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Contemporary contamination and risk of persistent organic pollutants in sediments of an urbanised estuarine and coastal ecosystem

Alex Billings [a,*], Francis Daunt [b], Justyna P. Olszewska [b], Amy Pickard [b], Maria I. Bogdanova [b], Helen Campbell [a], Heather Carter [a], M. Glória Pereira [a]

[a] *UK Centre for Ecology & Hydrology, Library Avenue, Bailrigg, Lancaster, LA1 4AP, UK*
[b] *UK Centre for Ecology & Hydrology, Bush Estate, Penicuik, EH26 0QB, UK*

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ABSTRACT

Estuaries are particularly at risk from persistent organic pollutants (POPs), since they form the boundary between freshwater and marine environments. We investigated spatial and seasonal trends of 7 organochlorine pesticides (OCs), 35 polychlorinated biphenyls (PCBs), and 25 polybrominated diphenyl ethers (PBDEs) in sediments ($n = 155$) from a range of sites in an urbanised and industrialised estuary (the Forth, south-east Scotland). PCBs ($\sum$PCB mean concentration 3.3 ng g^{-1} ww, detection frequency 86%) and OCs ($\sum$OC mean 2.5 ng g^{-1} ww; DF 95%) were the most abundant and frequently detected POPs, with PBDEs less widespread and at lower concentrations ($\sum$PBDE mean 0.17 ng g^{-1} ww, DF 59%). POP profiles reflected historic patterns of production and use, and, for PCBs, congener-specific degradation profiles. PCB congeners 28, 118, 149, 101, 153, and 138, and the pesticides DDE (a breakdown product of DDT) and hexachlorobenzene were amongst the most frequently detected and abundant compounds. We found no evidence for seasonal variation in $\sum$OC and $\sum$PBDE concentrations, although $\sum$PCB and some individual compounds, e.g. dieldrin, exhibited seasonal differences. Key drivers of POP fate were sediment organic matter and distance from source areas. The weight of evidence suggested that the majority of POPs pose a relatively low risk in the estuary. However some compounds, e.g. Lindane exceeded the Probable Effect Level in 8% of samples. This work demonstrates the spatial variation in presence and potential risk of POPs in the UK environment and the need to continue to monitor the levels of these contaminants.

1. Introduction

Persistent organic pollutants (POPs) include many halogenated organic compounds which have historically been widely used in a variety of applications. Polychlorinated biphenyls (PCBs) were amongst the widely produced halogenated organic compounds in the middle of the 20th century. Due to physical properties such as a low dielectric constant, low flammability, and chemical and thermal stability, PCBs were used in a number of applications, including heat transfer fluids in transformers and capacitors, plasticisers, lubricants, and dielectric fluids (Breivik et al., 2002; Environment Agency, 2007). PCBs were produced in the UK in the 1950s and 1960s. However, due to the impacts on the human health and the environment, the production of PCBs was phased out in the 1970s, with production ending in the UK in 1976 (Environment Agency, 2007). Due to their persistence, potential for bioaccumulation, and toxicity, PCBs are defined as POPs under the Stockholm Convention and listed for elimination as part of Annex A (Stockholm Convention, 2023).

Organochlorine pesticides (OCs) are another group of organochlorine compounds listed as POPs in the Stockholm Convention (Stockholm Convention, 2023). Introduced in the 1940s, organochlorine insecticides such as dichlorodiphenyltrichloroethane (DDT) and dieldrin, and fungicides such as hexachlorobenzene (HCB), were widely used in the UK until restrictions on their production and use came about in the 1970s and early 1980s (EEC, 1978). The use of OCs was phased out primarily due to their negative environmental impacts on non-target species, for instance DDT was linked to declines in populations of predatory birds in a number of continents (Mellanby, 1992).

Polybrominated diphenyl ethers (PBDEs) are organobromine flame retardants, the use of which peaked in the UK in the early 1990s (Environment Agency, 2019). However, concerns surrounding the bioaccumulation and endocrine disruption of PBDEs also led to legislation

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* Corresponding author.
E-mail address: alebil@ceh.ac.uk (A. Billings).

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heavily restricting their production in the 1990s (production of PBDEs in the UK ended in 1996), with their use declining in the early 2000s, when in 2004 restrictions on use were imposed (Environment Agency, 2019).

Many PCBs, PBDEs, and OCs are highly persistent, and despite the sharp decline in their production and use in the second half of the 20th century, many of these contaminants remain present in the environment (e.g. Montuori et al., 2020; Windsor et al., 2019), and numerous potential sources remain. For instance, PCBs and PBDEs were widely used in building materials, electrical infrastructure, and as additives in paints and polymer flooring, thus urban and industrial areas may represent a contemporary input of these legacy compounds into the wider environment.

In addition to potential inputs of POPs from sites of use in urban and industrial areas, there are also concerns around the remobilisation of compounds sequestered in the environment. For instance, inputs of POPs to estuarine and marine environments can occur through the remobilisation of POPs sequestered in riverine sediments following periods of high flow, e.g. storm events and dredging (Martins et al., 2012; Nadal et al., 2015). There are concerns that sea level rises coupled with increasing occurrence of storm events driven by climate change could increase the remobilisation of POPs from sites of historic disposal and storage (Brand and Spencer, 2019; Nicholls et al., 2021). For instance, POPs present in historic municipal and industrial waste sites (e.g. landfills) may be susceptible to release through leaching and subsequent lateral or vertical groundwater subterranean flows (Neuhold and Nachtnebel, 2011). Therefore, increasing remobilisation of POPs in the environment may constitute a dynamic, rather than static, pollution risk in freshwater and estuarine systems.

In this study, we aimed to assess the spatial and seasonal variations in concentrations of POPs (OCs, PCBs, and PBDEs) in estuarine and coastal sediments in order to elucidate potential links with areas of input into the estuary and understand the contemporary risk to organisms that these legacy contaminants still represent. The Forth estuary and the North Aberdeenshire coast in Scotland, UK, were selected as exemplar case studies to address this aim. The Forth estuary represents an area subject to historic inputs of POPs, and the North Aberdeenshire coastline was selected in order to provide a case study with putatively low historic POP inputs, against which the levels of contaminants in the Forth estuary could be compared. We measured the levels of POPs in bed sediments collected from these two regions. This allowed us to test the following hypotheses:

1) Profiles and relative concentrations of POPs in estuarine and coastal sediments are explained by legacy inputs and physicochemical properties (e.g. logK_{ow});

2) Seasonal and spatial variations in POP concentrations are driven by variations in estuarine dynamics, and variations in sediment properties and distance from source areas respectively;

3) The presence of OCs, PCBs, and PBDEs represents an ongoing risk to estuarine organisms based on comparison with effects metrics.

2. Materials and methods

2.1. Study area and sample collection

The Forth estuary in Scotland, UK, was selected as an exemplar area to address the aims of the study (Fig. 1). A number of potential historic and contemporary sources of POPs are located along the Forth estuary, e.g. legacy landfills and industrial sites. The Forth estuary also hosts internationally important breeding populations of seabirds such as European shags (*Gulosus aristotelis*), Atlantic puffins (*Fratercula arctica*), razorbills (*Alca torda*), and northern gannets (*Morus bassanus*) (Burrell et al., 2023; Wanless et al., 2018), which past work have shown to be at risk of persistent contaminant exposure, including POPs such as PCBs (Pereira et al., 2009; Yamashita et al., 2018). The channel flow of the

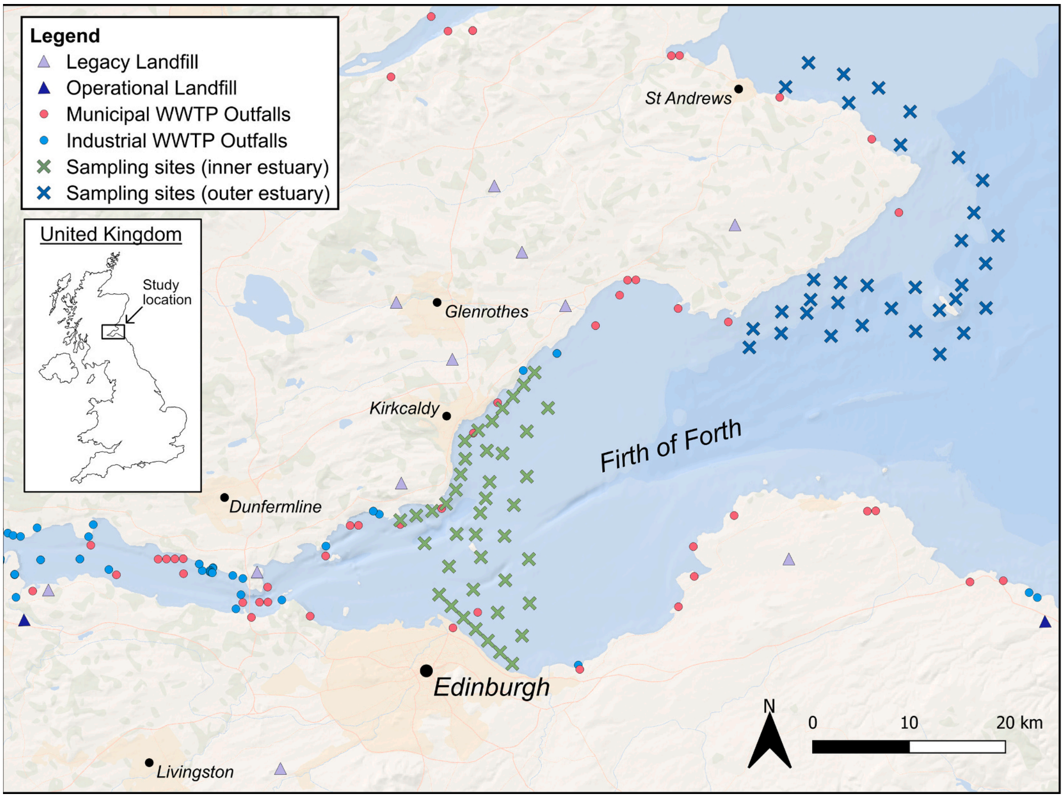

Fig. 1. Map of coastal landfill sites, wastewater treatment plants (WWTPs), and sediment sampling sites in the Forth estuary in Scotland, UK; landfill sites within 10 km of the Forth estuary and/or within 5 km of a tributary are shown; contains information from the public sector licensed under the Open Government Licence v3.0; a map of the background sampling area, the Aberdeenshire coast, is shown in Fig. S1.

Forth estuary averages ~65 m^3 s^{-}1 (range ~ 10–300 m^3 s^{-1}; Balls, 1992). The total urban population of settlements along the estuary is ~630,000 (National Records of Scotland, 2022).

A second study area was also investigated, specifically the North Aberdeenshire coastline, Scotland, UK (Fig. S1). The primary river that discharges in the vicinity of the North Aberdeenshire coastline sites is the River Deveron. The Deveron catchment is rural and lacks historic or contemporary sources of POPs, e.g. major industry, therefore the likelihood of input of POPs to the North Aberdeenshire coastline sites via remobilisation of riverine sediments was negligible. Thus, the North Aberdeenshire coastline provided a dataset from which background levels could be determined for the contaminants in question.

A total of 146 bed sediment surface samples were collected at a range of depths in the water column (2–57 m) in the Forth estuary from November 2020 to July 2021. Two sampling areas were selected, specifically the inner estuary channel (sites west of longitude −2.9; Fig. 1, green crosses) and the outer estuary channel (sites east of longitude −2.9; Fig. 1, blue crosses). Samples were collected from the surface of the estuary bed using a 250 cm^2 Van Veen grab sampler. Samples were stored in glass containers at −20 °C.

Samples were collected at three time periods: winter 2020–21 (n = 52; inner sites = 24; outer sites = 28; 03.11.20 - 03.03.21), spring 2021 (n = 53; inner = 27; outer = 26; 07.04.21–29.06.21), and summer 2021 (n = 41; inner sites sampled only due to logistical challenges; 14.07.21–23.07.21) from a total of 76 sites in the estuary and neighbouring coastal area (Fig. 1). A further 9 samples were collected from sites along the North Aberdeenshire coastline in winter 2023 (21.02.23–22.02.23; Appendix Fig. S1).

2.2. Sediment organic matter determination

Only a subset of samples (80%, n = 124) were analysed for organic matter due to limited sample availability (inner estuary, n = 70: winter = 23, spring = 27, summer = 20; outer estuary, n = 46: winter = 28, spring = 18; North Aberdeenshire coastline, n = 8).

Organic matter content in the sediments was measured by loss on ignition (LOI). In brief, 1 g of air-dried sediment was dried at 105 °C for 3 h, and heated in a muffle furnace at 550 °C for a further 3 h. Samples were cooled and weighed after each period of drying. In-house QC soil reference materials were analysed with each batch of samples as quality controls.

2.3. POPs extraction

Sediment samples were thawed and ~2–4 g ww of each sample was accurately weighed, homogenised, and dried with anhydrous sodium sulfate. Samples were spiked with ^{13}C-labelled recovery standards for PCBs (^{13}C-PCB 153, 180, and 209, Cambridge Isotope Labs, USA), OCs (^{13}C-α-HCH, Cambridge Isotope Labs, USA), and PBDEs (^{13}C-PBDE 28, 47, and 153, Wellington Labs, Canada) and Soxhlet-extracted with DCM for 16 h. Extracts were dried using anhydrous sodium sulfate, reduced to a known volume on a parallel evaporator and filtered through a 0.45 μm PTFE syringe filter. Extracts were cleaned using automated size-exclusion liquid chromatography (SEC; Agilent 1200 series, Agilent, USA) using a DCM mobile phase. Following SEC clean-up, extracts were loaded onto a glass column packed with Al_2O_3 deactivated with 5% deionised water (w/w) and analytes were eluted using hexane. Cleaned extracts were concentrated to a known volume and split into two fractions; one fraction to be analysed for PCBs and OCs, and the other for PBDEs. Prior to instrumental analysis, ^{13}C-labelled internal standards were added to each fraction: ^{13}C-PCB 8, 167 and 194 (Cambridge Isotope Labs, USA) and ^{13}C-HCB (Wellington Labs, Canada) to the PCB/OC fraction; ^{13}C-PBDE 77 and 138 (Wellington Labs, Canada) to the PBDE fraction. A full procedural blank was carried out with each batch of samples extracted (see Section 2.4).

2.4. POPs analysis

Sediment samples were analysed for a suite of 35 polychlorinated biphenyls (PCBs; di- to deca-PCBs), 25 polybrominated diphenyl ethers (PBDEs; tri- to octa-PBDE), and 7 organochlorine pesticides (OCs) (Table S1).

PCBs and OCs were analysed using an Agilent 7890B gas chromatograph coupled to an Agilent 5977B single-quadrupole mass spectrometer operating in electron ionisation mode. Samples were injected in splitless mode on to a Restek SGE HT8 analytical column (50 m length, 0.25 mm internal diameter, 0.22 μm film thickness). The inlet temperature was 60 °C, ramping at 600 °C min^{-1} to 325 °C. Following injection, the oven was held at 50 °C (2.5 min), followed by ramps to 200 °C (60 °C min^{-1}), 235 °C (1.5 °C min^{-1}), 240 °C (1 °C min^{-1}, held for 12.5 min), 250 °C (1 °C min^{-1}, held for 15 min), 280 °C (1 °C min^{-1}, held for 5 min), 310 °C (40 °C min^{-1}, held for 5 min). Helium was used as the carrier gas (1 mL min^{-1}). The MS source temperature was 250 °C, with a quadrupole temperature of 150 °C. The analysis was carried out in single ion monitoring (SIM) mode.

PBDEs were analysed using an Agilent 7890B gas chromatograph coupled to an Agilent 7010B triple-quadrupole mass spectrometer operating in electron ionisation mode. 4 μL of sample was injected in splitless mode on to a Restek SGE HT8 analytical column (12 m length, 0.25 mm internal diameter, 0.22 μm film thickness). The inlet temperature was 90 °C, ramping at 600 °C min^{-1} to 400 °C. Following injection, the oven was held at 50 °C (4 min), followed by ramps to 270 °C (50 °C min^{-1}), 290 °C (4 °C min^{-1}), 320 °C (15 °C min^{-1}, held for 6 min). Helium was used as the carrier gas (1 mL min^{-1}). The MS source temperature was 250 °C, with a quadrupole temperature of 150 °C. The analysis was carried out in multiple reaction monitoring (MRM) mode.

Quantification of all analytes was carried out using ^{13}C-labelled internal standards and calibration curves of unlabelled analyte standards (Chem Service & Cambridge Isotope Labs, both USA; Wellington Labs, Canada). Information regarding m/z values used for quantification of analytes is shown in Table S1. Recoveries of ^{13}C-labelled recovery standards ranged from 60 to 120% (Table S2). Concentrations were recovery-corrected in order to take into account potential matrix effects (both suppression and enhancement) and potential losses in the analytical procedure. Of the 12 procedural blanks carried out, only four compounds (DDE, PCBs 28, 29, and 206) were detected. Each of these compounds was detected only once. All concentrations were blank-corrected, and are reported in ng g^{-1} ww (wet weight). Mean limits of detection (LODs) ranged from 0.03 to 0.52 ng g^{-1} ww (median LOD 0.08 ng g^{-1}; see Table S3 for full list of LODs for each analyte), and were calculated from the mass of sample extracted, the dilution factor, and the lowest standard in the calibration curve.

2.5. Data analysis

2.5.1. Calculation of risk quotients

The relative risk posed by POPs in the Forth estuary was estimated by comparison against a number of environmental quality standards (EQS). Measured environmental concentrations of the POPs in sediments were compared against four sets of EQS values: 1) Experimentally-derived sediment predicted no-effect concentrations (PNECs) obtained from the NORMAN Network ecotoxicology database of collated PNECs (NORMAN, 2025) (data downloaded 03.06.24); 2) CEFAS action levels for disposal of dredged sediments in the UK marine environment (Marine Management Organisation, 2025, 2015); 3) Canadian interim sediment quality guidelines (ISQGs) and 4) Probable Effects Levels (PELs) (Canadian Council of Ministers of the Environment, 2001, 1999a, 1999b, 1999c). Where EQS values for a compound were available, risk quotients (RQs) were calculated by dividing the measured environmental concentrations in the sediments by the EQS in question. Concentrations for compounds in the study are reported on a wet weight basis, although EQS values were only available as dry weight values.

Thus, the RQs reported here are likely to be slightly underestimated, for instance freshwater sediments can be comprised of up to 66% water by weight (Fořt et al., 2025). When calculating the risk quotients for $\sum$PCB for comparison with Canadian ISQGs and PELs, it should be noted that all of the major components of the historically used Aroclor mixtures were included in our analytical suite (Frame et al., 1996), including those of Aroclor 1016, 1242, 1254, and 1260 (Environment Agency, 2007). One of the CEFAS action levels for PCBs is set for the sum of 25 congeners (Table S4), 18 of which were targeted in our study. Therefore, the RQs for PCBs based on the Canadian ISQGs, PELs, and the CEFAS action level for PCBs ($\sum$CEFAS 25 congener suite) may also be slightly underestimated. A full list of the EQS values used in our assessment is shown in Table S4.

2.5.2. *Calculation of PCB toxic equivalents*

To compare the relative risk of PCBs in the sediments, PCB toxic equivalents (TEQs) were calculated using the recently updated WHO toxic equivalency factor (TEF) values (DeVito et al., 2024). TEFs are derived by comparing the toxicity of each congener to a reference compound (specifically 2,3,7,8-TCDD) (Van Den Berg et al., 1998). The use of toxic equivalents is a well-established method of comparing the toxicity of different samples which contain dioxin-like PCBs in different concentrations, based on the additive toxicity of PCBs arising from a shared toxicity pathway across species (Denison et al., 2011; Denison and Faber, 2017; Van Den Berg et al., 1998). TEQ values for PCBs in sediments were calculated by multiplying the concentration of individual congeners by the TEF of the specific congener, with the sum of the resulting congener-specific TEQs giving the toxic equivalence for dioxin-like PCBs in the sediments.

2.5.3. *Statistical analysis*

POP concentrations are reported on a wet weight basis. For calculation of sum concentrations of POPs ($\sum$OC, $\sum$PCB, and $\sum$PBDE) for individual sites, and mean and median, compounds below the LOD were assigned a value of zero to avoid overestimation (Crosse et al., 2012; Pereira et al., 2021). Due to low detection frequencies of some compounds (see Tables S7-S9), $\sum$OC, $\sum$PCB, and $\sum$PBDE were used for statistical modelling instead of individual compound concentrations. In the case of $\sum$OC and $\sum$PCB it was necessary to carry out log10-transformation prior to statistical modelling to achieve approximate normality in the distribution of these variables. In the minority of instances where all compounds were below the limit of detection for OCs (5%) and PCBs (14%), $\sum$OC and $\sum$PCB concentrations were assigned half the median LOD for that suite of compounds prior to log10-transformation (Antweiler and Taylor, 2008). Statistical analyses were carried out using R (version 4.4.0) (R Core Team, 2024).

Relationships between $\sum$POP ($\sum$OC, $\sum$PCB, and $\sum$PBDE) concentrations in the Forth estuary and sampling season (winter, spring, summer), sampling area (inner or outer estuary), distance from the shoreline, and sample depth in the water column were investigated using linear mixed models (LMMs, for $\sum$OC and $\sum$PCB) and zero-inflation generalised linear mixed models (ZI-GLMMs, for $\sum$PBDE). ZI-GLMMs consist of two components: (1) a zero-inflation component which represents the probability of a concentration being below the limit of detection (assigned a value of zero), and (2) a conditional component which represents the expected concentration provided that the concentration is >LOD. Season and sampling area were included in the LMMs and ZI-GLMMs as fixed effects, distance to shore and sample depth were included as covariates. Sampling site ID was a random effect in all models as sites were sampled in different seasons (i.e. more than once). ZI-GLMMs, as opposed to LMMs, were used to model $\sum$PBDE due to a high frequency of non-detects in the PBDE dataset (41% of samples <LOD). ZI-GLMMs with a log link and gamma error structure were used. Throughout the text these models will be referred to as Model A.

In order to investigate the effects of organic matter (%OM) on POP occurrence in the estuary, for the subset of samples (80%) for which %OM data was available, additional LMMs ($\sum$OC and $\sum$PCB) and ZI-GLMMs ($\sum$PBDE) with the same model structure as described above were fitted, but with %OM included as an additional covariate. Throughout the text these models will be referred to as Model B1 (log10-transformed %OM) and Model B2 (untransformed %OM). PCB and OC were modelled using Model B1 and PBDEs were modelled using Model B2 due to improved model diagnostics for these models (see below for further details of how model performance was assessed).

LMMs were fitted using the ‘lme4’ package (Bates et al., 2003). ZI-GLMMs were fitted using the ‘glmmTMB’ package (Brooks et al., 2017). Marginal and conditional R^2 values for individual models were generated using the ‘performance’ package (Lüdecke et al., 2021). R^2 values for individual fixed effects in LMMs were estimated following the method established by Nakagawa and Schielzeth (2013) using the package ‘r2glmm’ (Jaeger, 2016). For all models, diagnostic plots were generated using the ‘performance’ package (Lüdecke et al., 2021). Appropriateness of model structure, and model validity and accuracy were assessed through comparisons of homogeneity of variance, uniformity of residuals, normality of random effects, influential observations, model linearity (for LMMs), predictor collinearity, and posterior predictive checks.

Outputs from all model analyses are provided in Tables S5 and S6.

3. Results and discussion

3.1. *Concentrations and profiles of POPs*

3.1.1. *Organochlorine pesticides (OCs)*

The majority of the organochlorine pesticides (OCs) measured in this study were banned for agricultural use in the UK in the early-mid 1980s, namely DDT, HCB and dieldrin (EEC, 1978). The insecticide lindane continued to be used until more recently, with agricultural use of lindane banned in the UK in 2002 (DEFRA, 2012). Despite this, ≥1 OC pesticide was detected in 95% of the sediment samples collected from the Forth estuary across all samples ($n = 146$), although no OCs were detected at the North Aberdeenshire coastal sites ($n = 9$). Mean seasonal $\sum$OC concentrations in the inner and outer Forth estuary ranged from 3.03 to 3.60 ng g^{-1} ww and 1.04–1.08 ng g^{-1} ww respectively (see Table S7).

The DDT breakdown product DDE was the most frequently detected OC in the estuary across the entire study (88% DF; mean 1.64 ng g^{-1} ww), with DDD less frequently detected (12% DF; mean 0.14 ng g^{-1} ww;

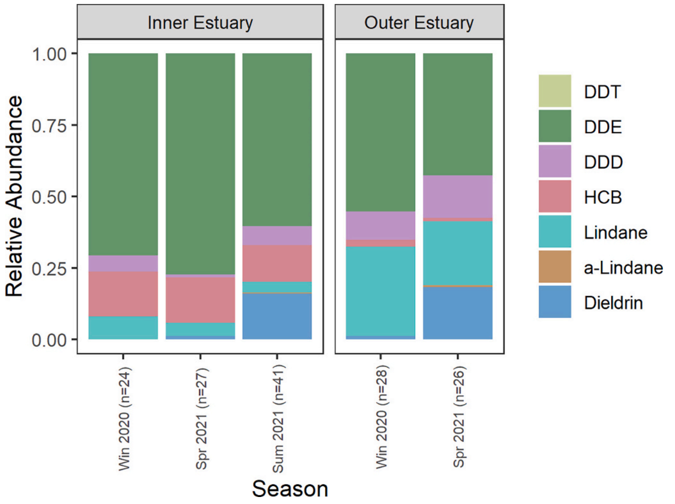

Fig. 2. Mean sum organochlorine pesticide profiles (mass-based) in sediments of the Forth estuary; “Win” = Winter, “Spr” = Spring, “Sum” = Summer; no OC pesticides were detected at the North Aberdeenshire coastal sites, hence they are not shown in this figure.

Fig. 2). DDT itself was not detected in any of the samples (mean DDT LOD 0.33 ng g^{-1} ww). DDE and DDD combined accounted for the majority (71.3%) of mean $\sum$OC across all samples, which is consistent with previous studies of the occurrence of legacy organochlorines in the UK environment (Jürgens et al., 2015; Morrissey et al., 2013).

Of the remaining pesticides to be banned alongside DDT in the 1980s, the fungicide HCB (57% DF; mean 0.31 ng g^{-1} ww) was more frequently detected than the insecticide dieldrin (10% DF; mean 0.18 ng g^{-1} ww) across all samples in the estuary. HCB was also the second most abundant OC behind DDE, contributing 12.6% of $\sum$OC across all samples. The widespread occurrence of HCB in Forth sediments reflects not only the legacy use in pesticide applications, but also historic local industrial discharges. For instance, HCB was a known component of effluents from the ICI Grangemouth manufacturing plant at the head of the Forth estuary in the late 1980s, and was detected in all surface water samples ($n = 39$) from surveys of the inner estuary in 1987 and 1990, although use of chlorobenzenes in the plant was almost eliminated in 1989 (Harper et al., 1992). The relative abundance of dieldrin and HCB is also consistent with previous reports of these compounds in the UK aquatic environment. For instance, dieldrin was detected in only 44% of samples in Welsh riverine sediments, in contrast to HCB (78% DF) and DDE (89% DF). Additionally, an earlier UK study of organochlorines in the eggs of the riparian Eurasian dipper found that the detection frequency of dieldrin decreased by over 50% between 1988–1992 and 2008–2010 (Morrissey et al., 2013). Thus the relatively low detection frequency of dieldrin seen in the Forth estuary may partly reflect continuing degradation or dispersal of this pesticide, in contrast to the continuing persistence of e.g. DDE and HCB.

Despite being banned relatively recently compared to the other OC pesticides (DEFRA, 2012; EEC, 1978), lindane (25% DF; mean 0.2 ng g^{-1} ww) and its production byproduct α-lindane (1% DF), were detected at relatively low levels in Forth estuary sediments (8.7% of $\sum$OC). These results are consistent with previous studies of OCs in UK sediments, for instance both lindane and α-lindane were not detected in any sediments collected from three Welsh river basins (Windsor et al., 2019). Lindane has a lower $\log K_{ow}$ (3.7) than other OC pesticides (e.g. DDE $\log K_{ow}$ 6.5), and a greater water solubility (7.3 mg L^{-1} vs 0.1 mg L^{-1} for DDE), therefore partitioning of lindane to sediments is less likely than the other legacy OC pesticides studied. These factors may have contributed to the lower levels of lindane observed in the Forth estuary sediments relative to e.g. DDE or HCB. Historic UK emissions inventories are not readily available for these compounds, therefore whilst it is possible that the relative occurrence of different OC pesticides in the Forth estuary is also related to past patterns of use, it was not possible to test this hypothesis.

3.1.2. Polychlorinated biphenyls (PCBs)

PCBs were detected in all study areas, with ≥1 PCB detected in all North Aberdeenshire samples ($n = 9$; mean $\sum$PCB 0.28 ng g^{-1} ww), and 96% and 70% at the inner ($n = 91$; mean $\sum$PCB 4.96 ng g^{-1} ww) and outer ($n = 54$; mean $\sum$PCB 0.44 ng g^{-1} ww) Forth estuary (see Table S8). The most frequently detected congeners (detected in >50% of samples) were PCBs 28, 101, 118, 138, 149, and 153. These congeners were also typically present in the highest concentrations and thus dominated the PCB profile across all sampling seasons and sites (Fig. 3, Fig. S2). Of the 35 PCB congeners analysed in this study, a group of 10 congeners (114, 123, 126, 156, 157, 167, 169, 189, 199, 205) were not detected or had detection frequencies of ≤5% in all samples.

The PCB profiles were generally dominated by penta- and hexa-chlorinated PCB congeners. For instance, PCB 118 (penta) was the dominant congener (16.6% of $\sum$PCB), with the greatest maximum and mean concentration (6.35 and 0.52 ng g^{-1} ww) across all samples. PCB 149 (hexa, max 2.66 ng g^{-1} ww, mean 0.39 ng g^{-1} ww), PCB 101 (penta, max 3.28 ng g^{-1} ww, mean 0.28 ng g^{-1} ww), and PCB 28 (tri, max 3.59 ng g^{-1} ww, mean 0.47 ng g^{-1} ww) were the next most abundant congeners, accounting for a further 36.9% of $\sum$PCB (Table S8).

The PCB formulations that were most commonly used or produced in source areas, e.g. the wider catchment, are likely to be key factors contributing to the profiles observed in this study. The PCB profiles observed in sediments in this study appear most similar to Aroclor 1254 and Aroclor 1260 (Fig. 3). Aroclors 1254 (dominated by penta- and hexachlorinated congeners; PCBs 101, 150, 118, 128, 138, 153) and 1260 (hexa and hepta; PCBs 138, 149, 153, 170, 180, 187) were amongst the most commonly used formulations in the UK (Environment Agency, 2007; Frame et al., 1996).

The occurrence in the Forth estuary of lighter congeners, such as PCBs 28 and 31, that were not present in Aroclors 1254 and 1260 (Fig. 3) may be partially explained by historic use patterns. Lighter congeners (di- to tetra-chlorinated) were abundant in Aroclors 1242 and 1016, which were also amongst the most commonly used formulations (Environment Agency, 2007; Frame et al., 1996). Aroclor 1016 was developed by Monsanto in the early 1970s as an alternative to Aroclor 1242 with a putatively lower environmental impact, due to lower

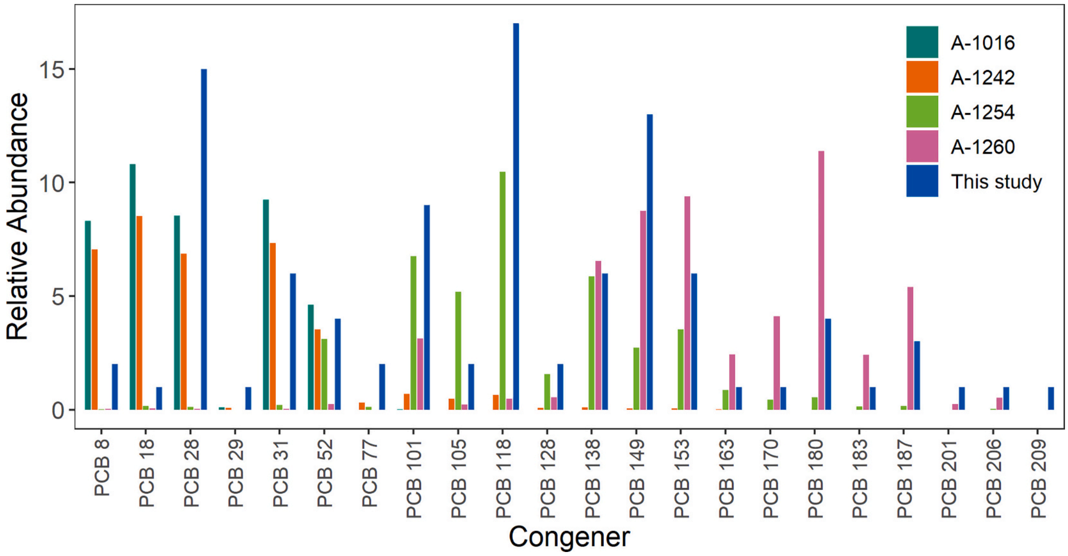

Fig. 3. Profiles of the PCBs in sediments analysed in this study; profiles of Aroclors 1016, 1242, 1254, and 1260 are also displayed for comparison (based on data from Frame et al., 1996); only PCB congeners with >1% relative abundance in sediments are shown, therefore data for PCBs 114, 123, 126, 141, 156, 157, 167, 169, 171, 189, 194, 199, and 205 are not displayed; data for all PCBs is shown in Table S8; profiles were calculated on a mass concentration basis.

concentrations of heavier congeners (Mayes, 1998).

However, whilst the profiles of PCBs in sediments of the Forth estuary appear to be related to the most commonly used Aroclors to some extent, there are discrepancies between these profiles. For instance, the relatively high abundance of PCB 28 in comparison to PCBs 8 and 18 is much higher than would be expected if Aroclors 1242 or 1016 were the primary contributors to the profile of the lighter congeners measured in the sediments. These differences may be due to the properties of individual congeners, such as rates of degradation and relative persistence, which are also known to affect PCB fate in sediments.

PCBs can be dehalogenated through microbial biodegradation in freshwater and estuarine sediments. The biological pathways required for degradation becoming increasingly anaerobic with increasing degrees of PCB congener chlorination (Beyer and Biziuk, 2009). Sediments in the Forth estuary are known to experience both oxic and anoxic conditions (Balls, 1992), therefore the profiles of PCBs in these sediments are also a result of dechlorination of PCB congeners.

PCBs with para- and meta-substituted rings are known to biodegrade more readily than ortho-substituted congeners, which can result in accumulation of lower congeners with ortho-substituted rings in the environment (Field and Sierra-Alvarez, 2008). This may partly explain the abundance of PCB 28 in sediments (Fig. 3, Table S8), as PCB 28 has chlorines in the ortho- and para- positions. PCB 18 and 8 were also relatively abundant in the Forth sediments, and also have ortho-/meta- and para-/ortho-substituted rings, respectively. Therefore, it is possible that the deviation of the less-chlorinated PCB profiles from the profiles from Aroclors 1242/1016 is explained by degradation of higher congeners. It should also be noted that PCB half-lives increase considerably with degree of chlorination. For instance, the sediment half-life of PCB 28 is 3 years, whereas for PCB 180 it is 38 years (Sinkkonen and Paasivirta, 2000). This therefore further suggests that the presence of lighter PCB congeners is a result of degradation of higher congeners, as lighter congeners are rapidly degraded compared to the heavier PCBs which dominated the profiles of the Forth estuary sediments (e.g. PCB 118, 149, 101). Remobilisation of sediments further upstream, which may have contained high levels of less chlorinated PCB congeners, could also have played a role. Lighter congeners are also likely to be more mobile in the environment relative to heavier congeners due to lower $\log K_{ow}$ values.

Given the persistence of PCBs in the environment and the widespread use of these formulations in the 1930s–1970s, the PCB profiles seen in the sediments of the Forth estuary are similar to those described in previous studies of Scottish marine sediments (Maes et al., 2012; Marine Scotland, 2020) and other European estuaries and rivers (Dendievel et al., 2020; Montuori et al., 2020; Van Ael et al., 2012). The concentrations of PCBs measured in the Forth estuary are broadly comparable to the handful of studies which have measured PCBs in other industrialised UK estuaries. For instance, the concentrations of ∑PCB in surface sediments of River Thames estuary were found to be in the range of 5–10 ng g^{-1} dw (Vane et al., 2020), comparable to the mean ∑PCB concentration of 4.96 ng g^{-1} ww found in our study in the inner Forth estuary. However, an earlier study reported higher ∑PCB concentrations in sediment of the River Mersey estuary in the range of 30–45 ng g^{-1} dw (Vane et al., 2007). This difference may be due to the greater degree of industrialisation in the Mersey catchment compared to the Forth or Thames.

That the PCB profile at the North Aberdeenshire coastal sites was composed primarily of lighter congeners (e.g. PCB 28) indicates that the main input of PCBs in these sites is aerial deposition, reflecting the lack of proximity to historic and current sources of PCBs (e.g. legacy landfill sites and industrial areas). This enrichment in lighter congeners at remote sites is consistent with the PCB soil profiles observed for rural areas in previous investigations of PCBs in the UK environment (Environment Agency, 2007).

3.1.3. Polybrominated diphenyl ethers (PBDEs)

PBDEs generally had low detection frequencies and concentrations in the studied sediments relative to other POPs (Table S9). Of the 25 PBDEs analysed in this study, 15 were detected in the Forth estuary, with no PBDEs detected at the Aberdeenshire coastal sites (Fig. S3). The most frequently detected congeners were components of the penta-PBDE and octa-PBDE technical mixtures used widely in commercial and industrial items in the UK in the 1980s and 1990s (Environment Agency, 2019; La Guardia et al., 2006). 10 PBDE congeners were not detected in any samples (BDEs 30, 32, 37, 49, 71, 128, 138, 153, 154, 190; mean LODs 0.03–0.28 ng g^{-1} ww). No PBDEs were detected at the North Aberdeenshire coastal sites.

Penta-PBDE components were the most frequently detected, specifically BDE 47 (50% DF; 28.5% of ∑PBDE), BDE 99 (50% DF; 29.4% of ∑PBDE), BDE 51 (20% DF; 5.4% of ∑PBDE), and BDE 100 (18% DF; 4.0% of ∑PBDE). BDE 47 and 99 were the two major components (total >85% *w*/w) of penta-PBDE technical mixtures (Environment Agency, 2019; La Guardia et al., 2006). This widespread use is reflected in their relatively high detection frequencies, albeit generally at lower concentrations than other POPs in this study, e.g. the mean seasonal concentrations of ∑BDE 47 + 99 in the inner and outer estuary were 0.11–0.20 ng g^{-1} ww and 0.01–0.04 ng g^{-1} ww.

Aside from those congeners present in penta-PBDE technical mixtures, the next most commonly detected PBDEs in the estuary were those present in octa-PBDE mixtures. BDE 183 (15% DF; 13.9% of ∑PBDE) was the most abundant and the most frequently detected octa-PBDE component. BDE 196 (also present in octa-PBDE) had a relatively high contribution to ∑PBDE in the estuary (12.3%) given its low detection frequency (4%), implying that this compound may have a heterogeneous distribution in the estuarine sediments. All other PBDEs had low detection frequencies (<5%) and relative abundances (<1% of ∑PBDE). Given that the historically most commonly used PBDEs dominate the sediment PBDE profiles, it appears that past patterns of use are the primary driver of contemporary concentrations of PBDEs in the estuary sediments.

It should be noted that, due to analytical constraints including a lack of sensitivity associated with thermal degradation and debromination of BDE 209 (deca-PBDE) in the inlet and GC column, it was not possible to reliably measure BDE 209 in this study. Given that BDE 209 is a frequently detected and abundant PBDE congener in UK estuarine sediments (e.g. Bignell et al., 2020), the true PBDE burden in sediments of the Forth estuary is likely greater than that reported in this study. Nevertheless, it is possible to draw conclusions based on the occurrence of the other dominant congeners measured in this study that were present in commonly used PBDE formulations (e.g. penta- and octa-PBDE). For instance, PBDE concentrations measured in the Forth estuary were at least one order of magnitude lower those reported by Bignell et al. (2020) for six UK estuaries located in England (Alde, Humber, Medway, Thames, Tyne, and Mersey). Excluding BDE 209, ∑PBDE concentrations measured by Bignell et al. (2020) ranged from 47 to 1013 ng g^{-1} dw, compared to the mean ∑PBDE in the Forth estuary of 0.23 ng g^{-1} ww. Similarly, concentrations of PBDEs (excluding BDE 209) in the Forth estuary were around one order of magnitude lower than those found in the Clyde estuary in Scotland (Vane et al., 2010). These results suggest that sediments of the Forth estuary may have a lower PBDE burden than other UK estuaries, although contemporary data of harmonised analytical suites is required to comprehensively characterise contemporary occurrence and risk.

3.2. Seasonal variation of POPs in the estuary

There was no evidence for seasonal differences in the concentrations of ∑OC in the estuary (spring relative to winter: estimate = −0.08, SE = 0.08, $t = -0.99$, $p = 0.32$; summer relative to winter: estimate = −0.16, SE = 0.09, $t = -1.72$, $p = 0.09$, winter coded as the reference season in the model; Model A, Table S5). Similarly, there were no seasonal differences in the concentrations of $\sum$PBDE (zero-inflation component: spring relative to winter: estimate $= 0.03$, SE $= 0.61$, z $= 0.04$, $p = 0.97$, summer relative to winter: estimate $= 0.55$, SE $= 0.77$, z $= 0.71$, $p = 0.48$; conditional component: spring relative to winter: estimate $= 0.32$, SE $= 0.18$, z $= 1.72$, $p = 0.08$, summer relative to winter: estimate $= -0.02$, SE $= 0.19$, z $= -0.1$, $p = 0.92$; Model A, Table S6). In contrast, there was some evidence that $\sum$PCB concentrations in the estuary were lower in summer (estimate $= -0.20$, SE $= 0.10$, $t = -1.97$, $p = 0.05$, Model A, Table S5), but not in spring (estimate $= 0.04$, SE $= 0.08$, $t = 0.47$, $p = 0.64$, Model A, Table S5), than in winter.

These results are consistent with previous studies which have observed higher concentrations of PCBs in bed sediments during periods of higher rainfall, attributed to increased urban runoff, riverine flux, atmospheric scouring, and resuspension of contaminated bed sediments (e.g. Nouira et al., 2013). The lack of a significant seasonal difference for $\sum$OC or $\sum$PBDE is also consistent with past assessments that have also reported that seasonal differences in estuarine concentrations of some POPs are rarely significant (e.g. Olaniyan et al., 2024; Tham et al., 2019; Wu et al., 2013). Channel flow is a key seasonal variable in the estuary, ranging from >300 m^3 s^{-1} in winter to <10 m^3 s^{-1} in summer (Balls, 1992), and therefore a lack of seasonal difference may reflect a lack of contemporaneous riverine input of POPs. Additionally, these results may suggest that the effects of flooding or storm events, such as upstream remobilisation of POPs, had a negligible impact on the flux of POPs in the sediments over the time-course of study.

In contrast to $\sum$OC, there was moderate statistical evidence that seasonal differences were observed in the concentrations of some individual OC compounds. Dieldrin exhibited the greatest relative significant difference in terms of mean concentrations. Specifically, dieldrin was more abundant in the inner estuary in summer (mean 0.49 ng g^{-1} ww; DF 24%) than spring (mean 0.05 ng g^{-1} ww; DF 4%; Kruskal-Wallis, Benjamini-Hochberg adjusted $p = 0.02$), and winter (not detected in any samples). The concentrations of dieldrin varied between seasons, despite the use of dieldrin in the UK having ceased in the 1980s (EEC, 1978), which indicates input of legacy contamination into the estuary. This may have occurred through remobilisation of dieldrin present in tributary or estuarine sediments via resuspension, transport and deposition of contaminated sediments in seasons with higher flow (winter, spring), followed by deposition in low flow conditions (summer). However, if remobilisation was the primary driver of this seasonal variation in dieldrin, it is unclear why this pattern was not seen for other POPs. Nevertheless, these results indicate that some POPs may continue to represent a dynamic, rather than static, pollution risk in freshwater and estuarine systems.

3.3. Spatial distribution of POPs in the estuary

There was very strong evidence that $\sum$POP concentrations were higher in the inner estuary than in the outer estuary (Fig. 4). $\sum$OC (estimate $= -0.74$, SE $= 0.14$, $t = -5.2$, $p < 0.0001$, Model A, Table S5) and $\sum$PCB (estimate $= -1.43$, SE $= 0.16$, $t = -8.9$, $p < 0.0001$, Model A, Table S5) had median concentrations of 3.05 and 3.21 ng g^{-1} ww in the inner estuary and 0.62 and 0.28 ng g^{-1} ww in the outer estuary. $\sum$PBDE were also significantly greater in the inner estuary, with a median value of 0.18 ng g^{-1} ww in the inner estuary compared to a median value $<$LOD in the outer estuary (Model A; zero-inflation component: estimate $= 5.1$, SE $= 1.84$, z $= 2.8$, $p = 0.006$; conditional component: estimate $= -0.85$, SE $= 0.42$, z $= -2.0$, $p = 0.04$; Table S6).

The rapid drop-off in contaminants concentrations along the course of the estuary suggests that the POPs are being retained in the sediments. Therefore, the inner estuary appears to be acting as a sink for OCs, PCBs and PBDEs in the Forth estuary. This may lead to particularly high exposures for individual organisms that breed or forage in the inner estuary itself, relative to more coastal organisms. There are a number of factors which may have contributed to the significantly higher levels of POPs in the inner estuary, including estuarine dynamics, distance from source areas, and sediment properties. These factors will be discussed in Sections 3.3.1 and 3.3.2.

3.3.1. Estuarine dynamics and distance from sources areas

The primary source of historic input of POPs into the estuary will be associated with industrial and urban areas and agricultural runoff (specifically for OCs) (e.g. Morrissey et al., 2013; Windsor et al., 2019), with these associated with either riverine inputs or direct overland flows into the estuary itself. Thus, the primary input of these compounds into the estuary will have occurred via input from upstream tributary rivers or waste outflows associated with the urban and industrial areas in the upper stages of the watershed and the estuary (e.g. the city of Edinburgh and Grangemouth industrial area; see Section 3.1.1). Potential contemporary sources of OCs, PCBs and PBDEs include, for instance, input from legacy landfill sites or upstream remobilisation of contaminated sediments (Brand and Spencer, 2019; Neuhold and Nachtnebel, 2011; Nicholls et al., 2021).

The transition from freshwater to saline water that occurs over the course of the estuary results in the sorption of contaminants to estuarine sediments ('salting out'). Previous studies have shown that sediment salinity is positively correlated with PCB concentrations (e.g. Simsek et al., 2026), therefore this process may explain the relative difference within the estuary, where the concentrations of PCBs, OC, and PBDEs in the inner estuary were significantly greater than at the outer estuary (Fig. 4, Section 3.3). Therefore, estuaries have the capacity to act as medium-term sinks for contaminants before they reach the marine

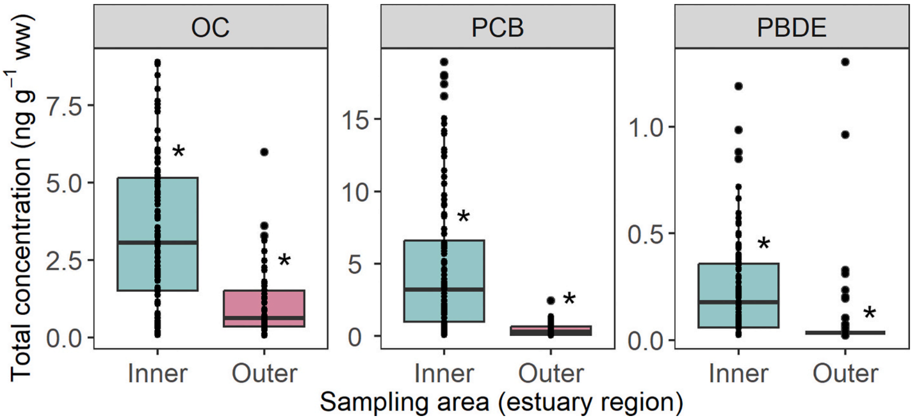

Fig. 4. Total concentrations of organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) in sediments of the Forth estuary, Scotland, UK; significant differences between sampling areas are indicated by an asterisk '*'.

environment.

The Forth estuary has a complex range of bed topologies Wanless et al., 2002 that may influence channel flow dynamics and thus affect the movement and subsequent distribution of contaminants in the estuary. There was moderate evidence to suggest that depth was positively correlated with $\sum$PCB concentrations ($R^2_{LMM} = 0.03$, estimate = 0.01, SE = 0.006, $t = 2.01$, $p = 0.05$, Model A, Table S5). However, there was no evidence of a relationship between depth and $\sum$OC (estimate = 0.003, SE = 0.005, $t = 0.6$, $p = 0.54$, Model A, Table S5) or $\sum$PBDE (zero-inflation component: estimate = −0.009, SE = 0.04, z = −0.24, $p = 0.81$; conditional component: estimate = 0.002, SE = 0.012, z = 0.17, $p = 0.86$; Model A, Table S6). Given that the variation in $\sum$PCB explained by depth was an order of magnitude lower than that for sample area (i.e. inner vs outer estuary, $R^2_{LMM} = 0.39$, Model A), and no relationships between depth and $\sum$OC or $\sum$PBDE were identified, it appears that depth does not play a major role in controlling the distribution of POPs in the estuary relative to e.g. distance from source areas or salting out dynamics.

There was weak evidence that the distance of sampling sites from the shoreline was significantly related to concentrations of PBDEs in sediments. The probability of detecting PBDEs ($\sum$PBDE >LOD) increased slightly with increasing distance from the shoreline (zero-inflation component: estimate = −0.31, SE = 0.19, z = −1.66, $p = 0.097$, Model A, Table S6), however $\sum$PBDE concentrations above LOD were not related to distance from the shoreline (conditional component: estimate = 0.04, SE = 0.06, z = 0.70, $p = 0.48$, Model A, Table S6). There was no correlation between distance from the shoreline and $\sum$OC (estimate = 0.02, SE = 0.02, $t = 0.90$, $p = 0.37$, Model A, Table S5) or $\sum$PCB (estimate = 0.03, SE = 0.03, $t = 0.97$, $p = 0.34$, Model A, Table S5). The weak positive correlation between the probability of detecting PBDEs and distance from the shoreline is unexpected, given that sites closer to the shore may be expected to be more highly contaminated with diffuse inputs from urban and industrial areas. One possible explanation is that the effects of tidal currents may have contributed to this relationship, by resuspending shoreline-associated contaminated sediment and depositing these POP-containing sediments further from the shoreline.

Given that relationships between POP concentrations and distance from the shoreline were absent (in the case of PCBs and OCs), or weak relative to those between $\sum$POP and sampling area (in the case of PBDEs), it appears that estuarine dynamics (e.g. salting out), inputs from the primary tributary into the estuary (i.e. the Forth river itself), and inputs from industrial/urban areas at the head of the estuary (e.g. from the city of Edinburgh, Fig. 1) are greater drivers of the spatial variability of POPs in the estuary than inputs from the shoreline itself.

In addition, as discussed in Section 3.1, there are known historic inputs of POPs and likely undocumented inputs in the Forth estuary. Therefore, given the environmental persistence of these compounds and the lack of demonstrable significant contemporary sources, it is likely that the occurrence of POPs in the inner estuary is related primarily to legacy contamination sequestered in the estuary sediments themselves or deposited through remobilisation of contaminated sediments further upstream, as opposed to contemporary input from the shoreline.

3.3.2. *Relationships between POP concentrations and sediment organic matter*

There was evidence for a strong positive relationship between organic matter and $\sum$OC ($R^2_{LMM} = 0.13$, estimate = 0.76, SE = 0.19, $t = 4.0$, $p = 0.0001$, Model B1, Table S5) and $\sum$PCB ($R^2_{LMM} = 0.25$, estimate = 1.33, SE = 0.22, $t = 6.0$, $p < 0.0001$, Model B1, Table S5) (Fig. 5).

The positive relationship between POPs and organic matter can be explained by the relatively high $\log K_{ow}$ values of these compounds (Table S1), resulting in stronger binding to the organic components of the sediments. Organic matter exhibits a negative correlation with grain size in estuarine sediments (e.g. Christiansen et al., 1997), therefore these results also indicate that sediment grain size would exhibit an inverse relationship with the concentrations of POPs in the estuary. The relationship between $\sum$OC or $\sum$PCB and organic matter was broadly comparable to the association with sample area (e.g. for $\sum$PCB: %OM $R^2_{LMM} = 0.25$, $p < 0.0001$; sample area $R^2_{LMM} = 0.14$, $p = 0.0001$; Model B1, Table S5). Assuming that sample area is a proxy for source intensity (see Section 3.3 and Fig. 1), these results suggest that sediment organic matter and the distance from potential sources are relatively similar in the extent to which they control the occurrence, and thus relative exposure risk, of POPs in the estuary. The marginal and conditional R^2 values (R^2_m and R^2_c) for Model B1 were higher for PCBs ($R^2_m = 0.61$, $R^2_c = 0.80$) than for OCs ($R^2_m = 0.39$, $R^2_c = 0.70$), indicating that our models explained a greater proportion of the variation in concentrations of PCBs in the estuary than in OCs. Furthermore, the relatively substantial contribution of fixed effects (as measured by R^2_m) compared to the contribution of fixed and random effects combined (as measured by R^2_c) observed in Model B1 for PCBs, and to a lesser extent OCs, suggests that a significant portion of the spatial variability in the levels of these compounds in the estuary is explained by the fixed effects (see Section 2.5.3).

The trends observed in the relationships between organic matter and $\sum$OC and $\sum$PCB are consistent with those previously reported by other studies (e.g. Gardes et al., 2020; Huang et al., 2018; Yuan et al., 2024; Zhang et al., 2007). Whilst the general patterns may be comparable

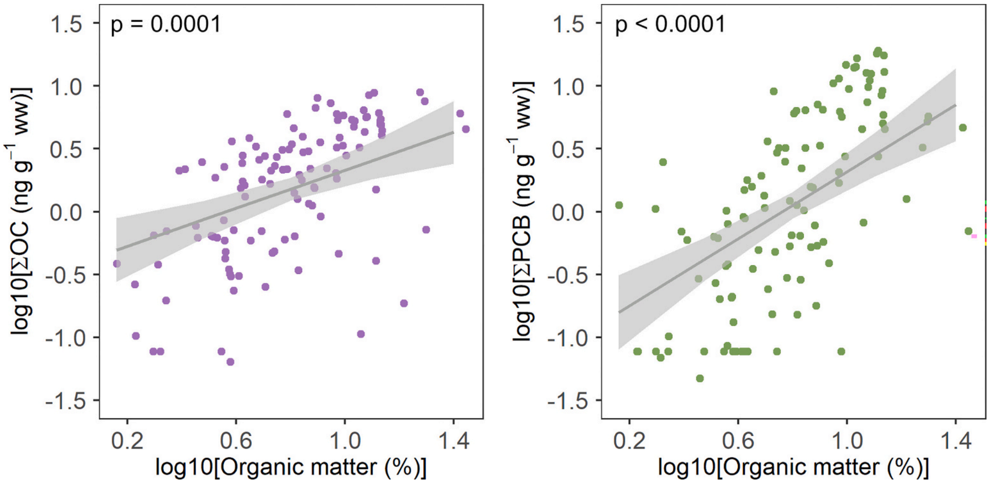

Fig. 5. Relationships between $\sum$OC and $\sum$PCB with organic matter; grey lines indicate the predicted values as determined by LMMs (Model B1, Section 2.5.3, Table S5), with 95% confidence intervals indicated by grey shading; $\sum$PBDE was not modelled using LMMs due to a high frequency of values <LOD.

between different studies, the exact nature and strength of the relationships will also depend on other local factors (e.g. estuary discharge, seasonality of flows, sediment types, and redox potential).

There was no evidence for a relationship between $\sum$PBDE and %OM (zero-inflation component: estimate = −1.28, SE = 1.27, z = −1.0, $p =$ 0.31; conditional component: estimate = 0.03, SE = 0.02, z = 1.42, $p =$ 0.16; Model B2, Table S6). The detection frequency of $\sum$PBDE in the samples that were also analysed for OM was only 26%, therefore it is possible that any effects of organic matter could have been masked due to these low levels of PBDEs relative to other contaminants. The fact that the PBDEs measured in this study were less abundant than PCBs or OCs may have resulted from the fact that the use and production of PBDEs in the UK was relatively low and short-lived compared to PCBs and OCs (see the Introduction). Furthermore, $\sum$PBDE concentrations in the estuary are likely higher than those measured, due to analytical constraints limiting the number the extent to which heavier congeners such as BDE 209 could be measured (see Section 3.1.3). For these reasons, detection frequencies and absolute concentrations of measured PBDEs are considerably lower than the other POPs measured in the estuary sediments, especially in the outer estuary which is further from historic sources (Section 3.1.3).

Based on the results discussed in Section 3.3, it can be concluded that primary factors controlling the distribution of POPs in the estuary include the distance from the estuary head, driven by distance from source areas and salting out associated with changes in salinity (and subsequent deposition of contaminants in bed sediments), in addition to sediment organic matter. Therefore, an understanding of the effects of sediment properties on POP occurrence and fate is a key component in assessing the risk posed to benthic organisms in the estuaries such as the Forth.

3.4. Risks associated with OCs, PCBs, and PBDEs in Forth estuary sediments

In order to compare and contextualise the risks associated with the presence of POPs in the sediments of the Forth estuary, the concentrations of these compounds were compared to environmental quality standards (EQS). Summary statistics of the risk quotients (RQs) are shown in Table S10 (NB: EQS information was not available for all compounds, hence only those compounds with reliable EQS values are shown in Fig. 6 and Table S10). It should be noted that the RQs reported here are likely to be slightly underestimated as concentrations for compounds in the study are reported on a wet weight basis, although EQS values were only available as dry weight values.

Based on the calculated risk quotients, OCs represent the highest risk to organisms in the Forth estuary relative to PCBs or PBDEs (Fig. 6, Table S10). The insecticides lindane and dieldrin, and the DDT breakdown product DDE, were amongst the compounds with the highest risk quotients. Lindane generally had the highest RQ values, with 25% of sediments exceeding a value of 100 for RQ_{PNEC} (i.e. the concentration of lindane in these sediments was >100 times greater than the lowest PNEC in the NORMAN database). It should be noted that the PNECs used in this assessment represent the lowest empirically-derived PNECs in the NORMAN database. Therefore, in order to contextualise the likely risk posed by these compounds it is important to consider a weight of evidence approach based on all of the EQS frameworks used in our assessment (PNECs, ISQGs, and PELs). Lindane also represented the highest risk based on ISQGs and PELs (18% of samples $RQ_{ISQG} > 1$; 8% of samples $RQ_{PEL} > 1$). Concentrations of DDE were also found to be at levels exceeding a number of EQS (27% of samples $RQ_{PNEC} > 1$; 29% of samples >1 RQ_{ISQG}). Although dieldrin exceeded RQ_{PNEC} and RQ_{ISQG} values of 1 in only 10% and 8% of samples respectively, 8% of samples

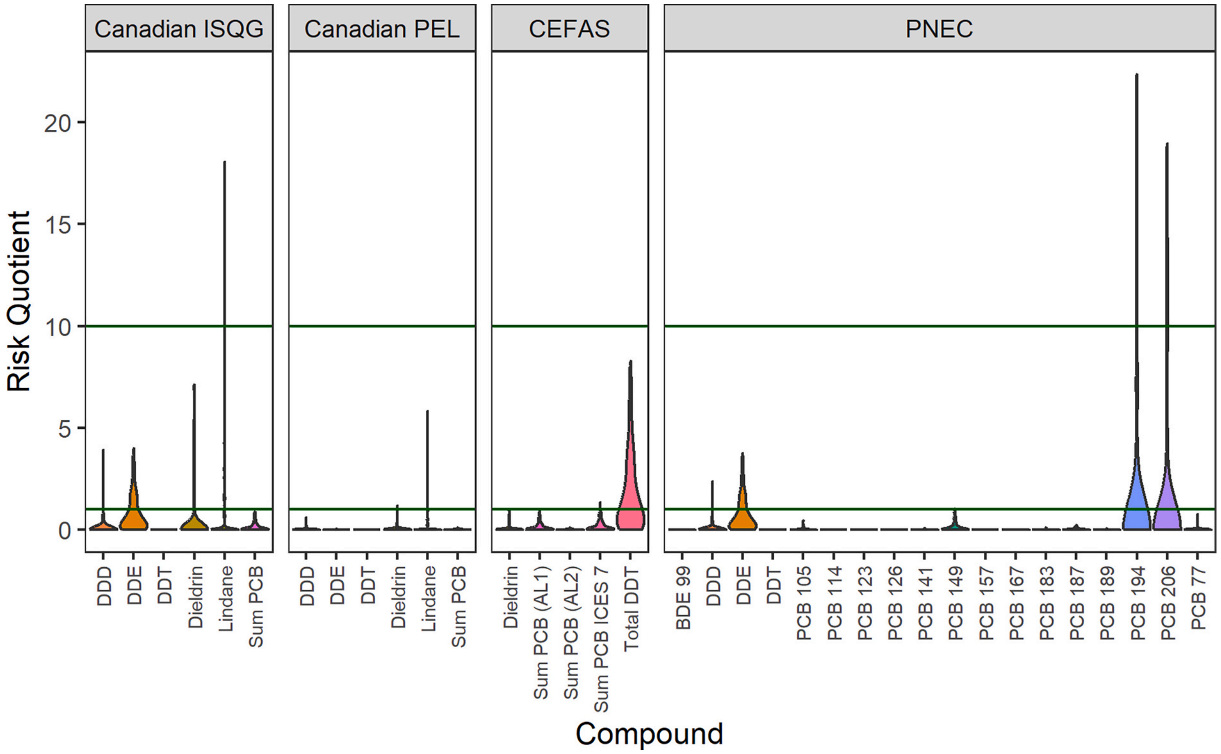

Fig. 6. Risk quotients (RQs) for selected compounds in sediments of the Forth estuary. Green lines indicate RQ values of 1 (i.e. concentration in sediments is equal to environmental quality standard) and 10 (i.e. concentration in sediment is 10× greater than environmental quality standard). RQs were based on: experimentally-derived lowest predicted no-effect concentrations (PNECs) in the NORMAN Network database (NORMAN, 2025); CEFAS action level 1 for marine sediments (Marine Management Organisation, 2025, 2015); Canadian interim sediment quality guidelines (ISQGs) and probable effects levels (PELs) (Canadian Council of Ministers of the Environment, 2001, 1999a, 1999b, 1999c); RQ_{PNEC} for dieldrin or lindane can be found in Table S10. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

had $RQ_{PNEC} > 100$ for this compound.

The high RQ_{PNEC} values associated with lindane and dieldrin are likely due in part to the fact that the PNECs for these compounds represent very conservative estimates of risk. These low PNECs may reflect the relatively potency of these compounds as insecticides, in addition to conservative estimates of risk arising from application of large assessment safety factors (Hampel et al., 2007). Some of these conservative PNECs were even below the sample LOD (for lindane: 0.001 ng g^{-1} dw PNEC vs 0.08 ng g^{-1} ww LOD; for dieldrin: 0.005 ng g^{-1} dw PNEC vs 0.29 ng g^{-1} ww LOD; Tables S3 and S4), thus whenever these compounds were detected, the RQ was by definition >1. The PNEC of DDE, by contrast, was higher than the LOD (2.2 ng g^{-1} ww vs 0.08 ng g^{-1} ww) and this is reflected in the fact that DDE exceeded an RQ_{PNEC} of 1 in 27% of all samples, despite having a detection frequency of 88%.

The risk quotients for PCBs were generally lower than for those of OCs, with the majority of compounds having a maximum RQ_{PNEC} of <1 (Fig. 6, Table S10). The two exceptions to this pattern were PCB 194 and PCB 206, which exceeded $RQ_{PNEC} > 1$ in 14% and 17% of cases respectively, with both compounds exceeding $RQ_{PNEC} > 10$ in 8% of samples (although neither exceeded $RQ_{PNEC} > 100$). These exceedances are primarily due to the low PNECs for these two compounds relative to other PCBs (0.01 ng g^{-1} dw vs 2.6 ng g^{-1} dw), in addition to the PNEC for PCBs 194 and 206 being below the sample LOD for these compounds (Tables S3 and S4). Despite these relatively high RQ_{PNEC} values for PCB 194 and 206, PCBs appeared to pose a relatively low risk based on either CEFAS action levels or Canadian interim sediment quality guidelines or probable effects levels. For instance, RQ_{ISQG} and RQ_{PEL} for $\sum$PCB never exceeded 1, and RQ_{AL} was for $\sum$PCB (ICES 7) was >1 in only 2% of cases. These results indicate that the risk posed by the additive effect of PCBs in the sediments is relatively low.

The mean TEQ for $\sum$PCB (11 dioxin-like congeners) was 0.0503 pg TEQ g^{-1} ww (median 0.0080 pg TEQ g^{-1} ww, maximum 0.8473 pg TEQ g^{-1} ww). As toxic equivalency factors are derived primarily from oral studies, comparison of sediments TEQs with those in organisms are challenging as the bioavailability of PCBs in sediments will be reduced through binding to organic matter and particulates. However, a conservative sediment quality guideline value for dioxin-like compounds of 70 pg TEQ g^{-1} dw has recently been proposed (Manning and Batley, 2023). Taking into account the fact that freshwater sediments can be comprised of up to 66% water by weight (Fořt et al., 2025), this value of 70 pg TEQ g^{-1} dw is at a minimum 2 orders of magnitude greater than the mean TEQ value for $\sum$PCB in the sediments analysed in our study. These results further indicate that PCBs, in isolation, likely represent a relatively low risk to organisms in the Forth estuary.

Due to a lack of established EQS values for PBDEs, RQs could be calculated for only one congener (PBDE 99). Based on the data in this study, PBDE 99 appeared to exhibit a very low risk in the sediments (Mean $RQ_{PNEC} = 0.00004$; Max $RQ_{PNEC} = 0.0003$). This is in accordance with the low abundance and detection frequency of PBDEs relative to other POPs in the estuary.

Based on the risk quotients calculated using the available EQS values (NORMAN lowest PNECs, CEFAS action levels, and Canadian sediment quality guidelines), the weight of evidence suggests that the majority of the POPs measured in this study pose a relatively low risk in the Forth estuary. However, some compounds exceeded multiple EQSs in sediment samples. For example, the OC pesticide lindane represented the greatest risk, exceeding the PNEC, ISQG, and PEL thresholds in 25%, 18%, and 8% of samples respectively. These results highlight the importance of continued efforts to monitor the levels of higher-risk compounds such as Lindane in the estuaries such as the Forth. Efforts to understand the potential mixture effects resulting from exposure to multiple legacy (e.g. POPs) and emerging contaminants (e.g. *per*- and polyfluoroalkyl substances, PFASs) in estuaries and other freshwater environments may also be warranted, given the continued presence and non-zero risk of POPs in some of these ecosystems.

4. Conclusions

Despite historic bans on their production and use, the results of this study illustrate the continuing presence of POPs in the UK environment. Our study of the Forth estuary and surrounding coastal area (south-east Scotland) provides evidence for widespread contamination of sediments with organochlorine pesticides and PCBs, although PBDEs were less abundant and less frequently detected. The profiles and levels of these contaminants reflect historic use patterns (e.g. the formulations of PCB Aroclors and PBDE mixtures) and compound-specific fate of contaminants in sediments (based on the physicochemical properties of individual POPs). However, despite their apparent persistence in sediments, the lack of a strong seasonal variation in the majority of POP concentrations may reflect a lack of significant contemporaneous riverine input and runoff of POPs into the estuary. Spatial variability in the levels of POPs in the sediments appears to be linked to distance from source areas and the transition from fresh to saline water. Additionally, there was strong evidence that sediment organic matter was positively correlated with POP concentrations, irrespective of distance from historic inputs, implying that organic matter could play a key role in the retention and occurrence of POPs in sediments. The presence of POPs in the sediments appears to represent a low risk to organisms in the study areas, with the exception of a small number of compounds such as lindane which exceeds multiple EQSs in a minority (8%) of samples. However, based on their widespread occurrence, persistence, and potential risks to ecosystems and human health, continued efforts to monitor these contaminants is warranted. Despite an apparent lack of significant contemporary input, future work is required to understand the potential risks to estuaries and other low-lying aquatic ecosystems that may be susceptible to remobilisation and input of POPs from site of legacy contamination due to increasingly extreme weather and climate patterns.

CRediT authorship contribution statement

Alex Billings: Writing – review & editing, Writing – original draft, Visualization, Formal analysis. **Francis Daunt:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Justyna P. Olszewska:** Writing – review & editing, Resources, Methodology, Investigation. **Amy Pickard:** Writing – review & editing, Resources, Methodology, Investigation. **Maria I. Bogdanova:** Writing – review & editing, Resources, Methodology, Investigation, Formal analysis. **Helen Campbell:** Writing – review & editing, Investigation. **Heather Carter:** Writing – review & editing, Validation, Investigation. **M. Glória Pereira:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

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.

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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.2026.119924.

Data availability

The data associated with this study, including supporting data documentation, has been deposited with the NERC Environmental Information Data Centre (EIDC). The DOI of the data is https://doi.org/10.5285/475f098c-dcc4-4e77-b57b-8b9bdeb330a3 (Billings et al., 2026).

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