Legacy and emerging flame retardants in sediments and wastewater treatment plant-derived biosolids

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HIGHLIGHTS

- Environmental contaminations of emerging OPE flame retardants occurring.
- High levels of BFRs and OPEs reported in WWTP-derived biosolids.
- Moderate to high ecotox. risk for PCB-52 and -115, as well as TEHP, EDHPP and TBOEP.
- TBOEP and BDE-209 present at highest concentrations sediment and biosolid samples.
- Low levels of PCBs in sediments and biosolids indicative of phase-out of their use.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

A baseline assessment of legacy and emerging flame retardant chemicals was performed in inland and transitional sediments as well as biosolids emanating from a selection of wastewater treatment plants (WWTPs) in Ireland. A selection of 24 polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and chlorinated organophosphate esters (Cl-OPEs) were quantified in: 81 inland and transitional sediment samples collected during 2023; 39 transitional sediments collected between 2018 and 2022; and 21 biosolid samples collected from 7 WWTPs over 4-month intervals in January, May, and September 2023. Highest concentrations of BDE-209 and several Cl-OPEs were detected in both sediment and biosolid samples, while most PCBs and penta-/octa-BDEs were comparatively low. Moderate levels of PBDEs and Cl-OPEs were detected in Irish sediments compared to similar studies conducted internationally. In biosolid samples, levels of BDE-209 were on the higher end of figured reported worldwide while levels of Σ_8Cl-OPEs were the highest relative to comparable international studies. PCBs meanwhile are on the lower end of international levels for both biosolids and sediments. Based on available predicted no-effect concentrations (PNECs), the majority of compounds assessed were found to be of low-risk based on their levels in sediments with the exception of TCIPP (Risk Quotient – RQ = 1.354 = high risk) as well as EHDPP, TEHP, PCB-118, and PCB-52 (RQ = 0.948, 0.576, 0.446, and 0.257 respectively = moderate risk). Similar risk assessment could not be performed on contaminants in biosolids,

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though levels of BDE-209 were on the higher end of figured reported worldwide (avg = 3155 ng/g) while levels of Σ_8Cl-OPEs were the highest relative to comparable international studies (avg$_8$ = 3290 ng/g). As the legacy PBDEs and PCBs have been listed as persistent organic pollutants (POPs) and replacement flame retardants such as Cl-OPEs have been flagged by programmes such as human biomonitoring for EU (HBM4EU) and the NORMAN Network as chemicals of emerging concern, continued monitoring of these moderate and high-risk contaminants in sediments, as well as an investigation of potential contamination of the food chain through land-spreading of biosolids on agricultural lands, would be warranted.

1. Introduction

Across the EU, there is much discussion regarding the utility and efficacy of fire safety standards for consumer goods and the use of additive flame retardants (FRs) as solutions to comply with such standards for at risk materials (Page et al., 2023). Halogenated flame retardants (HFRs) have been, and continue to be, extensively used in household furniture, electronics, and childcare items (e.g. prams, pushchairs, and cots) and insulation foams. Brominated flame retardants (BFRs) are largely used in hard plastics from electronic goods, as well as household insulation foams and some minor applications in textiles (Eljarrat and Barceló, 2011). Polychlorinated biphenyls (PCBs), while being used as FRs and plasticizers in some applications, were also widely used in dielectric insulating fluids for capacitors and transformers (Erickson and Kaley, 2011). Chlorinated organophosphate esters (Cl-OPEs) are more commonly found in foams from soft furnishings and childcare products (Harrad et al., 2023a; Wei et al., 2015), though have recently also been found in household insulation foams (Harrad et al., 2023a). Non-halogenated organophosphate esters (OPEs) have likewise been extensively used in these consumer goods as FRs, as well as being used as plasticisers, anti-foaming agents, and lubricants in a variety of other applications (Dou and Wang, 2023; Li et al., 2019). After many decades of use, research concluded that some HFRs, including polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), met the criteria for classification as Persistent Organic Pollutants (POPs), indicating their high risk in terms of environmental persistence and human and ecological toxicity (UNEP, 2024; Sharkey et al., 2020). While this led to the restriction of these particular chemicals over the last two decades, two prominent issues remain: (i) fire safety standards still require certain goods to pass strict safety tests, the simplest and cheapest way to achieve it being the addition of FRs; and (ii) replacements for banned substances have, to date, typically come in the form of other FRs such as Cl-OPEs and OPEs. These replacements are now seen as "regrettable substitutions", chemicals with similar properties to their banned predecessors many of whom are now under review by regulatory bodies such as the European Chemicals Agency and the US National Toxicology Programme (ECHA, 2023; NTP, 2023).

Due to the long lifespan of many of these goods, large volumes of materials containing legacy restricted or emerging HFRs remain in circulation in materials currently in use: in goods entering the waste stream, in newly manufactured goods made from recycled materials, or in goods exported from regions which have not yet restricted these chemicals (Sharkey et al., 2020). Meanwhile, goods which no longer use these restricted HFRs have shifted to these "regrettable substitutions" for which there is often insufficient ecotoxicological data but are nonetheless prominent in consumer goods. While high levels of PBDEs and Cl-OPEs have been detected in waste consumer goods (Harrad et al., 2019; Harrad et al., 2023b) and in the Irish indoor environment (Wemken et al., 2019), these chemicals are not known to be manufactured in Ireland. Sources of uptake to the outdoor environment would therefore likely a mix of diffuse emissions from their use in consumer articles, as well as their emissions from waste handling (e.g. landfills), WWTP discharges, domestic water discharges, and industrial emissions from processes where such chemicals are added to manufactured goods. Studies have shown that HFRs easily leach out of consumer products during everyday use, during recycling processes, and when disposed of

in landfills (Rauert et al., 2014; Stubbings, 2016; Harrad et al., 2020a). While the debate on the efficacy and safety of additive HFRs and discussions on their utility versus risk continues (Whaley et al., 2023; Page et al., 2023; ECHA, 2023; ECHA, 2024), such chemicals ultimately end up entering our waste systems most of which are not designed to screen or remove them. Due to their persistence and propensity for long-range transportation, their uptake into the environment is therefore highly likely.

Ireland has among the most stringent furniture fire safety standards worldwide (ECHA, 2023). Previous research has shown the presence of legacy hazardous BFRs such as PBDEs and hexabromocyclododecane (HBCDD), as well as replacement compounds such as deca-bromodiphenyl ethane (DBDPE), in many Irish indoor microenvironments, i.e. homes, offices, cars at concentrations significantly higher than those reported internationally (Wemken et al., 2019, 2020). In consumer products currently in circulation, it has been shown that legacy BFRs are still prevalent, though replacements such as Cl-OPEs are also extensively used in certain applications (Harrad et al., 2023a). It is therefore hypothesised that Cl-OPEs are likely also present in these indoor microenvironments (Keimowitz et al., 2016; Vykoukalová et al., 2017).

Despite previous research on legacy and emerging HFRs in indoor environments, there is comparatively less data available for the outdoor environment, particularly with regards to modes of environmental uptake. Certain pathways are likely to be of significance. For instance, an extensive study of landfills across Ireland found high levels of PBDEs and HBCDD in landfill leachate and highlighted that the transfer of BFRs from treated material to leachate readily occurs in landfill environments (Stubbings and Harrad, 2014; Harrad et al., 2020a). Studies in several other countries (Australia, South Africa, and Canada) similarly found BFRs to be present in landfill leachate (Gallen et al., 2016; Nomngongo et al., 2012; Li et al., 2012). Historically, landfills in Ireland operated under the "dilute and disperse" model resulting in uptake of contaminants directly into the environment. All currently operating landfills now dispose of leachate at wastewater treatment plants for the removal of targeted pollutants and microorganisms. While some investigations have been conducted into the efficacy of the current generation of wastewater treatment methods in removing some of flame retardant chemicals, current regulatory requirements and industry standards are not required nor designed to remove them during treatment.

Another potential contamination pathway is through the use of fertilisers produced from the solid fraction of wastewater treatment operations, also known as "biosolids". Given the high lipophilicity of many BFRs and partial lipophilicity of Cl-OPEs, it is conceivable that these biosolids contain HFRs which are then spread on agricultural lands as fertiliser (Gottschall et al., 2017). Currently, approximately 98 % of treated biosolids produced in Ireland are reused in this manner (Uisce Eireann, 2024a). However, the screening of chemicals/hazardous substances in Irish biosolids is currently limited to nitrogen, phosphorus, potassium, microbials, and heavy metals in accordance with the EU Sewage Sludge Directive (EU, 1986), as well as recommended screening for some emerging substances such as PCBs, polychlorinated dibenzo-dioxins/furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), and nonylphenol in accordance with the Code of Good Practice for the use of Biosolids in Agriculture (EU, 1986; DEHLG, 2008; Teagasc, 2024). Little is known about the chemical content of these biosolids beyond

these parameters or the implications of biosolid applications to agricultural land in Ireland which may contain emerging substances of concern (Healy et al., 2017), though data from other jurisdictions highlight the prevalence of some of these chemicals (see Section 3.2).

The European Green Deal (EC, 2020) and the Stockholm Convention (UNEP, 2019) both highlight an urgent need to protect human health and the environment from legacy and emerging organic contaminants such as flame retardants. It is therefore crucial that the levels of these chemicals in the environment are assessed and their potential sources identified so that effective measures can be adopted to reduce their impact. This research project aimed to investigate the presence of legacy restricted BFRs and PCBs, as well as replacement FRs in inland and transitional sediments samples collected from across Ireland. Concomitant with this, this project also involved a preliminary investigation into their presence in biosolids from a selection of seven WWTPs of varying size, treatment capacity, and treatment operations. In this paper we present: (i) concentration data for PBDEs, OPEs, and PCBs in inland sediments, transitional sediments, and biosolids from a broad selection of sites across Ireland; (ii) investigate variations in concentrations found (if any) between inland and transitional sediment sites; (iii) compare levels found in Irish sediments and biosolids with those found internationally in the context of the use, production, and regulation of FRs; (iv) determine statistically significant trends of FR concentrations with available metadata – population density of the local area, sediment type, and water flow speed for sediments; population equivalent (P.E.), treatment type, and seasonal variations for biosolids; (v) an evaluation of the ecotoxicological impacts of concentrations detected using available predicted no-effect concentrations (PNEC)s; and (vi) give indicative time trends for OPEs in transitional sediments where historical data is available.

2. Materials and methods

2.1. Sample collection and pre-treatment

The sampling campaign was split broadly into three threads: inland and transitional sediments collected by the project team during 2023; analysis of historical transitional sediment samples collected by the Irish Marine Institute between 2018 and 2022; and analysis of biosolid samples from Irish wastewater treatment plants (WWTPs).

2.1.1. Inland and transitional sediments 2023

Inland and transitional sediment samples ($n = 81$) were collected from a range of sites across Ireland (Fig. 1) including from rivers ($n = 62$) and estuaries ($n = 19$). Roughly 1 kg aliquots of surface sediments (0–5 cm) were collected from river sites which typically had a coarse (> 2 mm) grain size and approximately 0.5 kg each from the remainder with finer grain sizes. Samples were collected using either stainless steel digging implements or a Van Veen Grabber, both pre-cleaned before each sampling in a detergent wash and rinsed in triplicate with acetone, cyclohexane, methanol, and distilled water. Samples were collected into individual virgin HDPE containers and sealed in duplicate for transport to the lab for processing. Each sample was homogenised within their containers by constant stirring with a pre-cleaned stainless-steel spoon for a period of 8–10 min apiece. Homogenised samples were then sieved (via agitation, without any additional water) to a maximum 2 mm grain size using a stainless steel sieve and finally transferred to 50 mL polypropylene centrifuge tubes, sealed with parafilm and screw top caps. Freeze-drying was conducted in a Labconco Freezone freeze-dryer (Mason Technologies), under a maximum vacuum of 0.133 mBar, to a uniform temperature of $-40\ ^\circ$C, and over a period of approximately 6 days to ensure total dryness. Prior to loading samples into the freeze-dryer, the screw top caps were removed, the parafilm was perforated several times, and the cap placed lightly back on top of the tube to allow
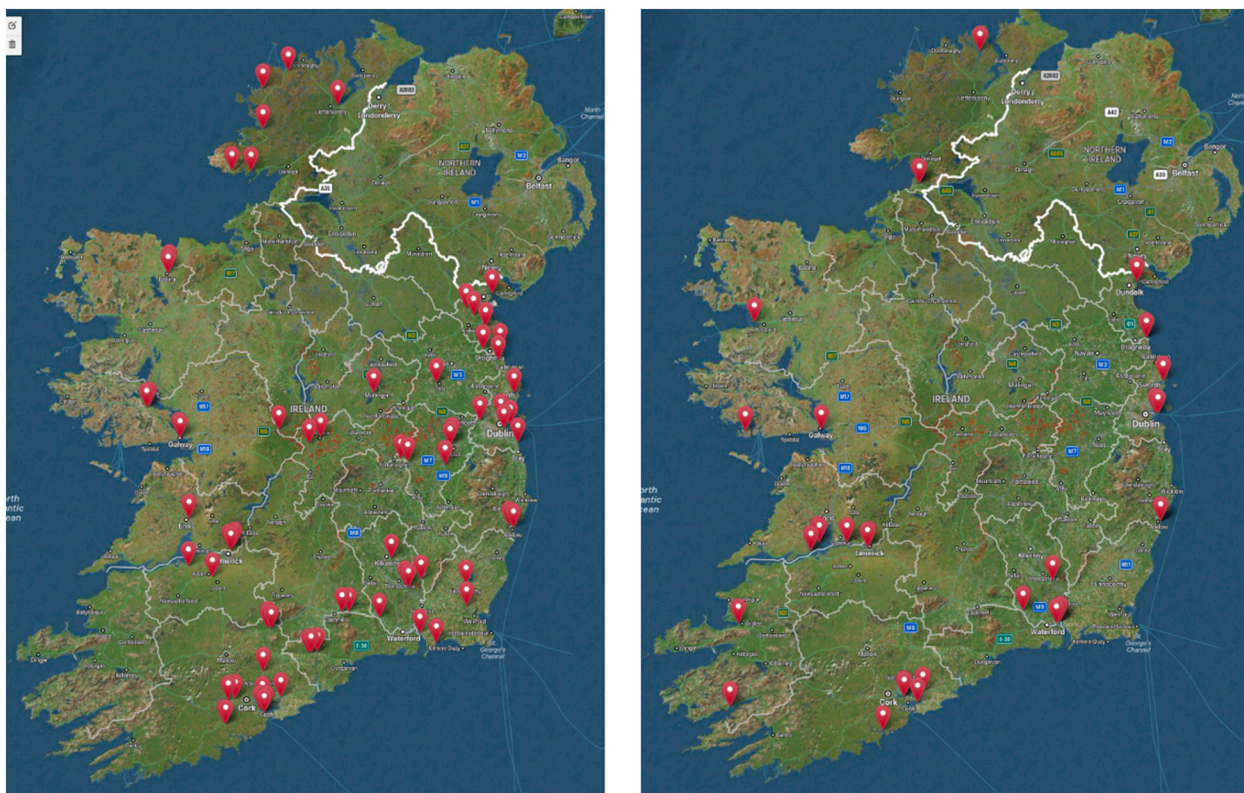
Fig. 1. Sampling points for 2023 campaign of Inland and transitional sediments (left) and 2018–2022 campaign by the Marine Institute for transitional sediments (right) [maps adapted from irishgridreferencefinder.ie].

for drying of multiple samples simultaneously while preventing cross-contamination of dried solids between containers. Dried samples were then resealed using parafilm and stored in preparation for analysis.

2.1.2. Transitional sediments 2018–2022

The Irish Marine Institute's annual monitoring campaign (Marine Institute, 2024) includes in its remit the annual or triennial sampling of transitional sediments from a selection of 26 sites around the Republic of Ireland for the purpose of routine monitoring of environmental contaminants as outlined in the Water Framework Directive (EU, 2000). Historical transitional sediment samples were made available to the TERRAChem project. In total, 39 samples from 23 sites over the five-year period 2018 to 2022 were available in sufficient volume for the purposes of analysis for the full suite of target chemicals ($n = 6, 13, 10, 8$, and 2 for each year respectively); in some cases, insufficient sample was remaining for analysis of OPEs within TERRAChem. Annual average concentrations of OPE compounds are used for temporal trend analysis in Section 3.3, though results may be subject to spatial variations as well as temporal. Sample collection for these sediments followed roughly the same procedure as outlined in Section 2.1.1, with the exception that non-metallic apparatus were used (due to the necessity to avoid heavy metal contamination) and samples were stored in pre-rinsed amber-glass containers. Samples in this instance were sieved to <63 μm grain size (in accordance with their monitoring requirements): initially oven dried at 104 °C and sieved through 2 mm, 1 mm, 125 μm, and 63 μm sieves respectively using sparing amounts of distilled water and with gentle brushing. The resulting 63 μm fraction was then placed in an oven at 104 °C and dried to a constant weight.

2.1.3. WWTP-derived biosolids

In collaboration with Uisce Éireann (UÉ, 2024), seven WWTP sites were selected for the collection of biosolid samples used as agricultural fertilisers. Table 1 shows a summary of the characteristics of the WWTPs sampled for biosolids which are relevant to the analysis and interpretation of data. In total, 21 biosolid samples were collected from the seven WWTPs: three samples were collected from each site at four-month intervals (January, May, and September 2023) to assess any seasonal variations, along with nuances relating to relative size and types of treatment occurring at each site. Collected samples were then freeze-dried using the same procedure as outlined above in Section 2.1.1.

2.2. Chemicals and standards

Individual native OPE standards (TPHP, TCIPP, TDCIPP, TCEP, TBOEP, EHDPP, TEHP, TNBP) and internal (surrogate) standards ($^{13}C_{18}$-TPHP, d_{15}-TDCIPP, d_{12}-TCEP, $^{13}C_2$-TBOEP, d_{27}-TNBP) were purchased from Wellington Laboratories (Guelph, ON, Canada). The internal standards (d_{18}-TCIPP and d_{51}-TEHP) were purchased from Chiron and Toronto Research Chemicals respectively. In addition, PCB-62 is used as a recovery determination (syringe) standard. Iindividual native PCBs (PCB-11, PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-

180), internal (surrogate) standards (PCB-34, PCB-62, PCB-119, PCB-131, and PCB-173), and recovery determination (syringe) standards (PCB-29 and 129) were purchased from Greyhound Chromatography (Birkenhead, Merseyside, UK). Individual native PBDE standards (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-209), internal standards (BDE-77, BDE-128 and ^{13}C-BDE-209), recovery standards (^{13}C-BDE-100) were purchased from Wellington Laboratories (Guelph, ON, Canada). High purity (HPLC grade) solvents and reagents were used for all analytical procedures and were purchased from Fisher Scientific (Loughborough, UK) and Sigma- Aldrich (St Louis, MO, USA).

2.3. Sample extraction

Prior to instrumental analysis, samples were subjected to solvent extraction and extract purification as follows. For OPEs: 2 g of sediment (0.1 g for biosolids) were spiked with 50 ng of mixed internal standard, and 2 g of copper powder added. The samples were mixed with 5 mL n-hexane:acetone (1,1 v/v), vortexed for 1 min, followed by ultra-sonication for 15 min, before centrifugation at 3500 rpm for 5 min. Following this, the supernatant was transferred into a centrifuge glass tube. This extraction procedure was then repeated twice. The combined extracts were concentrated to a volume of ~1 mL and loaded onto Florisil SPE cartridges (2 g, 15 mL) which were preconditioned with 6 mL hexane. Following sample loading, the cartridge was washed with 10 mL of hexane (discarded), and eluted with 10 mL of ethyl acetate to obtain the target contaminants. The elute was concentrated to incipient dryness and reconstituted in 100 μL toluene with 50 ng of the recovery standard PCB-62.

For PCBs and PBDEs: 1 g of sediment samples (0.1 g for biosolids samples) were spiked with 15 ng BDE-77, BDE-128 and 13C-BDE-209, 20 ng mixture PCB internal standards, and treated with 1 g copper powder. The samples were mixed with 5 mL n-hexane:acetone (3:1 v/v), vortexed for 5 min, sonicated for 20 min and centrifuged at 3500 rpm for 5 min. Supernatants were transferred to a clean tube and the extraction process repeated three times. After extraction, the combined supernatants were reduced to incipient dryness under a gentle stream of N_2 and reconstituted in 1 mL of n-hexane. To this concentrate was added 4 mL sulfuric acid (95 %), which was vortexed and left overnight for the layers to separate. After this the sample was centrifuged at 3500 r/min for 5 min, the organic layer removed, and the acid layer was washed twice with 2 mL n-hexane. The washes were combined with the organic layer and evaporated under N2 to ~0.5 mL. Sample concentrates were then transferred onto a 1 g Florisil SPE column pre-cleaned with 10 mL n-hexane. The column was eluted with 10 mL hexane:DCM (1:1 v/v). The eluate was evaporated under nitrogen flow to incipient dryness before reconstitution in 50 μL of toluene containing ^{13}C-BDE-100 at 300 pg/μL and PCB-29, PCB-129 at 400 pg/μL as recovery standard.

2.4. Instrumental analysis

Analysis of the target OPEs and PCBs was carried out on a GC Agilent 6850/5975C MSD with 1 μL of extract introduced via splitless injection onto a Restek Rxi-5Sil MS column (30 m × 0.25 mm × 0.25 μm film thickness). Analysis of PBDEs was carried out on Trace 1310 GC coupled to an ISQ single quadrupole mass spectrometer (Thermo Scientific, TX, USA) with a capillary fused silica column (RESTEK, USA, 15 m × 0.25 mm inner diameter, 0.1 μm film thickness). All the compounds were analysed in electron ionisation (EI) and selected ion monitoring (SIM) mode. GC/MS conditions for the analysis of OPEs and PCBs were as follows.

For OPEs, 1 μL sample extract was injected at 290 °C in splitless mode for 1 min. The flow of He was 1 mL/min. The oven program was 65 °C for 0.75 min, ramp at 20 °C/min to 250 °C, hold for 1 min, ramp at 5 °C/min to 260 °C, ramp at 30 °C/min until 305 °C, and hold for 1 min. Temperatures of the ion source, quadrupole and interface were set at: 230 °C, 150 °C and 300 °C respectively. For PCBs, 1 μL sample extract

Table 1
Available metadata for biosolid samples collected from 7 WWTPs in Ireland.

WWTP Site Reference #	Population equivalent (PE) Band	Output flow band (m³/day)	Types of biosolids treatment
WWTP 1	> 100,000	> 30,000	Advanced AD
WWTP 2	> 100,000	> 30,000	AD, TD
WWTP 3	> 100,000	> 30,000	AD, TD
WWTP 4	>100,000	>30,000	THP, AD
WWTP 5	2000 - 50,000	1000 - 10,000	AD, P
WWTP 6	2000 - 50,000	1000 - 10,000	AD, TD
WWTP 7	50,000-100,000	10,000 - 30,000	LS

AD = Anaerobic Digestion; TD = Thermal Drying; THP = Thermal Hydrolysis Processing; P = Pasteurization; LS = Lime Stabilisation.

was injected at 250 °C in splitless mode for 1 min. The flow of He was set at 1 mL/min. The oven program was 80 °C for 3 min, ramp at 20 °C/min to 180 °C, and hold for 2 min, ramp at 10 °C/min to 290 °C, hold for 8 min. Temperatures of the ion source, quadrupole and interface were set at: 230 °C, 150 °C and 280 °C respectively. For PBDE: 1 μL sample extract was injected at 90 °C in splitless mode for 1 min. The flow of He was set at 1.5 mL/min. The oven program was 80 °C for 2 min, ramp at 20 °C/min to 170 °C, and hold for 5.5 min, ramp at 25 °C/min to 320 °C, hold for 10 min. Temperatures of the ion source and MS transfer line were set as 280 °C and 320 °C.

2.5. Data analysis and risk assessment

For comparisons of mean concentrations determined with various metadata recorded (population density, sediment type, river flow speed, and year of collection for sediments; population equivalent (PE), treatment type, and month of collection for biosolids) non-parametric statistical tests are used as data cannot be assumed or are not observed to follow a specific distribution. For two sample means, Mann-Whitney *U* tests were used while for greater number Kruskal Wallis H tests were used (confidence interval of 95 %, Significance Level (p) of 0.05). Where data was recorded to be below the limits of detection (LoD), for the purposes of statistical analysis calculations, proxy values were determined using {LOD × Detection Frequency}. Where appropriate and noted, graphed data omits data points below limits of detection and reports the statistical metrics along with the detection frequency for the relevant parameter(s).

Risk Quotients (RQs) were employed to evaluate ecotoxicological risks for targeted compounds in sediment samples collected in inland and transitional sediments in 2023 (Carvalho et al., 2015). RQs were calculated per the following equation:

$$RQ = \frac{MEC_{95}}{Lowest\ PNEC}$$

where MEC$_{95}$ is the 95th percentile of the maximum measured environmental concentration from collected samples herein and lowest predicated no-effect concentrations (PNEC) in sediments are taken from the Norman Ecotoxicology Database (NORMAN, 2024). Degree of risk was assessed based on resulting risk quotient: RQ > 1 high risk; 1 > RQ > 0.1 = moderate risk; RQ < 0.1 = low risk.

3. Results and discussion

### 3.1. Flame retardants in inland and transitional sediments

Table 2 and Fig. 2 report concentration data for 24 PBDEs, OPEs, and PCBs in transitional and inland sediment samples collected in 2023 (full breakdown available in SI 1.1). No significant differences were shown between inland and transitional sediments for any of the BFRs or OPEs (SI 3.2, 3.3). Uniquely among the contaminants targeted in this study, most PCB congeners measured were more likely to be found at higher concentrations in transitional compared to inland sediments (p-value: PCB-11, -52, -101, -153, -138 << 0.05; PCB-180 = 0.051; PCB-28, -118 > 0.05). This trend remains even when accounting for several samples which have much higher PCB concentrations – 2-10 times higher than the next highest $\sum$PCB$_8$ level. This is potentially due to the reduction in use of PCBs over the last 20 years since their formal restriction in Ireland (EPA, 2021) and the washing-out of PCBs from rapidly moving inland waters to transitional waters where slower turnover is occurring (Nisbet and Sarofim, 1972). Meanwhile for more recently restricted FRs (e.g. PBDEs) as well as those increasing in use as replacements (OPEs), uptake is likely still occurring and accumulating in both types of water bodies. However, no clear trends were identified in magnitude or speed of river flow with measured concentrations (SI 3.4), though relatively low sample number and the samples being superficial grabs in nature may limit the significance of this test. Two coastal sites had elevated PCB concentrations perhaps related to significant shipping and industrial activity, though no such obvious sources exist at other areas of elevated concentration.

Concentrations reported in this study are higher than reported environmental background concentrations for in inland and transitional sediments (OSPAR, 2022). Samples taken near to known WWTP discharge points were not shown to have higher overall concentrations compared to samples taken from isolated areas (p > 0.05). These findings align with Onoja et al. (2023) on OPE concentrations in UK freshwater sediments, which found that concentrations of OPEs in sediments taken upstream and downstream from WWTPs did not differ significantly. Martinez-Carballo et al. (2007) similarly showed no significant differences in OPEs upstream and downstream from a WWTP in Vienna, though indicate that higher concentrations of TCIPP and TBEB may be linked to WWTP outfalls. Data presented herein find that population size showed little significance in terms of concentration trends. Even for those chemicals for which there were statistically significant differences in regions (TEHP, TCEP, and EHDPP), there were no clear indicators as to which population sizes would result in higher levels of target

Table 2
Summary statistics for BFRs (PBDEs), OPEs, and PCBs in 81 inland and transitional sediment samples collected in 2023.

ng/g	BDE-28	BDE-47	BDE-100	BDE-99	BDE-153	BDE-154	BDE-183	BDE-209
Mean	<0.26	0.07	0.19	0.28	0.37	0.04	0.08	6.93
Median	<0.26	0.04	0.04	<0.19	0.05	<0.03	<0.03	0.79
Range	–	<0.02–0.38	<0.02–4.44	<0.19–2.95	<0.02–4.24	<0.03–0.30	<0.03–0.83	<0.15–110
DF (%)	0	77.8	90.1	12.3	69.1	49.4	49.4	86.4

ng/g	TCEP	TCIPP	TDCIPP	TBOEP	TEHP	TNBP	TPHP	EHDPP
Mean	1.83	5.19	0.24	27.64	3.93	0.25	0.41	0.88
Median	1.13	2.24	0.04	24.54	1.15	0.14	0.27	0.28
Range	<0.02–33.8	<0.03–70.2	<0.04–15.3	<0.1–214	<0.02–58.9	<0.02–3.19	<0.01–23.7	<0.01–23.7
DF (%)	75.9	61.7	88.9	71.6	59.3	97.5	61.7	95.1

| ng/g	PCB-11	PCB-28/31	PCB-52	PCB-101	PCB-118	PCB-153	PCB-138	PCB-180
Mean	0.003	0.035	0.267	0.128	0.118	0.179	0.181	0.091
Median	<0.016	<0.008	0.095	0.046	0.081	0.086	0.084	0.034
Range	<0.016–0.061	<0.008–2.333	<0.013–4.339	<0.015–5.262	<0.013–2.010	<0.013–4.773	<0.045–4.582	<0.021–1.366
DF (%)	4.9	11.1	98.8	74.1	72.8	75.3	66.7	70.4
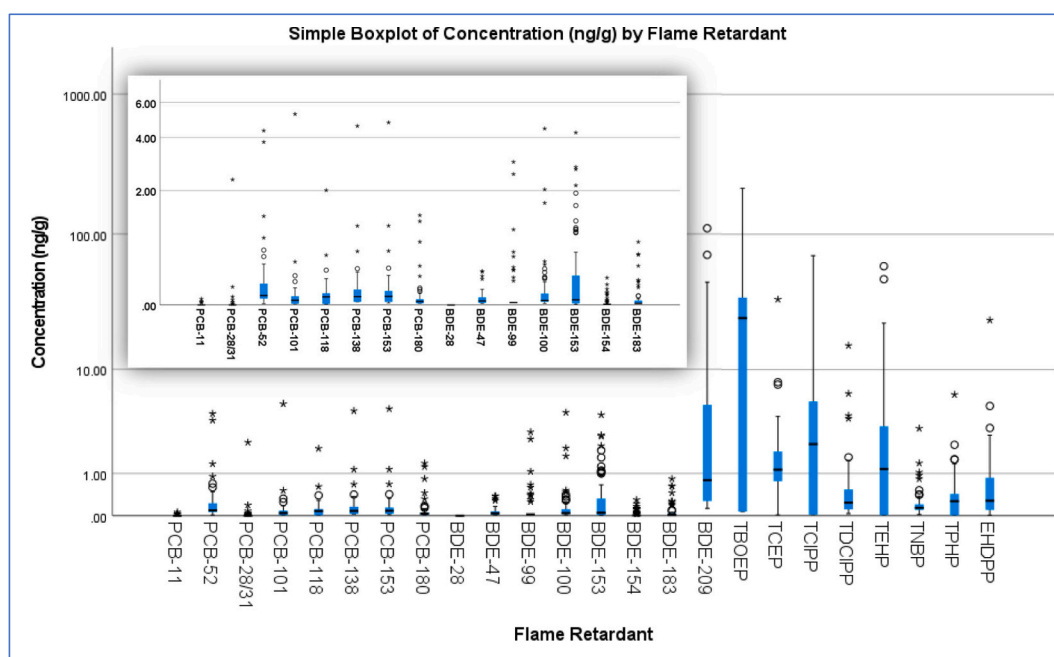
Fig. 2. Average concentrations of PCBs, PBDEs and OPEs in 81 inland and transitional samples collected around Ireland. Embedded graph shows blown-up view of PCB and PBDE compounds (sans BDE-209) for clearer discernment of lower concentration values. Blue shaded bars with central black lines denote the median and interquartile range (IQR); lower whiskers denote minimum values; upper whiskers denote [1.5 × IQR]; open circles denote outliers (> 1.5 × σ); stars denote extreme outliers (> 3 × σ).

contaminants overall (*SI 3*). Though low sample numbers per population group are a likely contributor to the lack of a clear trend and a number of other variables such as treatment type may also factor in, the lack of correlation may indicate that population alone is not the major factor in high concentrations of these contaminants. This is supported by trends seen in biosolid samples (see Section 3.2) where elevated levels of certain FRs were not correlated with higher WWTP population equivalents. Onoja et al. (2023) furthermore found highest levels of OPEs in an urban location not impacted by a WWTP, suggesting that OPEs may be removed or broken-down by certain WWTP processes. Contrastingly,

results found in this study showed elevated concentrations of OPEs and BDE-209 in samples taken both near to and isolated from WWTP outfalls. These disparate findings highlight that the behaviour of these compounds within WWTPs and their exact sources of environmental uptake are not yet fully understood.

Comparing levels of target contaminants in sediments in Ireland with other studies worldwide, overall levels of BFRs and OPEs are on the moderate range compared to similar surveys: levels of PBDEs in Ireland are significantly lower than those seen in Japan, the Netherlands, and the UK, though slightly higher than in other areas of Europe; while levels
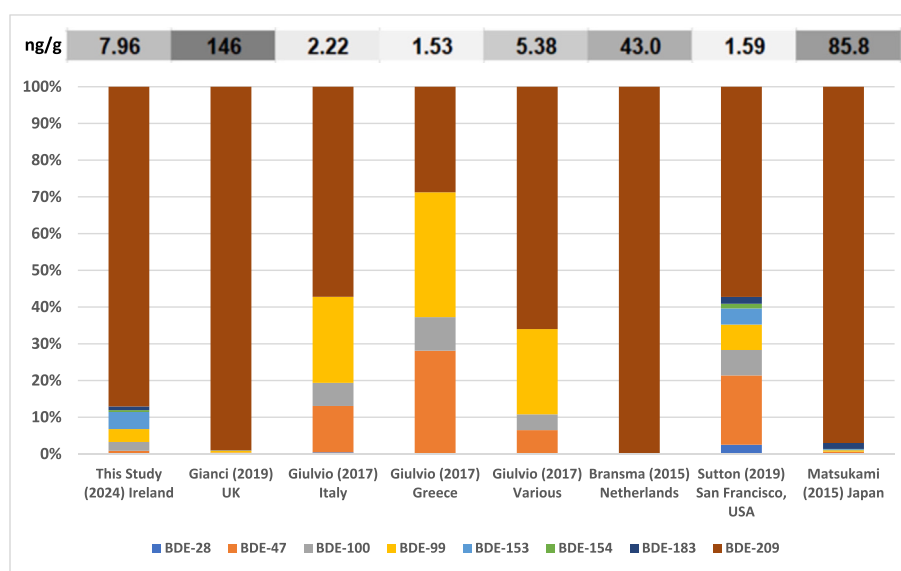
Fig. 3. Concentrations of PBDEs and percent contributions to ΣPBDEs in Ireland (this study) vs other studies worldwide. Values above the bars represent total average Σ$_8$PBDE concentrations (ng/g) quantified in each study (see S1.2 for in-depth information on Individual studies) (Gianci et al., 2019; Giulvio et al., 2017; Brandsma et al., 2015; Sutton et al., 2019; Matsukami et al., 2015). *"Various" samples taken by Giulvio et al. (2017) cover a range of locations in Slovenia, Croatia, Bosnia & Herzegovina, and Serbia.

of OPEs are higher than seen in Greece, the Netherlands, USA, and Japan, and lower than appear in other studies (Figs. 3 & 4; *SI 1.2 & 1.3*). The dominance of BDE-209 in Ireland aligns with other studies and reflects the phase-out of Penta- and Octa-BDE formulations following their restrictions in the early 2000s (Harrad et al., 2020b) compared to the more recent restriction and phase-out of Deca-BDE (Sharkey et al., 2020). The congener profile of OPEs are meanwhile less straightforward as the length and breadth of their usage and applications are not as well-known as the more studied PBDEs. Some specific OPE compounds such as TBOEP, TCIPP, and TEHP are prominent in Ireland as well as other EU countries, while TDCIPP is more prominently found in China, USA, Australia, and Japan. Irish and UK sediments are similar in terms of congener profile and magnitude, likely due to similar fire safety standards and the sizable UK market share in Ireland (CSO, 2017). It should be highlighted that not all OPEs included herein were analysed in all of these studies, TBOEP and TNBP being notably absent from the majority of these studies.

In the case of PCBs, a more direct comparison of levels in Ireland with other countries can be made via data reported through OSPAR's coordinated Environmental Monitoring Programme (CEMP), which currently has data and seasonal trend analysis for 7 countries in Europe (Ireland, UK, Spain, France, Germany, Belgium, and The Netherlands) (OSPAR, 2024). Concentrations reported in this study for both inland and transitional sediments are similar in magnitude to those reported to OSPAR in the years where data are available. While no clear upward or downward trends are yet discernible based on available data, for almost all PCBs these largely fall below Background Assessment Criteria (BAC) and Environmental Assessment Criteria (EAC). Concentrations in Ireland are low compared to other European countries, with the exception of a few sites where PCBs 101 and 118 are slightly above EACs. Where sufficient data is available and trends can be discerned, the majority of countries report decreasing levels over time of PCBs in sediments being monitored. While continued monitoring is warranted, with the restrictions currently imposed on PCBs and the global trend in reduction of use, it is unlikely that levels of PCBs in the Irish environment will increase significantly if at all. PCB-11 is somewhat distinct from other congeners analysed here, as a by-product from certain processes (e.g. pigment production) as opposed to deliberate use in applications (Vorkamp, 2016). Likely due to the comparatively small chemical manufacturing (of this type) industry in Ireland, PCB-11 is present here at a markedly lower detection frequency and mean

concentration compared to other congeners which, while not manufactured here, were used in various applications such as paints, anti-corrosive coatings, flooring compounds, and window sealants until their restriction (EPA, 2021).

In terms of ecotoxicological risk, risk quotients based on MEC_{95} concentrations for each compound (see *SI 1.4*) show moderate risk for in sediments for PCB-52, PCB-118, TEHP, and EHDPP, and PCB 118 ($0.1 < RQ < 1$) and high risk for TCIPP ($RQ > 1$). For individual sites, TCIPP, EHDPP, and PCB-118 are present at concentrations congruent with moderate or high risk at over half of sites assessed (60 %, 54 %, and 71 % respectively). While other compounds exceed the low-risk quotient at some sites, these are largely driven by a small number of samples with excess concentrations of multiple chemicals indicative of as-yet undetermined point source pollution at these sites.

3.2. Concentrations of FRs in WWTP-derived biosolids

Concentrations of target contaminants in biosolid samples are presented in Fig. 5 and Table 3 (detailed statistics available in *SI 2*). As expected, higher concentrations of all chemicals were present in biosolid samples compared to those found in inland and transitional sediments, likely due to the amalgamation and concentration of contaminants from influents entering WWPTs. By a significant margin, BDE-209 and TBOEP were found at the highest concentrations in biosolids. With restrictions only coming into force across the EU since 2019 (EU, 2019), BDE-209 has previously been reported as the most prevalent BFR in Irish waste furniture and electronics (Harrad et al., 2019; Harrad et al., 2023b) and landfill leachate (Harrad et al., 2020c). The high lipophilicity of BDE-209 means that more of this chemical will partition to the solid fraction of waste compared to the liquid, the fraction which in turn makes up the composition of biosolids. For TBOEP – as well as other OPEs present in relatively high abundance such as EHDPP, TEHP, and TCIPP – solid/liquid partitioning behaviour may not inform the levels found herein due to their being comparably less lipophilic than BDE-209. It is however notable that OPEs like TCIPP were found to be highly prevalent in Irish end-of-life furniture, furnishings, and childcare articles (Harrad et al., 2023b) at levels far exceeding those detected for BFRs, further suggesting their widespread use in consumer goods. TBOEP specifically has been shown to be among the most abundant OPEs in UK indoor dust (Gbadamosi et al., 2022) and sediments (Onoja et al., 2023). While landfill leachate is noted as a potential source of FRs into WWTPs and
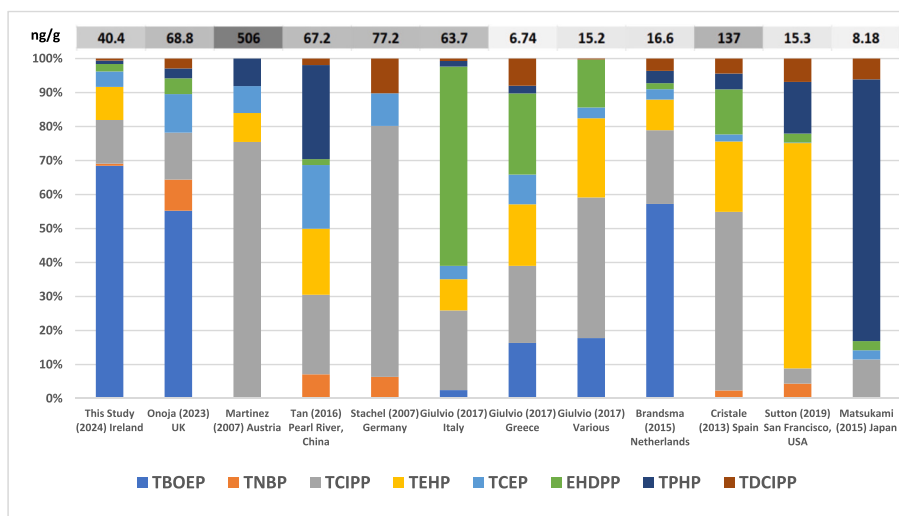

Fig. 4. Concentrations of OPEs and percent contributions to ΣOPEs in Ireland (this study) vs other studies worldwide. Values above the bars (ng/g) represent total average Σ_8OPE concentrations quantified in each study (see S1.3 for in-depth information on Individual studies) (Onoja et al., 2023; Martinez-Carballo et al., 2007; Tan et al., 2016; Stachel et al., 2007; Giulvio et al., 2017; Brandsma et al., 2015; Cristale et al., 2013; Sutton et al., 2019; Matsukami et al., 2015). *"Various" samples taken by Giulvio et al. (2017) cover a range of locations in Slovenia, Croatia, Bosnia & Herzegovina, and Serbia.
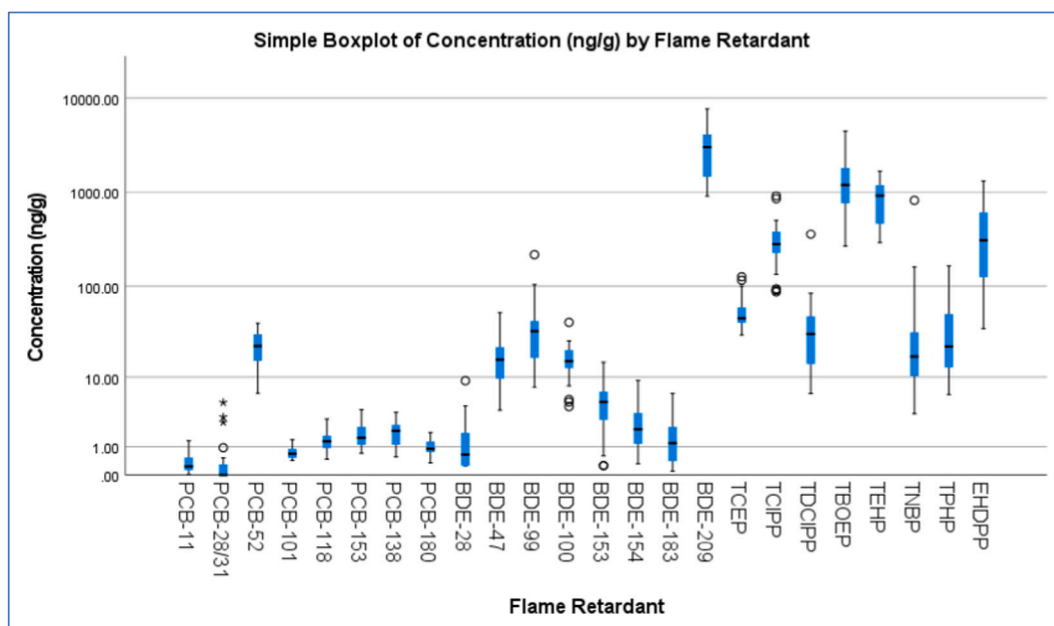
Fig. 5. Average concentrations of PCBs, PBDEs and OPEs in biosolid samples from 7 WWTPs around Ireland. Blue shaded bars with central black lines denote the median and interquartile range (IQR); lower whiskers denote minimum values; upper whiskers denote [1.5 × IQR]; open circles denote outliers (> 1.5 × σ); stars denote extreme outliers (> 3 × σ).

Table 3
Summary statistics for BFRs (PBDEs), OPEs, and PCBs in 21 biosolid samples collected in 2023.

ng/g	BDE-28	BDE-47	BDE-100	BDE-99	BDE-153	BDE-154	BDE-183	BDE-209
Mean	1.37	17.4	15.9	41.2	5.26	2.57	1.72	3160
Median	0.66	15.8	15.2	32.7	4.97	2.06	1.19	3030
Range	<LOD–9.1	3.9–51.8	4.34–40.8	7.57–217	0.26–14.7	0.33–9.12	0.1–6.33	908–7700
DF (%)	100	100	100	100	100	100	100	100

ng/g	TCEP	TCIPP	TDCIPP	TBOEP	TEHP	TNBP	TPHP	EHDPP
Mean	57.6	338	49.2	1410	900	66.9	42.1	423
Median	45.2	281	30.5	1200	917	17.1	22.3	309
Range	29.7–123	87.0–915	6.30–358	267–4460	292–1670	3.48–819	6.15–165	34.9–1320
DF (%)	100	100	100	100	100	100	100	100

ng/g	PCB-11	PCB-28/31	PCB-52	PCB-101	PCB-118	PCB-153	PCB-138	PCB-180
Mean	0.369	0.596	22.75	0.758	1.332	1.713	1.907	1.002
Median	0.238	<LOD	22.50	0.688	1.282	1.492	1.942	0.905
Range	<LOD-1.319	<LOD-4.896	39.93	1.380	2.946	3.952	3.648	1.830
DF (%)	95.2	28.6	100	100	100	100	100	100

resulting biosolids, other avenues may also exist for their uptake from source (i.e. treated materials) to wastewater, such as accumulation in household dust which are then taken into domestic wastewater while cleaning. Where data are available regarding the quantities of domestic, industrial, and landfill influent into the WWTPs where biosolid samples were obtained (Uisce Eireann, 2024b), no clear trends could be discerned relating a single influent stream (domestic, industrial, landfill, or other) to elevated levels of any FR. Limited sample numbers may play a factor in not seeing clearer trends, though this may also point to these FRs being prevalent across wastewater influents as opposed to solely from landfilling of contaminated wastes.

Concentrations of PBDEs reported in the current study are compared to international data in Fig. 6 and suggest that levels in Ireland are at the higher end of those internationally: comparable with levels detected in Australia, the UK, and South Korea, though markedly lower than levels found in the USA. The USA is notably one of the highest reported users of

BFRs worldwide (FMI, 2024; FRs-Online, 2020; ECHA, 2023) and likewise – as of 2020 – had not ratified the Stockholm Convention regarding the use of POP-BFRs in consumer goods or screening from waste materials (Sharkey et al., 2020). This disparity is further highlighted in Fig. 6 by the breakdown of PBDE congeners detected in wastes with most studies conducted in the last 20 years showing almost entirely BDE-209 while the USA also showing significantly higher levels of commercial Penta- and Octa-BDE congeners. OPE concentrations (Fig. 7) are meanwhile the highest in Irish biosolids compared to levels reported worldwide. TBOEP and EHDPP are dominant in Irish biosolids though this profile differs significantly from those in China, Spain, and the USA. While the overall higher levels in Irish biosolids are likely a result of the stringent furniture fire safety regulations which lead to higher levels of FRs, particularly OPEs, than the European average (ECHA, 2023), the specific profile of OPEs found are more likely related to types of materials treated/used as well as their manufacturing origin. Notably, while
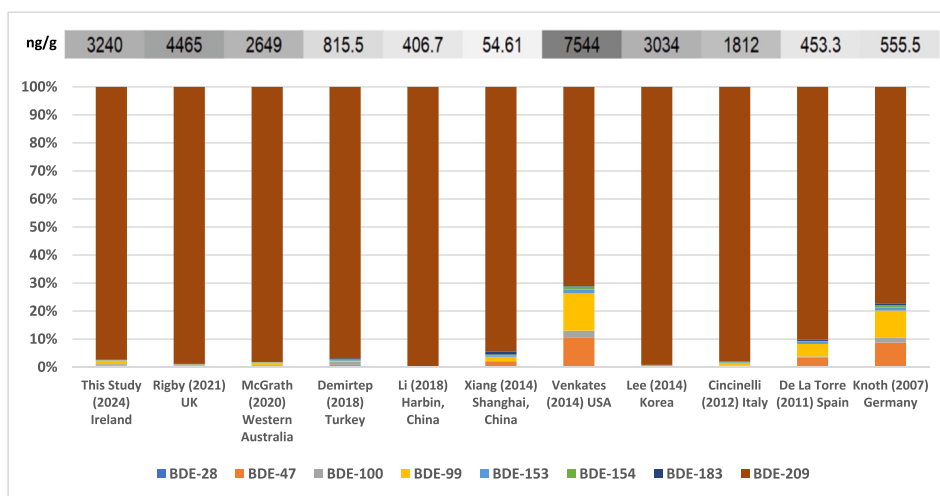
Fig. 6. Concentrations of PBDEs and percentage Σ₈PBDEs in WWTP-derived biosolids from similar studies conducted worldwide. Values above the bars (ng/g) represent total average concentrations quantified in each study (see S2.1 for in-depth information on Individual studies) (Rigby et al., 2021; McGrath et al., 2020; Li et al., 2018; Demirtep and Imamoglu, 2018; Xiang et al., 2014; Venkatesan and Halden, 2014; Lee et al., 2014; Cincinelli et al., 2012; De La Torre et al., 2011; Knoth et al., 2007).
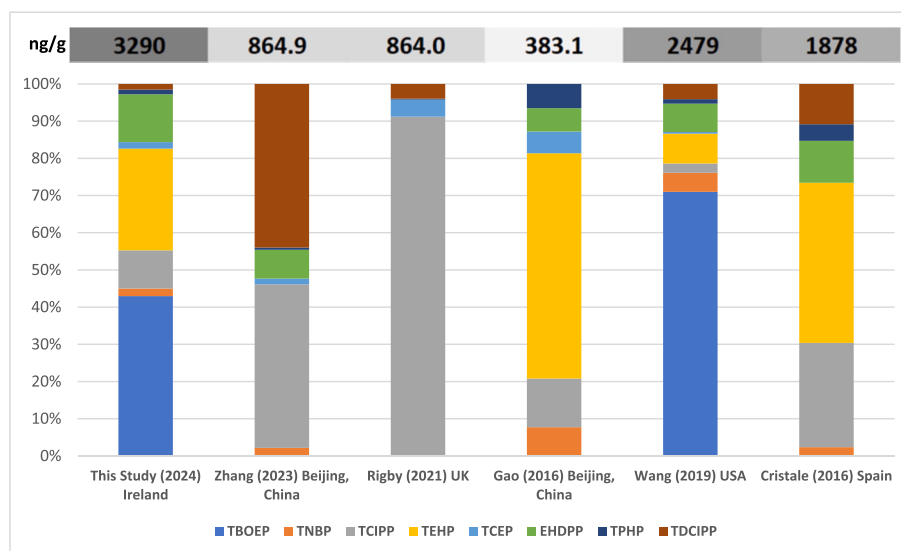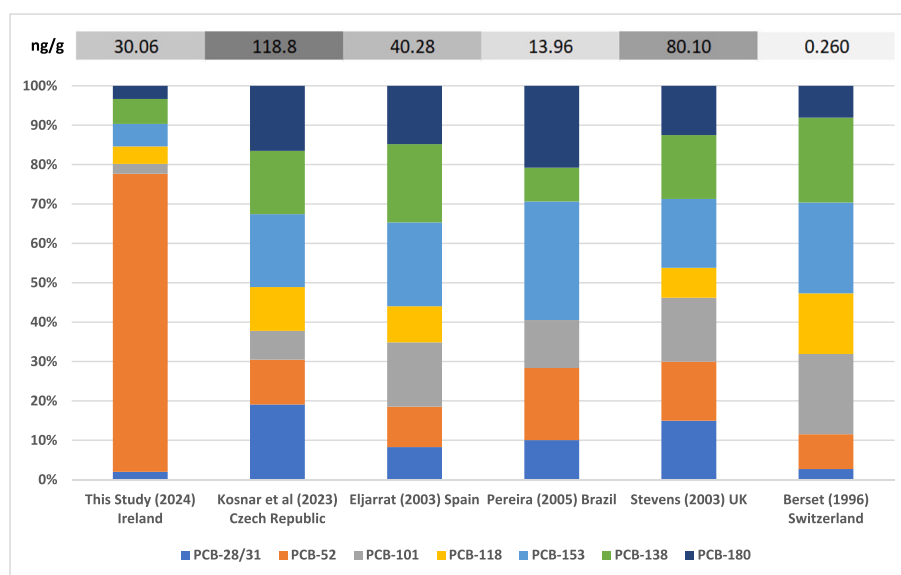

Fig. 7. Concentrations of OPEs and percentage Σ₈OPEs in WWTP-derived biosolids from similar studies conducted worldwide. Values above the bars (ng/g) represent total average concentrations quantified in each study (see SI 1.3 for in-depth information on Individual studies) (Zhang et al., 2023; Rigby et al., 2021; Gao et al., 2016; Wang et al., 2019; Cristale et al., 2016).

levels are higher than those in the UK, the profile of measured OPEs is similar: high levels of TCIPP, and comparably low levels of TCEP, TPHP, and TDCIPP. PCBs in Irish biosolids meanwhile are on the middle to lower end of levels found worldwide (Fig. 8). While stringent fire safety standards may point to the high usage of BFRs and OPEs, PCBs were used as FRs in a comparatively minor capacity being more typically used in other applications such as dielectric fluids and permanent elastic sealants. The similar lack of a manufacturing sector for PCBs as for other FRs in Ireland coupled with the less prevalent use may therefore point to the lower levels found in Irish biosolids. THE EPA's report on PCB Applications in Ireland (EPA, 2021) highlights the difficulty in linking specific commercial mixtures to certain applications, or obtaining profiles on the PCBs present in those mixtures. While many mixtures contain combinations of the seven PCB congeners studied herein (i.e. not including PCB-11), it is unclear as to why PCB-52 is comparatively more present in these samples. It is however notable that studies of UK indoor environments similarly revealed abnormally higher levels of PCB-52

compared to other congeners (Currado and Harrad, 1998). It should be noted that variations between sampling and analysis methodologies exist between studies such as different extraction methods, drying procedures, and analysis methods. Minor variations in quantified data could therefore occur, but a direct comparison is utilised here in-lieu of a harmonised methodology.

Comparisons were made for levels of target compounds found in samples based on treatment types (*SI 4.2*). However, low sample numbers ($n = 3$ each) mean that statistically significant trends were not discernible with the exception of those samples which underwent Anaerobic Digestion (AD) and Thermal Drying (TD) ($n = 9$). In these cases, AD/TD was not shown to result in significantly higher or lower levels than other treatment types. While it may still be possible that the specific WWTP treatment process may have an influence on treated water effluent and biosolids with regards to OPFRs and BFRs, resolute conclusions from results gathered herein cannot be drawn. Typical treatment methods (anaerobic digestion, thermal drying, etc.) are not

Fig. 8. Concentrations of PCBs and percentage Σ_8PCBs in WWTP-derived biosolids from similar studies conducted worldwide. Values above the bars (ng/g) represent total average concentrations quantified in each study (see SI 1.3 for in-depth information on Individual studies) (Kosnar et al., 2023; Eljarrat et al., 2003; Pererira and Kuch, 2005; Stevens et al., 2003; Berset and Holzer, 1996).

however designed to remove such chemicals during processing. Any correlations would therefore be incidental and are likely more prominently driven by the chemistry of the compounds themselves. This highlights that while initial trends may be discerned from grab samples such as conducted here and in comparable studies, much larger sample numbers and independent variable considerations are required to draw statistically significant conclusions. More significant trends were however observed related to the population equivalent of the WWTPs (*SI 4.3*). For several BFRs and PCBs, higher concentrations were frequently detected in WWTPs of "medium" size (PE of 50,000–100,000), while for OPEs higher concentrations were found in the largest WWTPs (PE > 100,000) with levels also following a generally linear trend.

Samples were taken from each of the seven WWTPs at four-month intervals ($7 \times 3 = 21$ total). Box plots of average concentrations and intervals are shown in *SI 4.4*. While plots superficially suggest increasing concentration trends from January and September, no statistically significant trends of this type are seen due to the relatively high variance in. Results do however show that the highest variance in concentrations detected for most FRs occurs in samples which were collected in September, possibly related to higher rainfall with average rainfall across all seven sites in January, May, and September recorded as 79.1, 47.8, and 121.5 mm respectively (MET Éireann, 2024). Higher levels of rainfall may significantly affect influent to WWTPs, potentially by dilution or by increasing of storm overflow diverting wastewater from treatment where capacity is exceeded A recent review in the UK concluded that there is a high likelihood that chemical contaminants in untreated wastewater are released via storm overflow during heavy rainfall or flood events where the capacity of sewage networks are exceeded (Tipper et al., 2024). Though exact figures are unavailable, storm overflows are reportedly regularly used in Ireland during periods of heavy rainfall (IRP, 2022; EPA, 2023).

3.3. Temporal trends of OPEs in transitional sediments

Reported here are concentrations of OPEs in transitional sediments from stored historical samples (2018–2022) with concentrations of PBDEs and PCBs reported elsewhere (ICES, 2024). Higher average concentrations are reported for these historical samples compared to those reported for samples collected in 2023 (both inland and transitional). However, as collection, preparation, and analytical procedures

were virtually identical, this difference is likely due to the difference in grain-size processed for each analysis: 2023 samples being sieved to 2 mm; historical samples being sieved to 63 μm (Fig. 9). This highlights that grain size is a key factor which should be considered when evaluating OPE concentrations in environmental matrices as smaller particles typically accumulate more pollutants, similar to the evaluation of toxic metals (Ozseker et al., 2022; Asomba et al., 2023).

To assess if any temporal variations in concentrations are evident between 2018 and 2022, Kruskal-Wallis H-tests were carried out for all OPEs comparing concentrations in historical transitional sediments as a function of year of collection. For each OPE, no statistically significant ($p \gg 0.05$) increase nor decrease in concentration as a function of year was determined (Table 4). Even omitting 2022 data, for which only two samples were collected, does not improve the significance sufficiently. Indeed, the change in calculated *p*-values when omitting these data points highlights volatility of these results. Table 5 below shows concentration data for replicate samples taken at roughly the same sampling points, using the same sampling and analysis methodologies, though in different years which highlights the moderate degree of variance though also the relative consistency of hotspots between years. At one site, three samples were taken within the same area in the same year showing a mean and standard deviation for Σ_8OPEs of 81.45 ± 26.36 ng/g. Several factors may influence this variance such as: slight spatial difference in the sampling locations between years; natural small-scale spatial variations in concentration which may be missed with grab sampling; or increased or decreased environment uptake of chemicals. As such, though reasonably reliable average concentration can be reported here and for sediments collected in 2023, temporal trends cannot be adequately discerned due to relatively high inter-site sample variance and potential spatial variances from different sites being assessed each year.

While variation is observed in samples collected, both between years and within this singular site, the nationwide averages do not appear to be appreciably changing between years for OPFRs. Significant increases over time would point either to increased usage of FRs in goods thus leading to increased environmental uptake, or accumulation in these matrices over time. Significant decreases would conversely point to less usage and/or rapid break-down over time; OPFRs being shown to metabolise much more rapidly when compared to PBDEs (Gibson et al., 2018). The relatively consistent levels therefore indicate a relatively
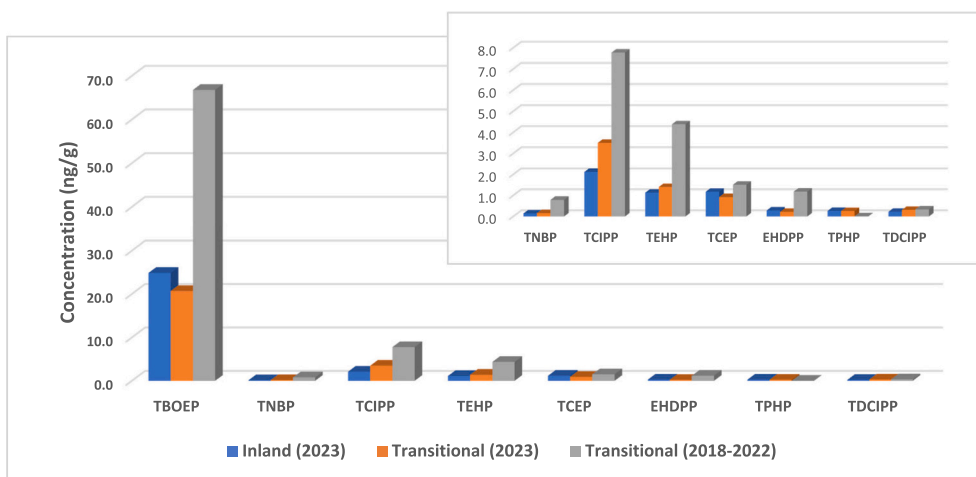
Fig. 9. Comparison of mean concentrations of OPEs in Inland and transitional sediment samples collected in 2023 and in 2018–2022 (inserted sub-graph (upper-right) highlights OPEs other than TBOEP for clarity).

Table 4
Statistical significance of differences of means between OPEs for marine and inland sediments (Mann-Whitney *U* Test).

	EHDPP	TBOEP	TCEP	TCIPP	TDCIPP	TEHP	TNBP	TPHP
p-value (2018–2022)	0.339	0.324	0.240	0.394	0.097	0.488	0.409	0.136
p-value (2018–2021)	0.200	0.901	0.616	0.669	0.225	0.217	0.133	0.063

Table 5
Replicate samples taken at the same site in different years between 2018 and 2022 (inclusive).

Site Ref #	Collection Year	Concentration (ng/g dw)							
		TBOEP	TNBP	TCIPP	TEHP	TCEP	EHDPP	TPHP	TDCIPP
1	2019	133	0.72	8.26	4.31	2.18	2.12	0.01	0.27
1	2020	54.0	0.02	8.43	2.48	2.11	0.48	0.01	0.07
1	2021	60.4	0.02	0.03	0.02	1.67	0.62	0.01	0.38
2	2018	80.8	1.08	7.99	5.98	0.02	0.97	0.01	3.90
2	2019	85.9	0.64	9.85	4.22	1.94	3.62	0.92	1.27
2	2020	86.4	0.98	7.56	3.18	2.04	0.66	0.01	0.24
2	2021	60.0	0.74	8.19	6.59	2.11	2.39	0.01	0.57
3	2019	78.7	0.46	4.88	7.55	0.02	0.67	0.01	0.88
3	2020	78.2	1.61	20.6	32.6	0.02	12.8	0.64	0.28
3	2021	167	6.55	25.9	30.7	1.77	14.0	1.03	0.82

consistent uptake of OPEs into the environment, likely due to the majority of these chemicals being unrestricted and fire safety standards leading to their continued use.

4. Conclusions

Concentrations of targeted BFRs, OPEs, and PCBs contaminants in sediments are broadly similar to those found in other countries worldwide, though their benthic sources of their uptake are as-yet unknown. Levels found in Irish sediments are shown to present a low ecotoxicological risk for the majority of contaminants assessed, with a few exceptions (TCIPP, EHDPP, TEHP, PCB-118, and PCB-52) which are at moderate to high risk in over half of the sites sampled. Levels of PBDEs and OPEs in biosolids are at the higher end of those reported internationally, though it is not known to what extent this may result in uptake into and bioaccumulation/biomagnification within the food chain following land-spreading on arable lands. Conclusions on the impact of parameters such as treatment methods (AD, TD, and THP) or the extent to which influent to WWTPs significantly affect the levels of contaminants in biosolids could not be conclusively drawn based on available data. Preliminary results does however indicate that minor variations in seasonal concentrations may occur, while higher levels of and the

dilution of influent to WWTPs may also effect the levels of FRs present in the biosolids produced. Despite restrictions on the use of Deca-BDE in 2019, elevated concentrations ae still found in sediments and biosolids along with high concentrations of replacement FRs such as TBOEP, TCIPP, and TEHP. This suggests widespread use of legacy FRs as well as high prevalence in goods still in circulation as well as high usage of novel replacements and, subsequently, a high degree of uptake of these chemicals into the environment. Risk Quotients quantified for OPEs in particular indicate a moderate to high risk from several of these emerging contaminants in sediments. While effective as a baseline assessment, this study data cannot infer the exact sources of higher concentrations of FRs in sediments or indeed any impact of land-spreading of biosolids on agricultural land and the environmental uptake thereof. A follow up study which includes a more in-depth investigation of regions where concentrations of contaminants approach or exceed PNECs for a given substance is recommended in order to more clearly identify pollution sources. Concomitant with this, an investigation into the potential uptake and impact of FRs to the environment following the land-spreading of biosolids on agricultural lands would be warranted.

CRediT authorship contribution statement

Martin Sharkey: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Shijie Wang:** Writing – review & editing, Validation, Methodology, Formal analysis. **Stuart Harrad:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **William A. Stubbings:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Mark G. Healy:** Writing – review & editing, Project administration, Methodology, Funding acquisition, Conceptualization. **Jingxi Jin:** Validation, Methodology, Formal analysis. **Ann Marie Coggins:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors wish to declare that they have no competing interests that could influence the work reported in this manuscript.

Data availability

Data will be made available on request.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.176582.

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