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Pyrethroids in sediments and wastewater treatment plant-derived biosolids from Ireland

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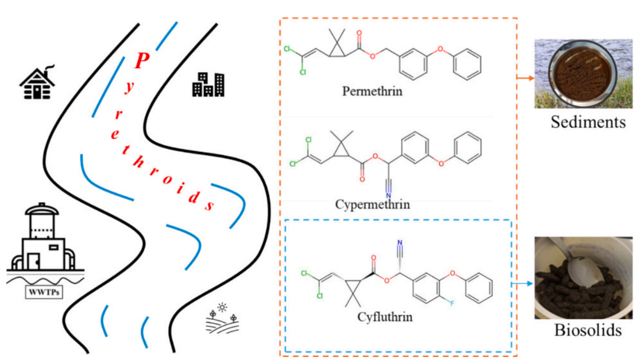
HIGHLIGHTS

- Pyrethroid contamination in Irish sediments and biosolids comprehensively assessed.
- Concentrations in Irish sediment generally within the ranges reported in other countries.
- Pyrethroids detected in all Irish biosolids samples analysed.
- Concentrations in some sediments present high ecotoxicological risk.

GRAPHICAL ABSTRACT



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ABSTRACT

Pyrethroids are widely used synthetic insecticides. This study reports the occurrence, distribution, and ecotoxicological risks of eight pyrethroids in sediments and biosolids from wastewater treatment plants (WWTPs) across Ireland. A total of 120 sediment samples were collected along with 3 biosolids samples from each of seven WWTPs (n = 21). The relative abundance of individual pyrethroids differed between sediment and biosolids samples. Permethrin, cyfluthrin, and cypermethrin were predominant in sediments, with cyfluthrin, permethrin and deltamethrin predominant in biosolids. Such disparities may reflect the anaerobic conditions and shorter residence times of biosolids within WWTPs compared to sediments, which may influence the extent of degradation of our target pyrethroids and drive differences in their relative abundance between biosolids and sediments. Pyrethroid concentrations in Irish sediments were generally within the global range. Among the four pyrethroids currently registered in Ireland (cypermethrin, esfenvalerate, deltamethrin, and λ-cyhalothrin), cypermethrin showed the highest concentrations in sediments, likely reflecting both agricultural, aquacultural, and indoor uses. Meanwhile, permethrin and cyfluthrin, although not registered for plant protection in Ireland, were also prevalent—permissible biocidal uses may explain the presence of permethrin, while cyfluthrin warrants further scrutiny. Risk quotient assessment of pyrethroid concentrations in Irish sediments, revealed that

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while bifenthrin and resmethrin posed low ecotoxicological risks, other pyrethroids such as permethrin, cyfluthrin, and cypermethrin presented moderate to high risk in many sediment samples. These findings highlight the widespread distribution and ecotoxicological risks associated with pyrethroid contamination in Ireland's aquatic environments, emphasising the need for continued monitoring and risk management strategies to mitigate their environmental impacts.

1. Introduction

Pyrethroids are a class of highly effective organic insecticides widely used around the world due to their excellent properties, such as broad spectrum, biodegradable, and low mammalian toxicity (Gu et al., 2024; Zhu et al., 2020). Structurally, pyrethroids are typically classified into two groups based on the absence or presence of a cyano (also known as nitrile) group at the α carbon of the 3-phenoxybenzyl alcohol moiety of the compound (Table S1): Type I pyrethroids, which do not contain the α-cyano moiety (e.g., bifenthrin, resmethrin, and permethrin), and Type II pyrethroids, which contain it (e.g., cyfluthrin, λ-cyhalothrin, esfenvalerate, deltamethrin, and cypermethrin) (Shafer et al., 2005). Due to their widespread use, pyrethroids have been frequently detected in various environmental compartments such as sediments (Chai et al., 2023; Liu et al., 2022), soil (Deng et al., 2020), and biological tissues from animals (Alonso et al., 2012) and human tissues (Babina et al., 2012; Feo et al., 2012).

Pyrethroids enter aquatic systems from multiple sources, including agricultural applications, aquaculture, landscaping, structural pest control, and indoor use (Hladik and Kuivila, 2012); with sources to marine and freshwater sediments likely differing (Méjanelle et al., 2020). Pyrethroids from indoor applications can enter wastewater systems via drain disposal, while outdoor sources may contribute through inflow and infiltration of runoff into the sewer network (Weston et al., 2013c). These pathways lead to the presence of pyrethroids in the influent of wastewater treatment plants (WWTPs) (Weston et al., 2013c; Wheeler et al., 2025). Since conventional WWTPs are not efficient at removing hydrophobic compounds like pyrethroids, they may also be present in treated effluent (Sutton et al., 2019). Sediments are often studied to assess the contamination characteristics of pyrethroids, because the relative hydrophobicity of pyrethroids (log Kow 5 to 7) predisposes them to partition readily into sediments in aquatic environments (Hladik and Kuivila, 2012). When pyrethroids accumulate in aquatic sediment, they may cause harm to organisms, producing severe oxidative stress and histopathological abnormalities (Ahamad and Kumar, 2023). Although studies have shown that pyrethroids are significantly less toxic to mammals than other types of insecticides such as organophosphates and carbamates, they have been linked with neurotoxicity, autism, and reproductive toxicity in humans (Barkoski et al., 2021; Yoo et al., 2016). Moreover, their potential for harm to other organisms in the aquatic environment cannot be ignored, especially to fish, to whom pyrethroids are highly toxic (Li et al., 2017). Once in sediment, pyrethroids are accumulated by benthic organisms and via biomagnification also pose a threat to organisms at higher trophic levels (Parolini et al., 2010). Knowledge of the presence of pyrethroids in sediments is thus crucial to understanding whether they pose an environmental threat and if so, at what level.

At present, research on pyrethroids in sediments is mainly concentrated in the United States (Amweg et al., 2006; Anderson et al., 2014; Anderson et al., 2006; Emert et al., 2023; Phillips et al., 2012; Phillips et al., 2010) and China (Chai et al., 2023; Sun et al., 2015; Yi et al., 2015), as well as in European countries such as Spain (Peris et al., 2022), the United Kingdom (Bonwick et al., 1995; Long et al., 1998), and Denmark (Kronvang et al., 2003). However, European data focus on fewer compounds than for other regions of the world, and to our knowledge data do not exist on concentrations of pyrethroids in sediments in Ireland. Cypermethrin, esfenvalerate, deltamethrin, and λ-cyhalothrin are currently registered for use in Ireland under the regulation of the Department of Agriculture, Food and the Marine (DAFM) (https://www.pcs.agriculture.gov.ie/pppd/Search/Substance). In contrast, several of the selected pyrethroids (bifenthrin, permethrin, resmethrin, and cyfluthrin) are not currently authorised for plant protection use in Ireland or the broader EU. Bifenthrin, for example, had its EU approval withdrawn in 2019 and is no longer authorised ((EU) 2018/291). Permethrin is not approved as a plant protection product in the EU. However, it remains in use under the EU Biocidal Products Regulation (EU) No.1090/2014 for applications such as insecticides, insect-repellent textiles, and wood preservatives. Its detection in the environment may therefore be attributable to non-agricultural uses. Similarly, resmethrin and cyfluthrin are not currently registered for use in Ireland, but their inclusion in this study reflects their relevance in international environmental monitoring programmes and risk assessments. Moreover, cypermethrin (as a mixture of 5 isomers) possesses acute and chronic Environmental Quality Standard (EQS) values in freshwater and transitional water and is listed as a Priority Substance under the European Union's Water Framework Directive (WFD) daughter directive 2013/39/EU. However, the proposed EQS for cypermethrin in sediment under the WFD is not endorsed by the Scientific Committee on Health, Environmental, and Emerging Risks (SCHEER) (SCHEER, 2022). The agricultural consumption of pyrethroids in Ireland (1.8 t in 2022) is notably lower than in other European countries such as the UK (17.9 t), Spain (142.9 t), and Denmark (28.8 t), representing a difference of one to two orders of magnitude (Fig. S1). Given the widespread global use of pyrethroids, country-level studies like this are essential for building a more comprehensive understanding of their environmental fate. In particular, the lack of data for Ireland highlights the need for targeted research to assess the environmental distribution and ecotoxicological risks of pyrethroids and may serve as a reference for broader risk assessment strategies and environmental monitoring frameworks.

Wastewater treatment plants (WWTPs) are also a sink for pyrethroids, with fertilisers produced from the solid fraction of wastewater treatment (also known as "biosolids") being a potential source of contamination to the terrestrial food chain of any chemicals present. Currently, around 98 % of processed biosolids generated in Ireland are spread on agricultural land as fertiliser (Uisce Eireann, 2024), including for crops such as cereals, oilseed rape, grass, and fodder beet (Nag et al., 2022; Department of the Environment, Heritage and Local Government, 2009). As such crops may enter the human food chain either directly or indirectly via animal feed, the presence of pyrethroids in biosolids represents a potential route of exposure.

Given this, our aims were to: (a) assess the concentrations of various pyrethroids in Irish sediment and biosolids samples from WWTPs, generating data to serve as a baseline against which future contaminant trends may be assessed; (b) compare the relative abundance of our target pyrethroids in surficial sediment with those in biosolids; (c) conduct an environmental risk assessment using a risk quotient (RQ) approach to investigate the impacts of pyrethroid contamination of sediment on organisms; (d) explore temporal trends in pyrethroid concentrations in transitional sediments at locations with repeated sampling over multiple years; and (e) investigate potential factors influencing pyrethroid contamination of sediments and biosolids in Ireland.

2. Methods

2.1. Chemicals and standards

Individual native pyrethroids standards (resmethrin (RES), bifenthrin (BIF), λ-cyhalothrin (CYH), permethrin (PER), cyfluthrin (CYF), cypermethrin (CYP), esfenvalerate (ESF), and deltamethrin (DEL)) (Table S1), internal (aka surrogate) standard $^{13}C_6$-cypermethrin, and recovery determination (syringe) standard PCB-62 (used to calculate internal standard recovery) were purchased from Chem Service, Inc. (West Chester, PA, USA) and 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).

2.2. Sample collection

Sampling sites were selected to provide broad geographic coverage, with the aim of capturing a representative overview of pyrethroid contamination across Ireland. The sampling campaign was broadly divided into three components: (1) inland and transitional sediments collected by the project team in 2023; (2) analysis of historical transitional sediment samples collected by the Marine Institute of Ireland between 2018 and 2022; and (3) analysis of biosolid samples from Irish WWTPs.

2.2.1. Inland and transitional sediments 2023

The project team collected inland and transitional sediment samples at 81 sites across Ireland between January and September 2023 (Fig. 1). Sediment samples were collected from rivers (n = 62) and estuaries (n = 19) using pre-cleaned collection equipment (cleaned with detergent and rinsed with acetone, cyclohexane, methanol and distilled water). Samples (approximately 0.5–1 kg, where relevant) were collected to a depth of 5 cm using a stainless-steel engraving tool or Van Veen Grabber and then transferred to HDPE containers and transported to the laboratory. Once at the laboratory, the samples were homogenised in the container by constant stirring for 8–10 min using a pre-cleaned stainless-steel spoon. The homogenised samples were passed through a 2 mm stainless steel sieve by stirring (without adding additional water) and then transferred to 50 mL centrifuge tubes, which were then sealed with parafilm and screw caps. Samples were stored at −80 °C until freeze-drying, which was carried out shortly after collection—typically within 1 to 2 weeks. Freeze-drying was performed using a Labconco Freezone freeze dryer (Mason Technologies) under a maximum vacuum of 0.133 mbar and at a temperature of −40 °C for approximately six days. Following freeze-drying, the dried sediments were stored in a cold room at 4 °C. All samples were analysed between June and July 2024.

2.2.2. Transitional sediments 2018–2022

To expand the range of sites examined and enable analysis of temporal trends in contamination, we measured pyrethroid concentrations in 39 transitional sediment samples (n = 39) collected from 23 sites between 2018 and 2022, as part of routine monitoring conducted by the Marine Institute of Ireland. Sampling procedures for these sediments were broadly similar to those sediment samples collected in 2023; however, non-metallic apparatus was used to avoid contamination with heavy metals, which are also monitored by the Marine Institute, and samples were stored in pre-rinsed amber glass containers. Unlike the samples collected in 2023, these were sequentially passed through 2 mm, 1 mm, 125 μm, and 63 μm sieves using minimal amounts of distilled water and gentle brushing. The 63 μm fraction was then oven-dried at 104 °C to a constant weight prior to contaminant analysis. The dried sediment was stored in a cold room at 4 °C. All samples were analysed between June and July 2024. Smaller sediment particles generally exhibit higher contaminant concentrations due to their greater surface area-to-mass ratio. Consequently, a direct comparison of pyrethroid concentrations or risk quotient (RQ_{Sed}) values between the two sample sets was not performed. Additionally, the samples were processed using different drying methods—freeze-drying and oven-drying—which may affect analyte recovery and introduce variability. These methodological differences represent a limitation for data interpretation; therefore, the two datasets were analysed separately.

2.2.3. WWTP-derived biosolids

Biosolid samples were collected from seven WWTPs. Table S3 summarises key characteristics of each WWTP. Overall, 21 biosolid samples

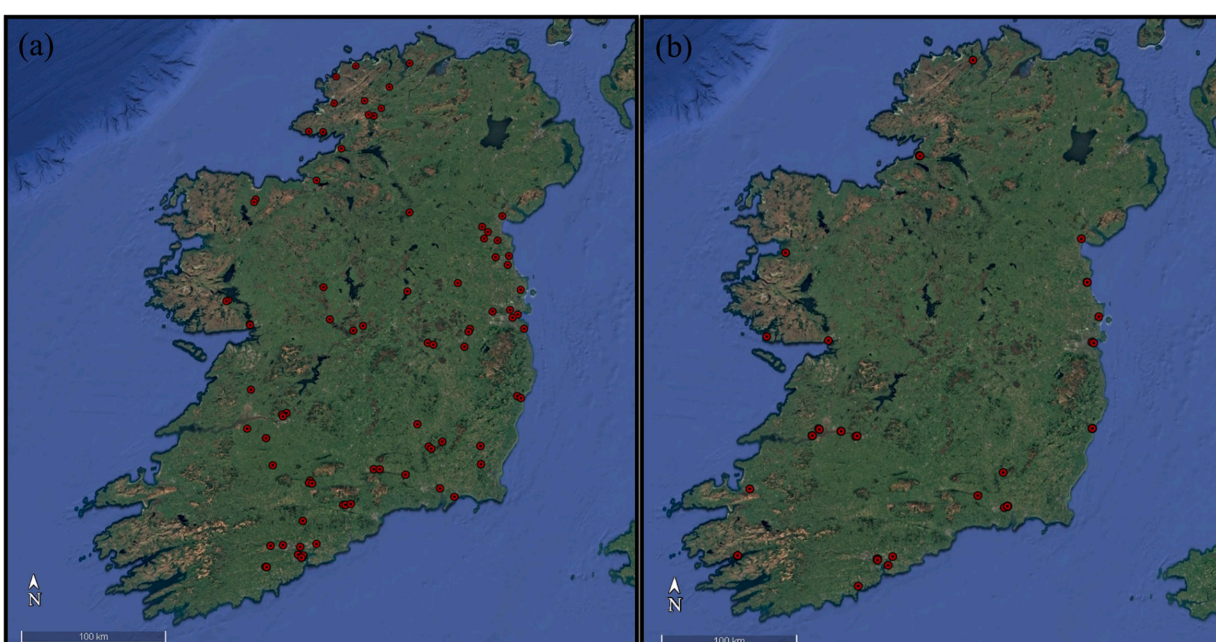

Fig. 1. Sampling locations for sediments: (a) collected in 2023 (b) 2018–2022 (Detailed information about sampling locations can be found in Tables S6 and S7). Map adapted from Google Earth Pro.

(n = 3 per WWTP) were collected from each WWTP in January, May, and September 2023 and prepared for analysis in line with the procedures described in sediment samples (2023).

2.3. Sample extraction and clean-up

Sediment samples (1 g) and biosolid samples (0.1 g) were spiked with 50 ng of internal (aka surrogate) standard and treated with 1 g of copper powder. The samples were extracted with 5 mL n-hexane: acetone (1:1, v/v), vortexed for 1 min and ultrasonic extraction for 30 min, before centrifugation at 4000 rpm for 10 min and transfer of the supernatant into a clean centrifuge glass tube. The extraction procedure was repeated twice, and the extracts combined and concentrated to a volume of about 0.5 mL (solvent exchange to n-hexane). A Florisil SPE cartridge (2 g, 15 mL) was used for cleanup of the sample concentrate. First, the cartridge was preconditioned with 6 mL of n-hexane, loaded with the concentrated sample, along with a 0.5 mL hexane rinse of the glass tube containing the concentrated sample. Finally, 10 mL of n-hexane: acetone (9:1, v/v) was used to elute the target pyrethroids (Sy et al., 2024). The eluate was concentrated to incipient dryness and reconstituted in 100 μL n-hexane with 50 ng of the recovery determination standard PCB-62, ready for GC–MS analysis.

2.4. Instrumental analysis

GC/MS analysis of target pyrethroids was carried out on a GC Agilent 6850 fitted with a Restek Rxi-5Sil MS column (30 m × 0.25 mm × 0.25 μm film thickness), coupled with a 5975C MSD operated in electron ionisation (EI) and selected ion monitoring (SIM) mode. One μL of sample extract was introduced via splitless injection with the injector held at 250 °C. Helium flow through the GC column was 1 mL/min. The GC oven programme was 50 °C for 1 min, ramp at 30 °C/min to 220 °C, ramp at 10 °C/min to 300 °C, and held for 10 min. Temperatures of the ion source, quadrupole and interface were: 230 °C, 150 °C, and 280 °C respectively. Further details on the GC–MS quantification procedure are provided in Text S2 and Table S2.

2.5. Data analysis and risk assessment

Statistical analyses were conducted using IBM SPSS 29.0. All data were first analysed for normality via a one-sample Kolmogorov–Smirnov test. Non-detects (values below the instrumental Limits of detection) were treated as zero for the purposes of statistical analysis and calculation of summary statistics (e.g., mean, standard deviation). Log-transformed data were used to perform an independent samples *t*-test comparing concentrations between estuarine/transitional (n = 19) and riverine (n = 62) sediments. Where data did not conform to a normal distribution, the nonparametric Mann–Whitney *U* test was applied instead.

The RQ_{Sed} concept was used to evaluate the ecotoxicological risk of target pyrethroids in sediments using (Eq. (1)):

$$RQ_{Sed} = \frac{MEC}{PNEC_{sed}} \quad (1)$$

where MEC is the measured environmental concentration and $PNEC_{sed}$ is the lowest predicted no-effect concentration (ng/g dw) for a given pyrethroid in sediments, taken from the Norman Ecotoxicology Database (www.norman-network.com/nds/ecotox). RQ values ranging from 0.01 to 0.1 are classed as low risk, those between 0.1 and 1 as moderate risk, while RQ values above 1 are considered high risk (Chai et al., 2023; Liu et al., 2024; Sánchez-Bayo et al., 2002; Sharkey et al., 2024; Wee and Aris, 2017).

2.5.1. Flow attenuation from rivers and lakes (FARL)

FARL is an index that weights each reservoir and lake area by the catchment area that feeds it. Values close to unity indicate the absence of attenuation due to lakes and reservoirs, whereas index values below 0.8 indicate a substantial influence on flood response. FARL data from the Irish EPA's GIS portal were obtained from https://gis.epa.ie/.

2.5.2. Standard average annual rainfall (SAAR)

The SAAR data were obtained from the Irish EPA's GIS portal (https://gis.epa.ie/). FARL and SAAR values were available for 57 samples in set B (n = 81), accounting for 70.4 %. Both the FARL and SAAR are based on monitoring points located within 1 km of each sampling site.

Population size data were from Central Statistics Office 2023 Census (https://www.cso.ie/en/census/). The population sizes are estimates of the townships/localities/cities surrounding each sampling site (set b, n = 81), with a 2 km radius defined as the upper limit for these estimates.

2.6. Quality control and quality assurance procedures

A procedural blank consisting of 1 g anhydrous sodium sulfate was analysed with every 5–7 samples. Acceptable method accuracy and precision for pyrethroids were demonstrated via replicate analysis (n = 4) of a river sediment (matrix spike) with more information provided in Table S4. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as the mass of analyte yielding signal-to-noise ratios of 3 and 10, respectively. The instrumental LOD range was 0.09–4.00 pg/injection, leading to LOQs in sediment and biosolids in the range 0.01–0.40 ng/g dw and 0.09–4.00 ng/g dw, respectively (Table S2). The recoveries of the internal (aka surrogate) standard in procedural blank samples were 79.8 % ± 18.3 % (mean ± standard deviation), and in sediments and biosolids samples were 104 % ± 26.2 % (mean ± standard deviation).

3. Results and discussion

3.1. Concentrations of pyrethroids in Irish riverine and transitional sediments and biosolids

Concentrations of pyrethroids in riverine and transitional sediments collected in 2023, along with the associated statistical analyses, are presented in Table 1. Average concentrations in these samples of: resmethrin (3.65 ng/g dw), permethrin (8.53 ng/g dw), cyfluthrin (8.06 ng/g dw), cypermethrin (7.12 ng/g dw), and deltamethrin (1.47 ng/g dw) were substantially higher than those of other targeted pyrethroids, including bifenthrin (0.07 ng/g dw), λ-cyhalothrin (0.10 ng/g dw), and esfenvalerate (0.60 ng/g dw). Among the four compounds currently registered under the Pesticide Registration and Control Divisions (PRCD) of the Department of Agriculture, Food and the Marine (DAFM) for agricultural use in Ireland—cypermethrin, esfenvalerate, deltamethrin, and λ-cyhalothrin—cypermethrin exhibited the highest concentrations, indicating a likely contribution from its agricultural and indoor domestic applications. Notably, permethrin and cyfluthrin—neither of which is registered for plant protection in Ireland—were also detected at relatively high concentrations. In the case of permethrin, its authorised use in biocidal products such as wood preservatives likely accounts for its environmental occurrence (EC, 2014). The comparatively elevated levels of cyfluthrin, despite its non-registration, warrant closer scrutiny. By contrast, bifenthrin concentrations were relatively low, which is consistent with its withdrawal from the EU market in 2019 and may indicate that regulatory actions have been effective (EU, 2018).

The concentrations of pyrethroids in sediments collected between 2018 and 2022 are also provided in Table 1. Average concentrations in sediments collected between 2018 and 2022 of permethrin (9.06 ng/g dw), cyfluthrin (8.89 ng/g dw), cypermethrin (9.51 ng/g dw), and deltamethrin (2.22 ng/g dw) exceeded by one to two orders of magnitude those of our other target compounds.

Table 1
Summary of concentrations (ng/g dw) of pyrethroids in sediment samples from Ireland collected in 2023 (inland (n = 62) and transitional (n = 19) sediments) and 2018–2022 (transitional sediments collected by the Marine Institute, n = 39).

Sediment category	Statistical parameter	Resmethrin	Bifenthrin	λ-Cyhalothrin	Permethrin	Cyfluthrin	Cypermethrin	Esfenvalerate	Deltamethrin	Σ_8-Pyrethroids
Sediments collected in 2023[a]	Minimum	0.23	ND	ND	ND	ND	ND	ND	ND	0.44
	Maximum	22.5	1.73	1.07	74.5	68.5	76.1	5.5	11.6	162
	Median	2.27	0.01	0.05	5.07	4.65	2.51	0.23	0.54	17.2
	Mean	3.65	0.07	0.10	8.53	8.06	7.12	0.60	1.47	29.6
	SD	4.25	0.24	0.17	10.6	10.4	12.9	0.92	2.35	30.6
	Detection frequency (%)	100	64.2	74.1	97.5	95.1	93.8	82.7	61.7	
Sediments collected between 2018 & 2022[b]	Minimum	ND	ND	ND	3.84	4.17	4.60	ND	ND	18.2
	Maximum	2.09	0.28	1.71	16.7	21.0	31.0	4.25	10.9	59.2
	Median	0.56	0.03	0.04	7.87	7.40	8.45	0.19	1.22	26.6
	Mean	0.73	0.05	0.10	9.06	8.89	9.51	0.54	2.22	31.1
	SD	0.52	0.06	0.27	3.20	3.98	4.70	0.90	2.39	10.1
	Detection frequency (%)	92.3	79.5	94.9	100	100	100	89.7	94.9	
	$PNEC_{Sed}$[c]	18.3	105,078	0.2	0.84	0.52	0.15	0.0045	0.0046	

[a] Sieved to 2 mm mesh.
[b] Sieved to 63 μm mesh.
[c] $PNEC_{Sed}$: Predicted No Effect Concentration. Sediment PNECs taken from the NORMAN database in January 2025 (www.norman-network.com/nds/ecotox).

A statistical summary of pyrethroid concentrations in biosolid samples collected from seven Irish WWTPs is provided in Table 2.

3.2. Concentrations of pyrethroids in Irish sediments compared to similar studies worldwide

Table 3 compares pyrethroid concentrations in sediments from this study with data from previously published research. Compared with other studies, the concentration of resmethrin, which has a very high detection rate, accounts for a high proportion of total pyrethroids in the two sets of sediments collected in this study. Hladik and Kuivila (2012) reported concentrations of resmethrin to fall in the range ND–18.8 ng/g dw, similar to the range in this study (0.23–22.5 ng/g dw, in 2023 samples; ND–2.09 ng/g dw, in 2018–2022 samples). In contrast, concentrations of bifenthrin in Irish sediments are relatively low in both sets (median concentrations: 0.01 ng/g dw in 2023 samples; 0.03 ng/g dw, in 2018–2022 samples), compared to other studies in which median concentrations were 4.21 ng/g dw (USA; You et al. (2008)), 6.95 ng/g dw (USA; Harwood et al. (2013)), and 4.67 ng/g dw (China; Liu et al. (2022)). The median concentrations of permethrin, cyfluthrin, cypermethrin, and esfenvalerate generally fall within the ranges reported in the literature. λ-Cyhalothrin concentrations in this study were at the low end of the global range, while the median concentration of deltamethrin exceeded those reported in previous studies, suggesting the influence of local sources or differing environmental conditions.

3.3. Year-on-year variations in concentrations of pyrethroids in estuarine sediments collected between 2018 and 2022

Of the 39 transitional sediment samples collected between 2018 and 2022, four samples were obtained from the same location in consecutive years (2018–2021). Additionally, samples were collected from two sites across three different years and from seven sites in two different years. These time-series samples provide preliminary insights into the temporal variation of pyrethroid concentrations in Irish sediments.

The concentrations of Σ_8-pyrethroids in samples from the three sites from which samples were available for 3 or more years are shown in Fig. 2. At each individual site, concentrations in 2021 were lower than in any other year for which samples were available. We performed an independent samples *t*-test by grouping the 2021 data from all three sites and comparing them with data from the same sites in earlier years (2018–2020). The result indicated statistically significant lower Σ_8-pyrethroids concentrations in 2021 compared to previous years (p = 0.042). To evaluate whether this is an indicative downward trend and to support effective environmental management, long-term monitoring at these and additional sites is recommended.

3.4. Comparison of concentrations and relative abundance of individual pyrethroids in riverine and transitional sediments collected in 2023

A one-sample Kolmogorov–Smirnov test revealed concentrations of pyrethroids collected from the sediment samples (n = 81) in 2023 to display a log-normal distribution. There was no significant difference in concentrations between estuarine/transitional (n = 19) and riverine (n = 62) sediments (independent sample *t*-test, $p > 0.05$), both for Σ_8-pyrethroids and for each individual target pyrethroid.

Fig. 3 shows that on average, the relative abundance of our target pyrethroids is similar in both riverine and estuarine/transitional sediments collected in 2023. The primary contributing compounds in the estuarine/transitional sediments are: cyfluthrin (31.4 %), permethrin (28.2 %), and cypermethrin (21.0 %), while in the riverine sediments, the main contributors are permethrin (29.0 %), cyfluthrin (25.7 %), and cypermethrin (25.2 %). This pattern contrasts to varying degrees with that observed elsewhere. For example, a recent study on the distribution

Table 2
Summary of concentrations (ng/g) of pyrethroids in biosolid samples from Ireland collected from 7 WWTPs in 2023.

Statistical parameter	Resmethrin	Bifenthrin	λ-Cyhalothrin	Permethrin	Cyfluthrin	Cypermethrin	Esfenvalerate	Deltamethrin	Σ_8-Pyrethroids
Minimum	2.16	0.51	0.23	43.1	540	28.0	11.5	25.6	740
Maximum	48.8	6.43	60.7	485	1740	360	294	672	3319
Median	9.75	1.90	3.53	268	920	77.8	107	147	1570
Average	13.4	2.31	8.79	265	1027	143	121	215	1795
SD	10.7	1.55	13.3	135	396	109	72.7	181	754
Detection frequency (%)	100	100	100	100	100	100	100	100	

Table 3
Comparison of pyrethroid concentrations (range (median) ng/g dw) in Irish sediments with those elsewhere in the world.

Reference	Location	Resmethrin	Bifenthrin	λ-Cyhalothrin	Permethrin	Cyfluthrin	Cypermethrin	Esfenvalerate	Deltamethrin
This study (2023)	Ireland	0.23–22.5 (2.27)[b]	ND[a]–1.73 (0.01)	ND–1.07 (0.05)	ND–74.5 (5.07)	ND–68.5 (4.65)	ND–76.1 (2.51)	ND–5.5 (0.23)	ND–11.6 (0.54)
This study (2018–2022)	Ireland	ND–2.09 (0.56)	ND–0.28 (0.03)	ND–1.71 (0.04)	3.84–16.7 (7.87)	4.17–21.0 (7.40)	4.60–31.0 (8.45)	ND–4.25 (0.19)	ND–10.9 (1.22)
Bonwick et al. (1995)	UK	NM[c]	NM	NM	ND–335 (214)	ND	NM	NM	NM
Long et al. (1998)	UK	NM	NM	NM	ND–5451[d] (15)	NM	ND–1140 (ND)	NM	ND (ND)
House et al. (2000)	UK	NM	NM	NM	50–300 (NA[e])	NM	NM	NM	NM
Kronvang et al. (2003)	Denmark	NM	NM	ND–30 (NA)	ND	NM	NM	ND–10 (NA)	ND–50 (NA)
Feo et al. (2010)	Spain	ND	ND	ND	ND	ND	8.27–71.9 (NA)	ND	ND
Peris et al. (2022)	Spain	NM	NM	NM	NM	NM	ND–327 (NA)	NM	NM
Hladik and Kuivila (2012)	USA	ND–18.8 (ND)	ND–30.1 (0.6)	ND–0.3 (ND)	ND–180 (ND)	ND–14.6 (ND)	ND–21.8 (ND)	NM	ND–12.1 (ND)
Amweg et al. (2006)	USA	NM	ND–429 (NA)	ND–10.7 (NA)	ND–172 (NA)	ND–60.4 (NA)	ND–30.6 (NA)	ND–4.4 (NA)	ND–57.0 (NA)
Anderson et al. (2006)	USA	NM	NM	ND–59.4 (9.25)	ND–107 (ND)	NM	NM	ND–32.6 (ND)	NM
Ensminger et al. (2011)	USA	NM	ND–74.4 (2.9)	ND–8.98 (ND)	ND	ND–4.19 (ND)	ND	ND	ND
Harwood et al. (2013)	USA	NM	1.2–329 (6.95)	ND–11.0 (1.42)	ND–58 (3.3)	ND–32 (ND)	ND–36 (ND)	NM	NM
Holmes et al. (2008)	USA	NM	2.19–219 (13.5)	ND–24.2 (ND)	ND–97.8 (23.9)	ND–127 (6.53)	ND–30.4 (ND)	ND–6.90 (ND)	ND–9.31 (ND)
Phillips et al. (2010)	USA	NM	24.7–172 (86.0)	2.5–9.7 (4.77)	13.8–53.1 (32.1)	ND–67.5 (ND)	ND–102 (18.8)	NM	NM
Phillips et al. (2012)	USA	NM	ND–375 (ND)	ND–125 (1.45)	ND–1279 (ND)	ND–214 (ND)	ND–499 (3.25)	ND–5.5 (2.1)	NM
Weston et al. (2013a)	USA	NM	ND–32.2 (ND)	ND–11.7 (ND)	ND–158 (ND)	ND–3.0 (ND)	ND–6.7 (ND)	ND–203 (ND)	ND
Weston et al. (2013b)	USA	NM	ND–35.5 (1.8)	ND–4.2 (ND)	ND–12.8 (ND)	ND–7.7 (ND)	ND–5.4 (ND)	NM	NM
You et al. (2008)	USA	NM	ND–52.5 (4.21)	ND–6.55 (ND)	ND–107 (4.26)	ND–38.5 (ND)	ND–33.0 (ND)	ND–5.56 (ND)	ND–7.86 (ND)
Ding et al. (2010)	USA	NM	ND–46 (3.4)	ND–25 (ND)	ND–51 (ND)	ND	ND	ND	ND
Emert et al. (2023)	USA	NM	ND–0.82 (0.52)	ND–5.33 (1.82)	ND–3.57 (0.83)	NM	NM	ND–9.41 (3.78)	NM
Miranda et al. (2008)	Brazil	NM	NM	ND–5.0 (1.65)	ND–7.0 (3.5)	NM	ND	NM	ND–20.0 (ND)
Allinson et al. (2015)	Australia	NM	ND–59 (ND)	NM	ND–34 (ND)	NM	NM	NM	NM
Xue et al. (2008)	China	NM	NM	NM	NM	NM	ND–0.009 (0.006)	NM	ND–0.524 (0.345)
Hu et al. (2015)	China	NM	NM	0.04–6.40 (0.35)	ND–3.4 (0.38)	ND–5.7 (1.6)	ND–7.6 (1.75)	NA	ND–0.19 (ND)
Qi et al. (2015)	China	NM	ND	0.03–0.06 (0.04)	0.06–0.15 (0.12)	ND	ND–0.04 (ND)	ND–0.03 (ND)	ND
Wang et al. (2012)	China	NM	ND–0.062 (0.002)	ND–0.064 (0.005)	ND–108 (0.937)	ND–0.203 (0.004)	ND–11.3 (0.082)	ND–187 (0.182)	ND–0.334 (0.026)
Li et al. (2011)	China	NM	ND–135 (ND)	ND–13.2 (0.65)	ND–91.4 (1.53)	ND–2.83 (ND)	1.44–219 (18.3)	ND–15.7 (ND)	ND–83.3 (ND)
Sun et al. (2015)	China	NM	ND–1.76 (0.02)	ND–7.44 (0.03)	ND–48.5 (0.39)	NM	ND–29.8 (0.25)	ND–4.08 (0.04)	NM
Yi et al. (2015)	China	NM	0.63–3.48 (1.81)	9.87–90.7 (14.0)	20.4–132 (71.1)	ND–5.77 (ND)	18.0–130 (115)	NM	ND–227 (0.39)
Cheng et al. (2017)	China	NM	0.38–6.54 (1.17)	0.29–1.87 (0.59)	0.88–35.4 (8.66)	ND	0.14–20.4 (2.46)	ND	ND–1.29 (0.36)
Gu et al. (2024)	China	NM	0.12–5.59 (NA)	NM	ND–9.85 (NA)	NM	ND–25.4 (NA)	NM	13.8–476 (NA)
Chai et al. (2023)	China	NM	5.96–10.12 (NA)	1.77–3.77 (NA)	NM	NM	4.02–6.14 (NA)	NM	7.68–28.6 (NA)
Liu et al. (2022)	China	NM	ND–55.6 (4.67)	0.23–78.3 (4.07)	ND–10.2 (0.62)	ND–1.02 (ND)	1.37–198 (9.92)	ND–7.32 (0.63)	ND–14.5 (0.16)

[a] ND: not detected.
[b] Median concentration.
[c] NM: not measured.
[d] Cis-permethrin.
[e] NA: not available.

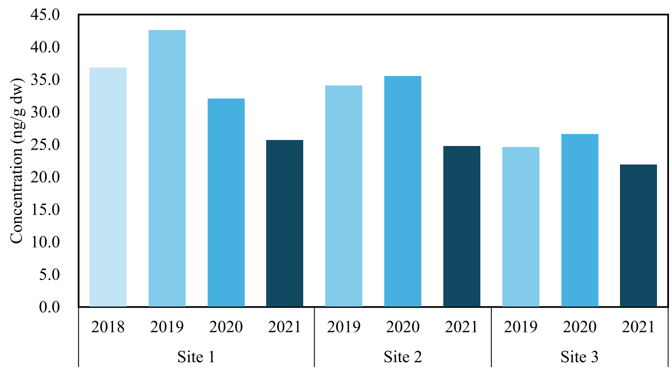

Fig. 2. Annual variation in Σ_8-Pyrethroids concentrations (ng/g dw) in sediment at 3 locations (Each bar represents one sample).

of pyrethroids in the sediments of Yangcheng Lake, China, revealed that deltamethrin was the primary contributing compound (Gu et al., 2024); while a study in California, USA, found that permethrin and cypermethrin were the primary contributing compounds, with cyfluthrin a relatively low contributor (Delgado-Moreno et al. (2011). Such variations in composition across different regions likely reflect differences in use patterns. Our data suggest the principal pyrethroids used in Ireland are permethrin, cyfluthrin, and cypermethrin. Moreover, compared to other pyrethroids targeted in this study, permethrin, cyfluthrin, and cypermethrin exhibit high detection rates (97.5 %, 95.1 %, 93.8 %, respectively). Due to their prevalence, these three pyrethroids warrant increased attention in future studies.

3.5. Ecotoxicological risk assessment of pyrethroids in Irish sediments

Logarithmically transformed RQ_{Sed} values of each target pyrethroid in sediment samples are presented in Fig. 4. For transitional sediment samples collected between 2018 and 2022, bifenthrin exhibited low risk levels ($RQ_{Sed} < 0.1$) in all samples (n = 39). However, we note the much higher PNEC for binfenthrin—at least 3 orders of magnitude higher than those of our other target pyrethroids—and further study of bifenthrin's ecotoxicity appears warranted given reports elsewhere of its impacts on freshwater benthic invertebrates (Hasenbein et al., 2015). Resmethrin presented a low risk in most samples (94.9 %), with the remaining 5.1 % falling into the moderate risk category ($0.1 < RQ_{Sed} < 1$). In contrast, λ-cyhalothrin posed a moderate risk in 76.9 % of the samples, while concentrations in 5.1 % of the samples presented high risk ($RQ_{Sed} > 1$). Concentrations of permethrin, cyfluthrin, and cypermethrin were categorised as high risk in all samples, while those of esfenvalerate and deltamethrin were categorised as high risk in 89.7 % and 94.9 % samples respectively, with the remainder deemed low risk.

In transitional sediment samples from 2023, concentrations of bifenthrin fell into the low-risk category in all samples, with the same caveat regarding the elevated $PNEC_{Sed}$ as described for the samples collected in 2022. However, those of resmethrin and λ-cyhalothrin were deemed moderate risk in 50.6 % and 59.26 % of samples respectively. Moreover, concentrations of permethrin, cyfluthrin, cypermethrin, esfenvalerate, and deltamethrin were categorised as high risk in 97.5 %, 93.8 %, 91.4 %, 82.7 %, and 61.7 % of samples, respectively. It is important to note that the smaller sediment particle size (<63 μm) of these samples provided by the Marine Institute, leads to higher pyrethroid concentrations with concomitantly higher RQ_{Sed} values.

These findings underscore the importance of continued monitoring

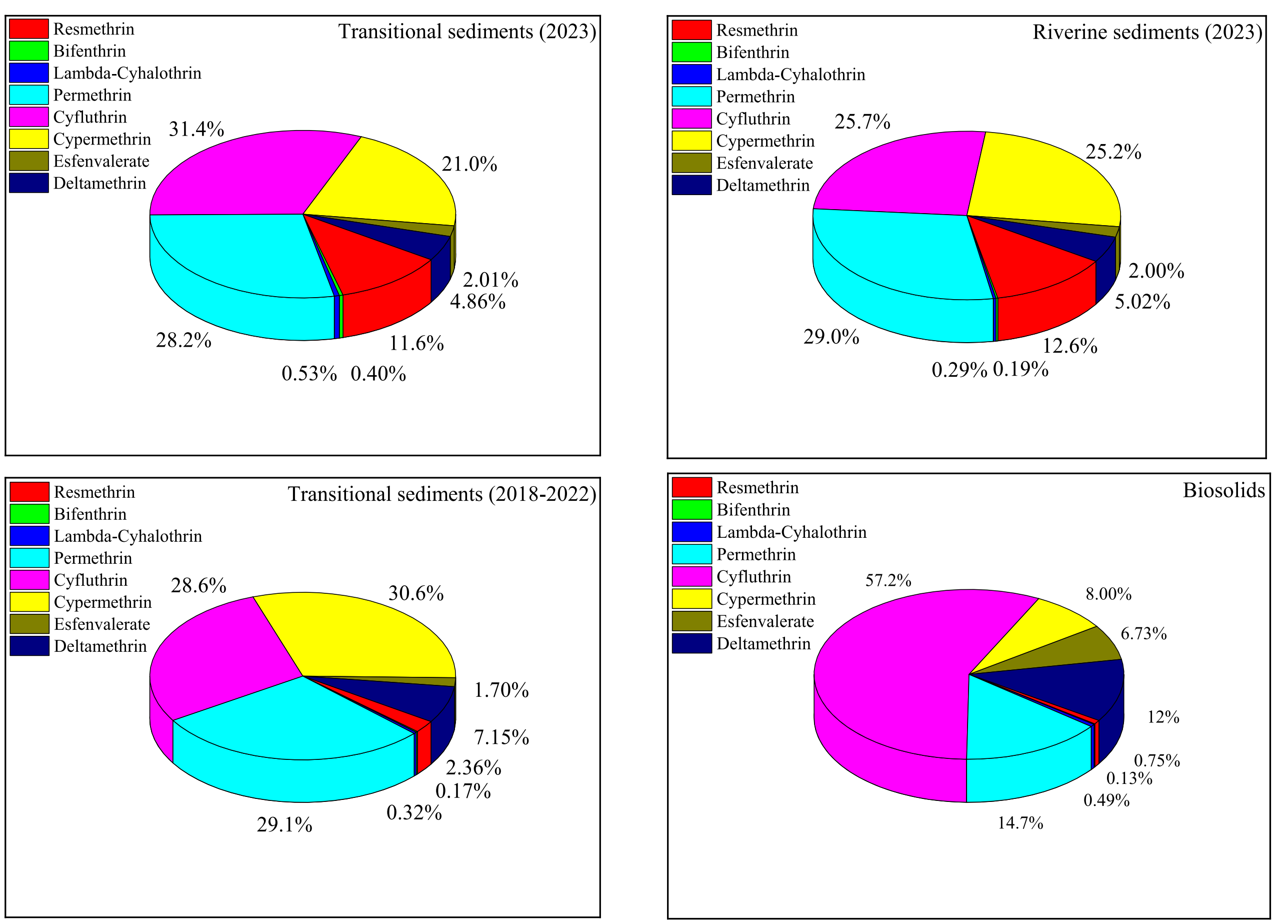

Fig. 3. Pyrethroids pattern (expressed as percentage of Σ_8-Pyrethroids) in biosolids and surficial sediments from Ireland.

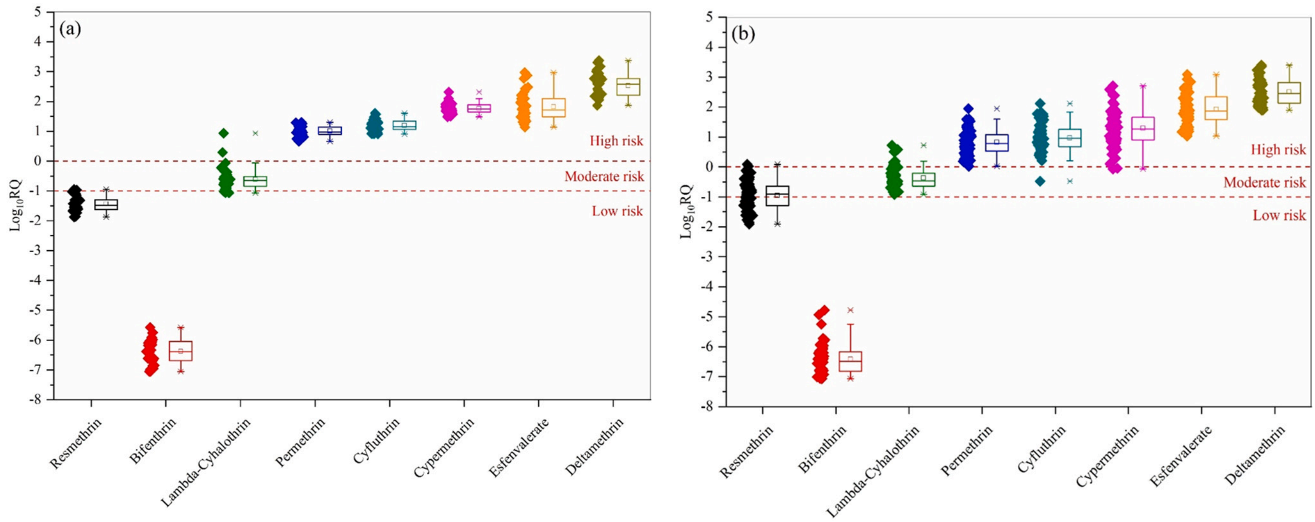

Fig. 4. Log_{10}Risk quotient (RQ_{Sed}) values for the target pyrethroids in: (a) transitional 2018–2022 and (b) inland and transitional 2023 sediments from Ireland (Box (rectangle): represents the interquartile range (IQR): the middle 50 % of the data. The bottom of the box = Q1 (25th percentile). The top of the box = Q3 (75th percentile). Line inside the box: this is the median (Q2), or 50th percentile. In box plot, the small square represents the average value of the dataset. Whiskers (lines extending from the box): extend from the box to the smallest value within 1.5 × IQR below Q1; extend from the box to the largest value within 1.5 × IQR above Q3. Anything outside this range is considered a potential outlier).

and assessment of pyrethroids, considering their potential ecotoxicological impacts and the complex interactions of multiple pollutants within aquatic ecosystems.

3.6. Potential influences on pyrethroids concentrations in Irish sediment

There was a positive correlation between FARL values and concentrations of resmethrin ($r = 0.513$, $p < 0.001$) and cypermethrin ($r = 0.274$, $p = 0.039$), as determined by the Spearman correlation analysis. No significant correlation was found for other pyrethroids ($p > 0.05$). As higher FARL values indicate little flow attenuation due to presence of a lake/reservoir, while <0.8 indicates a substantial impact on flow of flood response, this positive correlation suggests that stable (low flow) river states may contribute to the accumulation of pyrethroids in sediment.

Related to this, cypermethrin concentrations were significantly negatively correlated with the standard average annual rainfall (Spearman correlation analysis, $r = -0.333$, $p = 0.011$). This finding suggests higher rainfall leads to lower cypermethrin accumulation in sediments. No significant correlation was found for other pyrethroids (p > 0.05).

In addition, λ-cyhalothrin exhibited a significant positive correlation with population size (Spearman correlation analysis, $r = 0.266$, $p = 0.016$), as did cyfluthrin ($r = 0.277$, $p = 0.012$). These findings indicate that concentrations of λ-cyhalothrin and cyfluthrin in sediment are positively associated with population size, suggesting anthropogenic activities linked to higher population size may contribute to elevated concentrations of these compounds.

3.7. Concentrations of pyrethroids in Irish WWTP-derived biosolids compared to previous studies elsewhere

Among the four compounds currently registered for agricultural use in Ireland—cypermethrin, esfenvalerate, deltamethrin, and λ-cyhalothrin—the mean concentration of λ-cyhalothrin (8.79 ng/g dw) was much lower than the other three, which were 143 ng/g dw, 121 ng/g dw, and 215 ng/g dw, respectively. Compared to earlier data, the concentrations of pyrethroids in biosolids in this study are higher, but similar to those seen elsewhere in recent years. In addition, previous studies have focused on fewer pyrethroids in biosolids, primarily limited to permethrin. Kupper et al. (2006) determined the permethrin concentration in sludge after digestion treatment from a sewage treatment plant to be 290 ng/g dw (Switzerland). Plagellat et al. (2004) determined the mean concentration of permethrin in sewage sludge from Swiss wastewater treatment plants was 49.1 ng/g dw, while the mean concentration of permethrin in 12 UK sewage sludge samples was 5600 ng/g dw (Rogers et al., 1989). Table 2 summarises the concentrations of pyrethroids in biosolids samples collected from seven wastewater treatment plants in Ireland in 2023. Concentrations of permethrin in this study ranged from 43.1 to 485 ng/g dw, with an average concentration of 265 ng/g dw. These concentrations were much lower than those reported in the UK in the 1980s but closer to those reported in Switzerland in more recent years. More recently, Wheeler et al. (2025) conducted an extensive survey of biosolids from 17 WWTPs across California, USA. Their study detected multiple pyrethroids in 18 biosolids samples, with permethrin showing a 100 % detection frequency and a median concentration of 694 ng/g—substantially higher than the values reported in our Irish samples (median: 268 ng/g). Other frequently detected pyrethroids included bifenthrin (94 %), cyhalothrin (89 %), and cypermethrin (50 %) with median concentrations of 116 ng/g, 16 ng/g, and 39 ng/g, respectively. The median concentrations of these pyrethroids were higher or close to the median concentrations in this study. There appears currently little data on concentrations of pyrethroids in biosolids. Consequently, the data from this study not only provides an important point of comparison for Ireland but also a valuable comparator for other regions.

3.8. Relative abundance of target pyrethroids in biosolids and sediment

Sediment samples collected in 2023 (n = 81) and transitional sediment samples from 2018 to 2022 (n = 39) displayed different relative abundances of individual pyrethroids compared to biosolid samples. As shown in Fig. 3, cyfluthrin accounts for 57.2 % of Σ_8-pyrethroids in biosolid samples, followed by permethrin (14.7 %) and deltamethrin (12.0 %). This compares to the more equal distribution of cyfluthrin, permethrin, and cypermethrin in sediment samples. The differences in the patterns of pyrethroid compounds between biosolids and sediments suggest that biosolids/WWTP emissions are only one of many putative sources of pyrethroids in Irish sediments. This may be partly explained by the fact that biosolids typically have relatively short retention times in WWTP, in contrast to environmental sediments that accumulate contaminants over longer periods. Moreover, anaerobic digestion processes, commonly used in WWTPs, involve limited microbial activity and influence the bioavailability of hydrophobic compounds (Wheeler et al., 2025). In addition, the higher organic matter content and processing conditions of biosolids may favour accumulation of pyrethroids such as λ-cyhalothrin, while in sediments, environmental factors such as FARL, rainfall, and population size may affect pyrethroid contamination.

3.9. Influence of season, wastewater treatment technology, and size of population served by a given WWTP on concentrations of pyrethroids in biosolids

For three WWTPs, concentrations of Σ_8-pyrethroids in biosolids declined in the order Jan > Sep > May, while concentrations in the other followed the order Jan > May > Sep (Fig. 5). This indicates that concentrations of pyrethroids in winter (January) exceed those in other seasons. This could be due to lower pyrethroid inputs in spring (May) and late summer/early autumn (September) than in winter (January). Another possible reason is that the lower temperature in winter limits volatilisation and degradation of pyrethroids (ATSDR, 2003; Harwood et al., 2009). For the remaining three WWTPs (Fig. S2), two showed the highest concentration in September and one showed the highest concentration in May.

The mean concentrations of Σ_8-pyrethroids across the three sampling periods were also analysed in relation to the population equivalent (PE: One PE represents the organic biodegradable load having a five-day biochemical oxygen demand (BOD_5) of 60 g of oxygen per day) and flow band (FB) of each WWTP, using the minimum recorded values for PE and FB (Table S3). Spearman correlation analysis revealed a significant positive correlation between Σ_8-pyrethroids concentrations and both PE and FB ($r = 0.896$, $p = 0.006$). This suggests that higher PE and FB are associated with elevated pyrethroid concentrations in biosolids. The influence of PE and FB is underlined by the observation that in plants such as WWTP 2, WWTP 3, and WWTP 6, that employ the same treatment methods (anaerobic digestion (AD) and thermal drying (TD)); the positive correlation between concentration of Σ_8-pyrethroids and PE and FB remained (Fig. 5, Table S3). This suggests that the influence of PE and FB on pyrethroid concentrations is in addition to any attributable to the treatment processes themselves.

4. Conclusions

This study provides a comprehensive assessment of pyrethroid contamination in freshwater and transitional sediments and wastewater treatment plant derived biosolids across Ireland, offering valuable data for future environmental monitoring and risk assessment. Pyrethroids, particularly resmethrin, permethrin, cyfluthrin, and cypermethrin, were widely detected in both sediments and biosolids, with higher concentrations observed in biosolids. While pyrethroid concentrations in Irish sediments are generally within the ranges reported in other regions worldwide, RQ_{Sed} analysis indicated moderate-to-high ecotoxicological risks for several compounds, particularly permethrin, cyfluthrin, and cypermethrin. This suggests that even relatively low environmental concentrations may pose significant threats to aquatic ecosystems. Among the four pyrethroids currently registered in Ireland, cypermethrin showed the highest concentrations in sediments, likely reflecting both agricultural, aquacultural, and indoor uses. Permethrin and cyfluthrin, although not registered for plant protection, were also prevalent—permissible biocidal uses may explain the presence of permethrin, while cyfluthrin warrants further scrutiny. Conversely, bifenthrin concentrations were low, aligning with its regulatory withdrawal in 2019. Our findings highlight the need for greater regulatory controls on the use of certain pyrethroids, attention to contamination of biosolids and continued long-term monitoring to mitigate their

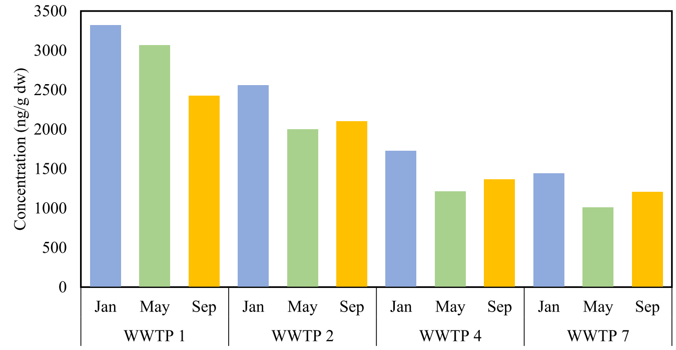

Fig. 5. Σ_8-Pyrethroids concentrations in biosolids from four selected WWTPs in January, May, and September 2023. (Each bar represents one sample. The four WWTPs were selected because they exhibited the highest Σ_8-pyrethroids concentrations in winter (January), highlighting seasonal variation. Data for all seven WWTPs are provided in Fig. S2 in the Supplementary Information.)

ecotoxicological impacts and protect aquatic biodiversity.

CRediT authorship contribution statement

Shijie Wang: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Martin Sharkey:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation. **Jingxi Jin:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **William Stubbings:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Conceptualization. **Habib Bagheri:** Writing – review & editing, Methodology, Investigation. **Mark G. Healy:** Writing – review & editing, Project administration, Methodology, Funding acquisition, Conceptualization. **Marie Coggins:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Mohamed Abou-Elwafa Abdallah:** Writing – review & editing, Methodology, Data curation. **Stuart Harrad:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, 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.scitotenv.2025.180108.

Data availability

Data will be made available on request.

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