

Innovative Monitoring to Prioritise Contaminants of Emerging Concern for Ireland

Authors: Imogen Hands, Helena Rapp-Wright, Marcin Penk, Damià Barceló Cullerès,
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2. Office of Environmental Enforcement
3. Office of Evidence and Assessment
4. Office of Radiation Protection and Environmental Monitoring
5. Office of Communications and Corporate Services

The EPA is assisted by advisory committees who meet regularly to discuss issues of concern and provide advice to the Board.

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Identifying pressures

Contaminants of emerging concern (CECs) can be defined as “any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects”. This project provides comprehensive insight into the occurrence, fate and impact of CECs in Irish receiving waters. Influent, effluent and receiving waters from an urban and a rural waste water treatment plant (WWTP), representing worst-case scenarios, were comprehensively screened for pesticides, pharmaceuticals and personal care and cosmetic products over 1 year. The pressures on WWTPs were investigated by analysing the nature and concentration of CECs in influent samples. WWTPs are not designed to remove CECs, but the extent to which they could successfully remove CECs from influent water was also investigated. The extent to which CECs not removed during processing were diluted on entering receiving waters was also determined. This work allows contaminants that are not efficiently removed during treatment of municipal effluents to be highlighted and enables an evidence-based prioritisation list of CECs to be developed.

Informing policy

Article 16(4) of the Water Framework Directive (WFD) requires that the list of priority substances (Annex X of the WFD) must be reviewed and adjusted as appropriate at regular intervals. This happened in 2013 when 12 substances were added to Annex X, through Directive 2013/39/EU. Article 8b of the 2013 directive created a “watch list”, which was defined as a “list of substances for which EU-wide monitoring data are to be gathered for the purpose of supporting future prioritisation exercises”. For example, three compounds – diclofenac, 17 β -estradiol and 17 α -ethnylestradiol – were added in 2013, and a further 10 were added in 2015. Article 16 of the WFD requires that the Annex X list of priority substances be reviewed in future and that these reviews be informed by monitoring data gathered for watch list data. The analyses carried out in this research will provide a database of monitoring data for Irish and EU water bodies, to directly inform review of Article 16(4).

Developing solutions

It is challenging to detect and monitor CECs using current analytical instruments. Two promising strategies highlighted in a recent EU Joint Research Centre report to overcome these issues were the use of modern mass spectrometric detection technologies and the sampling of greater volumes of water. We utilised the latest developments in both, including state-of-the-art instruments and methods at Imperial College London and the Catalan Institute for Water Research, to comprehensively analyse water samples from urban and rural WWTP influents and effluents, as well as receiving surface waters and freshwater river samples. In addition, we used passive sampling to monitor pesticide concentrations in surface waters, demonstrating the additional functionality of continuous monitoring as opposed to the point-in-time approach of grab sampling. This project demonstrated how utilisation of a range of sampling and analysis methodologies can result in a comprehensive overview of CEC presence and concentration, which in turn can be utilised to assess the environmental risk of these chemicals.

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This report is based on research carried out/data from June 2018 to May 2022. More recent data may have become available since the research was completed.

The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Executive Summary

The objectives of IMPACT (Innovative Monitoring to Prioritise Contaminants of Emerging Concern (CECs) for Ireland) were to detect, monitor and risk assess CECs, in particular pesticides, pharmaceuticals and personal care products, in the Irish aquatic environment. This project provides a comprehensive insight into the occurrence and fate of CECs in wastewater treatment effluent on entry to Irish receiving waters.

The temporal and spatial occurrence of more than 100 CECs were monitored for 1 year in the aquatic environment and in wastewater treatment plant (WWTP) influents and effluents (see Chapter 2). Two WWTPs in Ireland were chosen, one rural and one urban. These WWTPs were chosen as risks had previously been identified by Irish Water (now known as Uisce Éireann) in terms of CEC contamination, and therefore this study would enable a “worst case” scenario to be investigated (although it is noted that results may not be fully representative of the national profile for CECs, as only two sites were investigated). Among the compounds detected at the highest concentration in effluent were the pharmaceuticals propranolol, hydrochlorothiazide and venlafaxine. The contaminants showed a clear decrease in concentration once the effluent entered the aquatic environment. A risk assessment was performed for substances detected, and the highest risk values in effluent across both sites were from the following compounds: estradiol, 17 α -ethynylestradiol, carbamazepine, diclofenac, atorvastatin and venlafaxine.

Pesticides were explored in more detail (see Chapter 3), investigating influent, effluent and receiving waters, and examining both the efficiency of pesticide removal in the same WWTPs as those investigated in Chapter 2 and the risks posed by these compounds in surface waters. Total pesticide loads in both WWTP influent and effluent were predominantly composed of the pyrethroid compounds permethrin and cypermethrin. Permethrin was removed (either fully or partially, depending on the WWTP) through wastewater treatment; however, cypermethrin was not. The acid herbicides 2,4-D (2,4-dichlorophenoxyacetic

acid), mecoprop and MCPA (2-methyl-4-chlorophenoxyacetic acid), which were either not detected or detected at only very low concentrations in both influent and effluent, were shown to account for the majority of pesticides detected in receiving water samples, indicating potential sources beyond water treatment. The acid herbicide MCPA was found to be of moderate risk to rural receiving waters, alongside the neonicotinoid pesticides acetamiprid and imidacloprid.

Passive sampling deployment strategies were investigated for pesticide analysis (see Chapter 4). When compared with grab samples taken from the same locations, the additional benefits of passive samplers were immediately evident, with a number of compounds detected using the passive sampling devices that had not been detected in the corresponding grab samples. Of particular interest was the detection of cypermethrin. In recent years, there have been efforts to phase out the use of pyrethroid pesticides, including cypermethrin, by restricting its use to limited applications (DAFM, 2022); however, it is still frequently detected in environmental aquatic samples. The work reported in Chapter 4 demonstrates how cypermethrin was detected using passive sampling but was not found in grab samples. However, this work also demonstrates the practical limitations of passive sampling, with some devices stolen, damaged or moved during the study.

The impacts of the pesticides detected in this project on invertebrate communities in Irish rivers were investigated (see Chapter 5). While no clear pattern emerged, it was determined that the concentrations of both clothianidin and imidacloprid exceeded the draft maximum allowable concentration environmental quality standard (but not the annual average environmental quality standard), which has been derived to acutely safeguard aquatic ecosystems. This highlights the need for further research into their use and the environmental impact of this use. In addition, the need to consider the interactions between two well-documented challenges for Irish freshwaters – herbicide pollution and nutrient enrichment – was highlighted here. This project also explored the extent

of CEC risk in Ireland in an international context, comparing the environmental risk of endocrine-disrupting compounds (EDCs) in the River Liffey, Dublin, with the River Thames, London, and the River Ter in Girona, Spain (see Chapter 6). The EDCs

contributing the highest potential risk in all three rivers were caffeine and bisphenol A. Lastly, a list of CECs for prioritisation for further investigation and a series of recommendations are presented (see Chapter 7).

1 Introduction

Hazardous substances not routinely monitored are referred to as contaminants of emerging concern (CECs), and have been defined by the United States Geological Survey as “any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects” (Raghav *et al.*, 2013, p. 12). In recent years, thousands of CECs have been detected in wastewater treatment plant (WWTP) influents and effluents and in surface, ground and drinking water worldwide. CEC removal in current WWTPs is often incomplete and variable, ranging from 12.5% to 100% for some frequently reported compounds (Luo *et al.*, 2014). Of the CEC classes shown to have less than 100% removal, pesticides, pharmaceuticals and personal care products (PCPs) are most prevalent in the Irish aquatic environment, as discussed in detail below.

Regulations originating in the EU, such as the Sustainable Use of Pesticides Regulations (Government of Ireland, 2012a) and the Plant Protection Product Regulations (Government of Ireland, 2012b), concerning the sustainable and responsible use of pesticides, have been transposed into Irish law. These regulations aim to reduce pesticide contamination in the wider environment and include, for example, the times of year at which pesticides can be applied and minimum application distances from water bodies. These measures, and the Irish Surface Waters Regulations (Government of Ireland, 2015), intend to reduce the occurrence of pesticides in Irish water bodies, as control of pesticides is critical to achieving a designation of good chemical status (DHLGH, 2018), and the public water supply for over 10,000 people has levels of pesticides above the standard in the Drinking Water Regulations (EPA, 2023). The extent to which pesticides were detected during routine Irish drinking water monitoring indicates that pesticide contamination may be a concern in Ireland. Apart from a subset of CECs that are monitored within the EU Watch List (EC, 2022), routine monitoring of pharmaceuticals and PCPs has not been carried out to date. Their contamination of waters

is an emerging environmental issue in Europe (EC, 2019), and national consideration of their presence and magnitude in the Irish aquatic environment is urgently required (Bradley *et al.*, 2015). Antibiotic and antifungal/antibacterial compounds have been shown, for example, to be highly persistent and most likely to persist in wastewater effluent (Guerra *et al.*, 2014; Luo *et al.*, 2014).

Previous research (McEneff *et al.*, 2014) has explored the spatial occurrence and relative distribution of pharmaceutical residues in the Irish marine environment. This work demonstrated that pharmaceutical residues are present in the Irish aquatic environment, and that they persist beyond the wastewater treatment process in the receiving surface waters. As part of this work, an analytical method to monitor a number of pharmaceutical compounds in WWTP influent and effluent samples was developed (McEneff *et al.*, 2014). Recommendations for future research noted in a comprehensive review undertaken by Tiedeken *et al.* (2017) included the investigation of technologies such as passive sampling and of seasonal variations in CEC loading and removal efficiencies in WWTPs, both of which are considered in this report.

An EPA-funded risk assessment case study was carried out that demonstrated the usefulness of a semi-quantitative risk assessment model for determining the relative risks posed by Irish WWTPs with regard to the environmental consequences of contamination with pharmaceuticals of interest. Future extensions and developments of this risk assessment model could allow benchmarking with EU standards, e.g. environmental quality standards (EQSs), and be applied to a wide range of regulated and emerging aquatic pollutants, thus providing critical information to government, regulators, state agencies, service providers and stakeholders (Tiedeken *et al.*, 2017). This research also highlighted that Irish studies evaluating pharmaceutical levels in WWTP influents and effluents are also lacking and required.

The extent of the potential hazard of CECs to human health is not known. The focus of the work here was

to establish the occurrence, exposure and effects of pharmaceuticals in the aquatic environment to add to the evidence base that can support robust

decision-making regarding human and ecological health (as demonstrated in, for example, Voulvoulis *et al.* (2015)).

2 Temporal Occurrence, Frequency and Fate of Contaminants of Emerging Concern in Rural and Urban Influent, Effluent and Receiving Waters

2.1 Objectives

While the analysis of CECs has attracted attention across the world, limited research has been carried out in Ireland. In this study, more than 100 compounds, including pharmaceuticals, PCPs and pesticides, were monitored for 1 year in WWTP influent and effluent and in surface waters with a monthly grab sampling campaign (Table 2.1). Substances were classified based on EU Surface Water Watch List designations; indications in the 2017 draft river basin management plan; recent literature highlighting substances as potential CECs for influent or effluent European urban WWTPs or associated receiving waters; and negotiations with the EPA on the contract award. Spatial distribution and seasonal and geographical variations were investigated at two locations, one rural (population equivalent less than 2000) and one urban (population equivalent 50,000–100,000). Stage 3 phosphorus removal treatment (known as 3P or tertiary P removal treatment) takes place at WWTPs located at both sites. The sites were chosen in collaboration with the EPA and Irish Water (now known as Uisce Éireann) as “worst-case scenario” locations to gain insight into the likely maximum scale of occurrence, frequency and fate of CECs in effluent entering surface waters. It should be noted, however, that, as only two sites were chosen, the results may not be fully representative of the national CEC profile.

2.2 Sample Collection and Preparation

Grab samples of 1 litre of influent and effluent wastewater and downstream surface water were collected monthly from October 2018 to September 2019 from two WWTPs managed by Irish Water, one located in a rural site (population equivalent less than 2000) and the other in an urban site (population equivalent 50,000–100,000). Irish Water has more than 1000 WWTPs within its asset base, which equates to 66–70% of the population connected to the public sewers. Samples were collected in duplicate

using amber Nalgene bottles and were transported chilled on ice. On arrival in the laboratory, one set of samples was not pre-treated and did not receive any pH treatment. The other set was acidified to pH2, using hydrochloric acid (37% v/v). All samples were stored in the freezer at -20°C until further treatment to minimise sample degradation/adsorption, which could alter the compounds and reduce chemical concentration. Details of the full quantitative analysis can be found in Rapp-Wright *et al.* (2023a).

2.3 Environmental Risk Assessment Methodology

The assessment of risk associated with the contaminants detected at both sites (rural and urban) was carried out by estimating risk quotients (RQs) at three trophic levels: algae, daphnia and fish. RQs are typically used to assess the ecological risk of pesticides by comparing a predicted environmental concentration with predicted no-effect concentrations (PNECs). The latter are generally calculated from acute toxicity tests. In this study, to calculate RQs, the highest concentration quantified for the compound per site was used as the maximum environmental concentration (MEC) value. If any compound was detected below the limit of detection (LOD) or limit of quantification (LOQ), then half of the method limit (LOD or LOQ, respectively) was used as the MEC. The MEC value was then divided by the PNEC value. PNECs were calculated using no-observed-effect concentrations (NOECs) from chronic studies when possible, and, if not possible, the lowest median lethal concentration (LC_{50}) value from available acute toxicity studies was considered. Values were obtained from the NORMAN Ecotoxicology Database, quantitative structure–activity relationship models or the United States Environmental Protection Agency Ecological Structure Activity Relationships (ECOSAR) predicted model (v2.0) software. Assessment factors (AFs) were established as follows: an AF of 10 was applied when three NOECs were available, an AF of 50 when two

Table 2.1. Use classifications of pharmaceuticals, pesticides and PCPs analysed in this chapter

Pharmaceuticals										Pesticides				PCPs	
Anti-inflammatory	Heart disease/hypertension	Psychiatric/psychotropic	Antihistamines/bronchodilators	Hormones	Others	Fungicides	Herbicides	Insecticides	Antioxidants	UV stabilisers	Antibacterials				
Diclofenac	Atorvastatin	Ziprasidone	Antipyrine	Norethisterone	Tacrine	2-(Thiocyanomethylthio)benzothiazole	Ametryn	Nitenpyram	2,6-Di-tert-butyl-4-methylphenol (butylated hydroxytoluene)	2-Ethylhexyl-4-methoxycinnamate (octinoxate)	Triclosan				
Mefenamic acid	Warfarin	Amitriptyline	Tramadol	Medroxyprogesterone	Tamsulosin	Azoxystrobin	Atrazine	Diflufenuron		Octocrylene					
Fluocinonide	Verapamil	Venlafaxine	Lidocaine	Flutamide	Timolol	Dimethomorph	Terbutyn	Mephofofolan		Benzophenone-4 (sulisobenzone)					
Flurbiprofen	Amiodarone	Nordiazepam	Celecoxib	Estrone (E1)	Memantine	Famoxadone	Thiazopyr	Cyromazine							
	Ciprofloxacin	Diazepam		17 β -Estradiol (E2)	Methylphenidate	Picoxystrobin	Dimethametryn	Spinosyn D							
	Azelnidipine	Risperidone		17 α -Ethinylestradiol (EE2)	Hydrochlorothiazide	Pyraclostrobin	Cycloxydim	Spinosyn A							
	Valsartan	Clozapine			Ketoconazole	Pyracarbolid	Cyclouron	Pymetrozine							
	Nifedipine	Lorazepam			Levocabastine	Flutolanil	Isocarbamid	Flufenoxuron							
	Sulfamonomethoxine	Citalopram			Ronidazole	Fuberidazole	Simazine	Oxamyl							
	Spiramycin	Fluoxetine			Risatriptan	Oxycarboxin	Benoxacor	Neonicotinoids							
	Sulfadimethoxine	Carbamazepine			Levamisole	Propamocarb	Clocinafop-propargyl								
	Enalapril	Carbamazepine epoxide			Prenzepine		Pyralufen-ethyl	Acetamiprid							
		Bupropion					Carfentrazone-ethyl	Clothianidin							
		Buspiron					Bensulide	Imidacloprid							
							Fenoxaprop-ethyl	Thiamethoxam							
							Flurochloridone	Thiacloprid							
							Piperophos								
							Pretlachlor								
							Proclamine								
							Prometon								
							Prometyrn								
							Propazine								

NOECs were available and an AF of 100 when there was just one NOEC located. A value of 1000 was applied when there were no NOECs located and at least one LC_{50} value available (ECHA, 2012).

Substances for which the RQ values were below 0.1 were considered to pose an insignificant risk, and substances for which the RQ values were between 0.1 and 1 were considered to carry a low or negligible risk. If RQ values were between 1 and 10, a medium risk was assigned (Rivera-Jaimes *et al.*, 2018). If any compound present had an RQ value higher than or equal to 10, a high ecological risk was assigned. To assess the potential risk arising from chemicals detected at a site, i.e. rural and urban, ΣRQ_{site} was calculated, and if ΣRQ_{site} was below 0.01 then no risk was associated with the site. A low risk of harmful effects was associated with values ranging from 0.01 to 0.1, a medium risk was associated with values between 0.1 and 1, a high risk was expected for values greater than 1 and, finally, if the values obtained were greater than 10, a very high risk was assigned. An estimation of the contribution of each compound to the risk calculated was also determined by dividing the RQ of the compound by the total RQ of the investigated site (ΣRQ_{site}) (Iturburu *et al.*, 2019).

2.3.1 Statistical and data analysis

Statistical analysis was performed to assess possible temporal and geographical variations. Mean values for categories of contaminants were used, with the normality of data tested with the Shapiro–Wilk *W* test, applying a $p < 0.005$ significance level. Analysis of variance with the post hoc Tukey's test ($p < 0.05$) and independent samples *t*-test was used for parametric data where necessary. Kruskal–Wallis analysis of variance by rank and independent-sample Mann–Whitney *U*-tests were used for non-parametric data. Concentrations reported below the LOQ were assumed to be half of the value of the LOQ of the specific compound for the specific matrix in order to perform the data analysis. Results obtained below the LOD were set to zero. Microsoft Office Excel (Redmond, WA, USA), IBM SPSS Statistics v27 (Armonk, NY, USA), R v4.0.5, RStudio v1.4.1106 (Boston, MA, USA), EPI Suite version 4.1 (US Environmental Protection Agency's Office of Pollution Prevention and Toxics and Syracuse Research Corporation, Washington, DC, USA) and Python version 3.7.9 (Wilmington, DE, USA) were all used.

2.4 Results and Discussion

An overview of the compounds detected in this work is shown in Figure 2.1, and discussed in more detail in the relevant sections below.

2.4.1 Pharmaceutical occurrence

Most of the compounds detected were pharmaceuticals, mostly belonging to the psychiatric/psychotropic category (including antidepressants and antipsychotics) and heart disease/hypertension category. Of the 47 pharmaceuticals detected across all samples, 17 were included in the top 100 most prescribed drugs by the General Medical Service when the sample period campaign was carried out, including atorvastatin in position two. Pharmaceuticals were also found at higher concentrations than other types of CECs throughout the influent wastewater samples. The antidepressant venlafaxine was detected in the highest concentration, $8273 (\pm 1) \text{ ng L}^{-1}$, in October 2018, in influent at the rural site; its average concentrations across the year were $1133 (\pm 2267) \text{ ng L}^{-1}$ and $553 (\pm 101) \text{ ng L}^{-1}$ for the rural and urban site, respectively. According to the Health and Safety Executive Most Commonly Prescribed Products database (HSE, 2019), venlafaxine was consistently in the top 30 most prescribed drugs in Ireland during the sampling campaign, but the prescribing frequency did not vary significantly between months. Valsartan had the highest concentrations detected across both sites, with average concentrations in influent samples of $2894 (\pm 2283) \text{ ng L}^{-1}$ and $2423 (\pm 821) \text{ ng L}^{-1}$ for the rural and urban site, respectively, and it was noted that its prescribing frequency was just under half that observed for venlafaxine. Other compounds such as antipyrine, an analgesic, were detected at high concentrations (average of $1302 (\pm 826) \text{ ng L}^{-1}$ for the rural site) but were not ranked in the top 100 most prescribed drugs during the sampling campaign.

For effluent samples, hydrochlorothiazide was detected at the highest concentrations, with an average of $444 (\pm 251) \text{ ng L}^{-1}$ and $547 (\pm 99) \text{ ng L}^{-1}$ for the rural and urban site, respectively. The following compounds also had relatively high average concentrations for the rural and urban site, respectively: diclofenac at $253 (\pm 152) \text{ ng L}^{-1}$ and $519 (\pm 173) \text{ ng L}^{-1}$, carbamazepine at $159 (\pm 188) \text{ ng L}^{-1}$ and $276 (\pm 116) \text{ ng L}^{-1}$, tramadol at $267 (\pm 249) \text{ ng L}^{-1}$

Prioritising Contaminants of Emerging Concern for Ireland

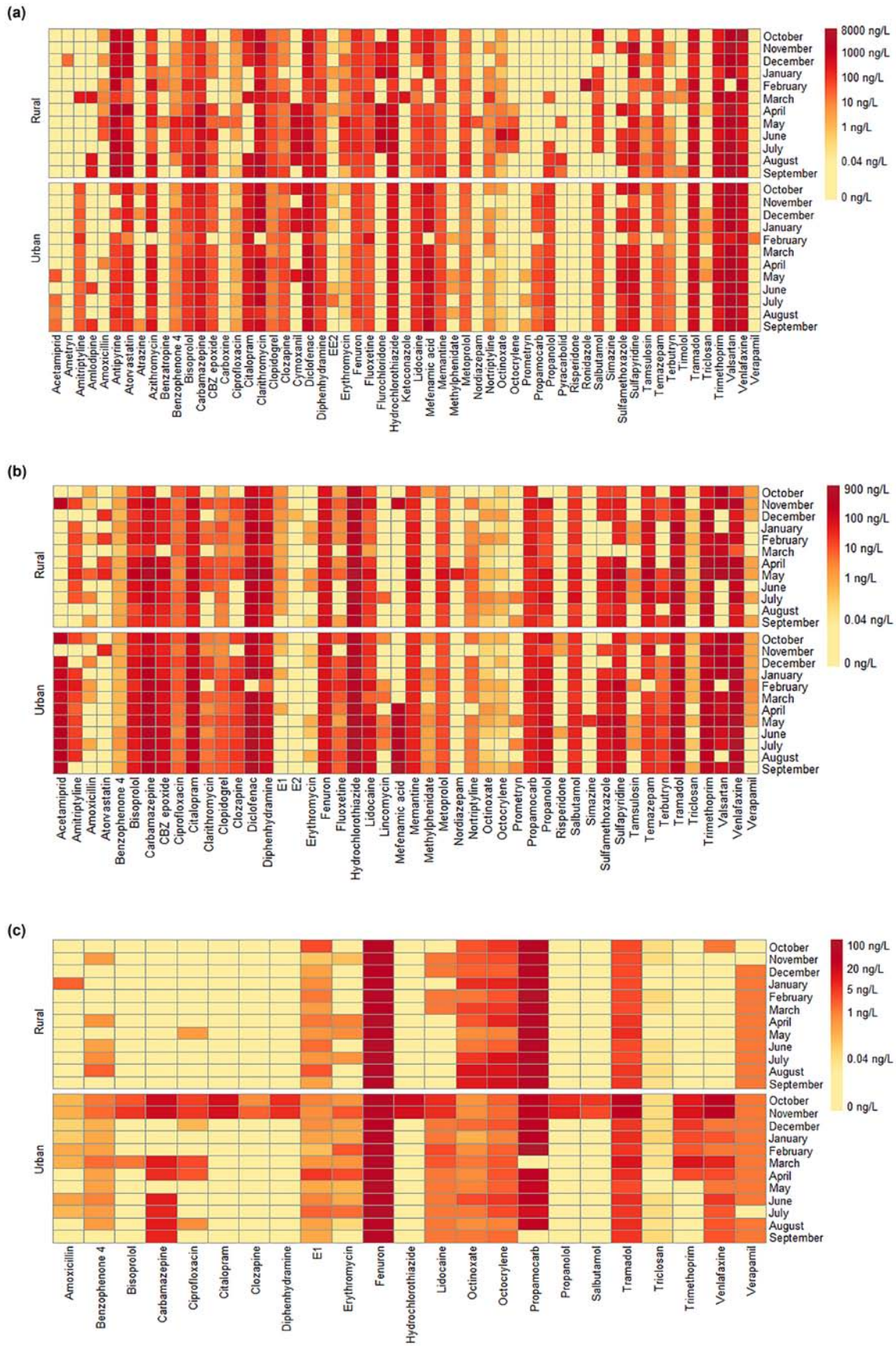


Figure 2.1. Heatmaps of compounds determined in the (a) influent, (b) effluent and (c) surface water samples for both sites, showing the ranges in concentrations, where darker colours indicate higher concentrations detected.

and $187 (\pm 78) \text{ ng L}^{-1}$, trimethoprim at $266 (\pm 269) \text{ ng L}^{-1}$ and $190 (\pm 75) \text{ ng L}^{-1}$, valsartan at $239 (\pm 161) \text{ ng L}^{-1}$ and $136 (\pm 64) \text{ ng L}^{-1}$, and venlafaxine at $163 (\pm 170) \text{ ng L}^{-1}$ and $448 (\pm 226) \text{ ng L}^{-1}$. Of these compounds, only venlafaxine belongs to the psychiatric/psychotropic category, which was the most detected category of pharmaceuticals. The psychiatric/psychotropic category accounted for 26% of all pharmaceuticals detected. Antibiotics accounted for 21% of the total pharmaceutical detections, but most detections were less than the LOD and LOQ. Antibiotics detected above the LOD were sulfamethoxazole, sulfapyridine, trimethoprim and ciprofloxacin, which were detected with average concentrations for both sites (i.e. urban and rural) of $44 (\pm 23) \text{ ng L}^{-1}$, $81 (\pm 67) \text{ ng L}^{-1}$, $228 (\pm 197) \text{ ng L}^{-1}$ and $6 (\pm 2) \text{ ng L}^{-1}$, respectively.

In surface waters, most pharmaceuticals were detected at less than the LOD and LOQ, in both the rural and the urban site. Of the pharmaceuticals, heart disease/hypertension drugs were detected most frequently (21% of total pharmaceutical detections), with propranolol detected at the highest concentrations, ranging from less than the LOD to 99 ng L^{-1} and 134 ng L^{-1} for the rural and urban site, respectively. All antibiotics were detected at concentrations below LODs and LOQs, except for ciprofloxacin in the urban site, where it was quantified up to $5 (\pm 26) \text{ ng L}^{-1}$. The same trend was observed for the heart disease/hypertension category, except for hydrochlorothiazide, which was detected at a maximum concentration of $18 (\pm 25) \text{ ng L}^{-1}$ for the urban site. This concentration was much lower than the maximum concentration of hydrochlorothiazide of $685 (\pm 15) \text{ ng L}^{-1}$ detected in the influent samples. Tramadol and carbamazepine were detected at maximum concentrations of $31 (\pm 6) \text{ ng L}^{-1}$ and $19 (\pm 10) \text{ ng L}^{-1}$, respectively, in surface waters in the urban site.

2.4.2 Personal care product occurrence

Four PCP compounds were investigated in this study (butylated hydroxytoluene was discontinued because of sensitivity issues), and all were detected across all matrices. The highest concentration of benzophenone-4 was detected in the influent at the

rural site ($242 (\pm 95) \text{ ng L}^{-1}$); however, the majority of samples noted concentrations of less than 2 ng L^{-1} in surface waters and effluents. Triclosan was also quantified at low concentrations, with a maximum of $7 (\pm 46) \text{ ng L}^{-1}$ in the influent at the urban site. Combined urban and rural influent samples showed maximum concentrations for octocrylene and octinoxate, up to $182 (\pm 66) \text{ ng L}^{-1}$ and $682 (\pm 153) \text{ ng L}^{-1}$, respectively. The concentrations of PCPs were observed as follows for the majority of compounds: influents greater than effluents greater than surface waters, with the highest concentrations in effluent and surface waters not exceeding $\leq 14 \text{ ng L}^{-1}$.

2.4.3 Pesticide occurrence

Across all samples analysed (as detailed in section 2.2), 11 pesticides were detected in influent, six in effluent and two in surface waters. Only propamocarb was found in all three matrices investigated; however, it was not detected in influent samples at the rural site. Occurrence frequencies were generally high for this compound in all matrices, but concentrations were relatively consistent and low overall, suggesting that this may have arisen from stormwater and/or leachate (generally less than 50 ng L^{-1}) (EPA, 2019). It was not clear in these sites what the usage patterns were across the year. Twenty-six out of the total 51 pesticides in this study are not approved by the European Commission as plant protection products (EU Pesticides Database, European Commission;¹ EU, 2009). Ametryn, atrazine, cyromazine, prometryn and terbutryn were detected mainly in wastewater influent, suggesting efficient removal during treatment. Only prometryn and terbutryn were further detected in effluent samples, but not in surface waters. Simazine, a Water Framework Directive (WFD) priority substance, was detected in effluent samples, but not in receiving surface water. Neonicotinoids are among the most widely used classes of insecticides in agriculture, although recent EU rulings (see, for example, CJEU (2023)) have restricted their use among flowering crops. From this group, acetamiprid was detected in only urban influent samples, with maximum concentrations of $27 (\pm 14) \text{ ng L}^{-1}$. In summary, all pesticides appeared to be removed before discharge

1 https://food.ec.europa.eu/plants/pesticides/eu-pesticides-database_en (accessed 15 September 2023).

from these WWTPs to the natural aquatic environment, apart from propamocarb.

2.4.4 Seasonal patterns

Temporal patterns were observed in the cumulative concentration values of all compounds detected across the year (see Figure 2.2, where cumulative concentrations were calculated for influent, effluent and receiving waters for both sites; values less than the LOD were set to zero). Regarding seasonal variations for surface waters, significant differences were determined for pharmaceuticals in the urban site only, specifically for the following categories: psychiatric/psychotropic (between summer–autumn and autumn–winter), heart disease/hypertension (between spring–autumn, summer–autumn and autumn–winter) and antibiotics (between autumn–winter and summer–autumn). For the psychiatric/psychotropic category, venlafaxine and citalopram were responsible for the significant change in the

concentration of these compounds in autumn. These two compounds were quantified in October and November, but in all other months were not detected or were not quantifiable. Antibiotics were detected in surface waters of the urban site at less than the LOD, except erythromycin, which was detected in July, but could not be quantified.

Although only grab samples were taken each month, an obvious increase in concentrations of ultraviolet (UV) filters were observed in the months with the most sun (May–July) (Kim *et al.*, 2017). In particular, octinoxate concentrations increased in the rural site and its detection has been correlated to seasonal use elsewhere (Carve *et al.*, 2021; O'Malley *et al.*, 2020). However, aside from its use in sunscreen products, octinoxate is also widely used in cosmetics, shampoos and lotions, and in industrial products such as insecticides, plastics and detergents (Carve *et al.*, 2021). Similarly, octocrylene was detected at higher concentrations overall in spring and summer, ranging

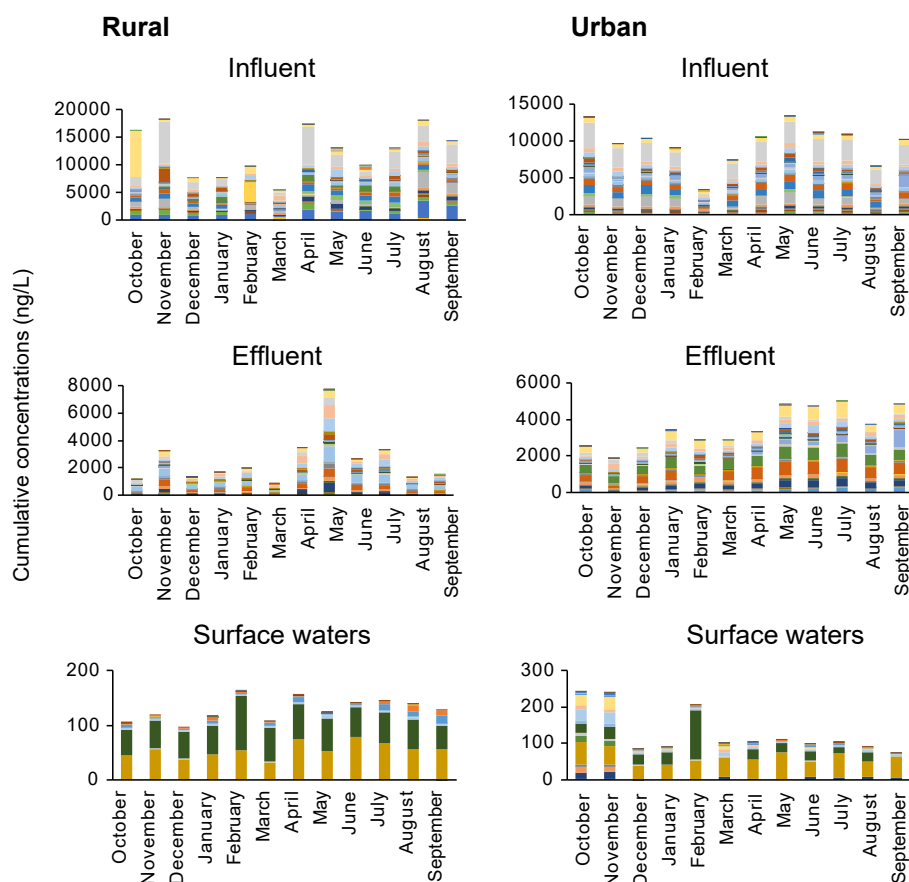


Figure 2.2. Cumulative compound concentrations detected during the sampling campaign for the three matrices tested at the urban and rural sites. Each colour represents a different compound detected, details of which can be found in Rapp-Wright *et al.* (2023a).

from not detected during winter and autumn to a maximum concentration of $182 (\pm 66) \text{ ng L}^{-1}$ in June.

Pesticide concentrations remained stable throughout the year, which is unexpected because of their application patterns from approximately May to August in Ireland. Pesticides could also be used in winter for weed control in winter cereals such as wheat, rye and barley; however, this is typically not the case in Ireland. Some pesticides are also used for manufacturing products, which happens throughout the year.

In summary, therefore, the main class of chemicals where a seasonal correlation was observed was PCPs, specifically UV filters, where an increase was observed in the summer months.

2.4.5 Geographical patterns

Two different catchment sites were sampled in Ireland, a rural site influenced predominantly by agriculture and a significantly more urbanised site. Influent, effluent and surface waters were investigated in both locations using the independent samples *t*-test on the two variables by category of contaminant to explore differences between the catchments.

In surface waters, the rural site showed 16 compounds detected overall, with 19% (i.e. three compounds) detected in every sample. In the urban site, 24 compounds were obtained overall, with 13% (i.e. three compounds) detected in every sample.

Two of them, fenuron and octocrylene, were common to both sites; however, the third compound was propamocarb for the rural site and octinoxate for the urban site. Carbamazepine, citalopram, clozapine, bisoprolol, hydrochlorothiazide, propranolol, trimethoprim, diphenhydramine and salbutamol were detected for the urban site only, and 17β -estradiol (E2) for the rural site only. The different categories were compared, and the pesticides ($t(44) = 1.715$, $p = 0.093$), psychiatric/psychotropic ($U = 11$, $p = 0.549$), heart disease/hypertension ($U = 75$, $p = 0.377$), antibiotics ($U = 74.5$, $p = 0.399$) and hormones ($U = 72$, $p = 1.000$) categories did not show any significant difference between the two sites, resulting in the same distribution of concentrations across both locations. However, analgesics and PCPs showed significant differences ($U = 148$ ($p = 0.001$) and $U = 456$ ($p = 0.012$), respectively). For the analgesics group, a clear example was tramadol, which was quantified

at a maximum concentration of $31 (\pm 6) \text{ ng L}^{-1}$ in the urban site, while in the rural location concentrations ranged from the LOD to LOQ and therefore no quantification was possible. However, PCPs showed the opposite results, where concentrations were higher for the rural site. It was not possible to carry out any statistical analysis for the category of antihistamines/bronchodilators, as no compounds were detected in any month for the rural site, and only two LOQ values were detected in the urban site, in October and November.

In effluent samples, 47 compounds were detected in both sites. E2 and nordiazepam were found in only the rural site, while risperidone and simazine were found in only the urban site. In this study, the presence of simazine was irregular, and it was detected, and also quantified, in only one effluent sample, for the month of May, from all matrices studied. The category of pesticides did not show any significant difference between the sites studied ($U = 757$, $p = 0.527$). The following categories also did not present significant differences between locations: antibiotics, antihistamines/bronchodilators, hormones, psychiatric/psychotropic, PCPs and others. However, the heart disease/hypertension ($U = 2110$, $p = 0.030$), analgesics ($U = 819$, $p = 0.031$) and anti-inflammatories ($t(28) = -3.510$, $p = 0.002$) categories showed significant differences between sites. Higher mean concentrations were detected for each category of pharmaceuticals for the urban sites.

Influent waters showed no significant difference between the sites investigated for the following categories: antibiotics, heart disease/hypertension, psychiatric/psychotropic, PCPs, antihistamines/bronchodilators and hormones. Analgesics as a group also did not present significant differences; however, antipyrine was studied independently due to its higher concentrations in the rural site. After statistical analysis, significant differences between the sites for antipyrine were clear ($U = 2$, $p = 0$). Anti-inflammatories ($U = 67$, $p = 0$), pesticides ($U = 516.5$, $p = 0.02$) and others ($U = 77$, $p = 0.034$) had significant differences between the sites studied. For the anti-inflammatories group, mefenamic acid was the main cause of the difference between sites due to the difference in the range of concentrations obtained for the rural and urban site, $59\text{--}336 \text{ ng L}^{-1}$ and $231\text{--}1463 \text{ ng L}^{-1}$, respectively. In the pesticides category, seven compounds were detected in the rural site and six in

the urban site. Flurochloridone (a herbicide) was detected in only the rural site and presented the maximum concentration for this group of compounds, with $1200 (\pm 12) \text{ ng L}^{-1}$ for the month of April; however, the maximum concentration obtained for the urban site was $367 (\pm 18) \text{ ng L}^{-1}$ for cymoxanil. Therefore, overall, higher concentrations were found in the rural site, as expected due to the influence of agriculture. However, three pesticides, acetamiprid (an insecticide), propamocarb (a fungicide) and atrazine (a herbicide), were found in the urban site only. Lastly, fenuron (an additive used in manufacturing for formulation or re-packing) was detected in both sites, in effluent and surface waters, with 100% of frequency across all matrices. However, it was not detected in influent wastewater, suggesting alternative sources of fenuron entering the environment (Miller *et al.*, 2019). Overall, there were more compounds detected in the urban influent samples, with higher analgesic concentrations in the urban site and higher UV filter concentrations in the rural site. There were also higher concentrations of certain categories of pharmaceuticals in the urban effluent and receiving waters, with, as expected, higher pesticide concentrations in the rural receiving water samples.

2.4.6 Fate and removal

Both sites involve 3P – Tertiary P removal treatments. The number and concentrations of compounds detected decreased in surface waters (Figure 2.3). This reduction was expected and can be attributed to dilution, degradation and partitioning to sediment. A clear example is temazepam, a prescribed pharmaceutical, which was found in influents at

concentrations ranging from 32 to 311 ng L^{-1} , effluents at less than LOQ to 149 ng L^{-1} and not detected in any sample of surface waters. Considering that WWTPs are not designed to remove CECs, it was observed that approximately 62% of total cumulative CEC concentrations were removed for the urban site. In addition, in the urban site, 95% of total cumulative CEC concentrations remaining in the effluent were further diluted in the surface waters. Higher removals were obtained for the rural site, where almost 84% of total cumulative CEC concentrations were removed during treatment (i.e. between influent and effluent), and 95% of those remaining in effluent were further diluted in receiving surface waters.

To fully understand the impact of CECs, it is essential to understand their transport and fate and also their removal in WWTPs, as they are the main point source (Wang *et al.*, 2020). A characterisation of influent and effluent wastewater samples was performed to determine the removal efficiency of both WWTPs selected, both of which have 3P – Tertiary P removal treatment. Removals varied overall, as they depend on the physicochemical properties of the molecules and the type of treatment performed (Burns *et al.*, 2018), and there might be some minor differences in the treatments applied at the sites investigated. For this reason, removals are treated separately, depending on the location. Overall, 19% and 24% of the total compounds detected in the urban and rural site, respectively, obtained $\geq 80\%$ removal efficiencies. High removal rates were achieved for the following compounds in the rural and urban site, respectively: amlodipine, 98% ($\pm 1\%$) and 94% ($\pm 1\%$); fluoxetine, 92% ($\pm 5\%$) and 86% ($\pm 5\%$); antipyrine, 99% ($\pm 1\%$)

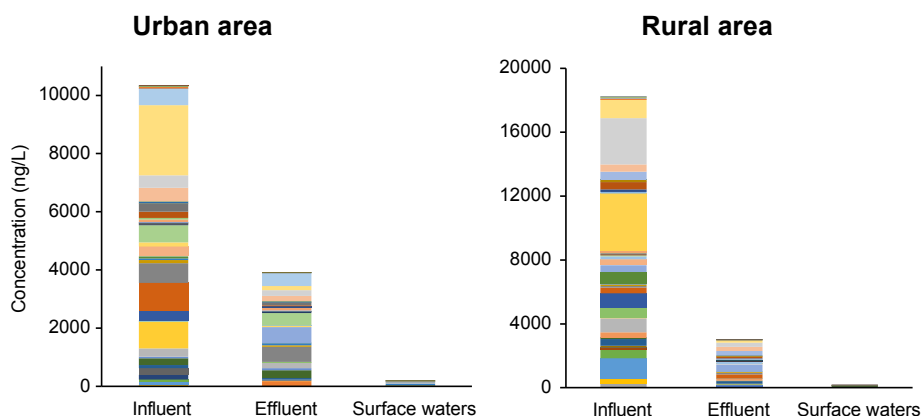


Figure 2.3. Cumulative results for average compound concentrations detected during the sampling campaign for the three matrices tested at each site. Each colour represents a compound detected.

and 92% ($\pm 3\%$); estrone (E1), 79% ($\pm 13\%$) and 88% ($\pm 4\%$). Compounds with log p -values less than 2.5 tend to remain in the aqueous phase (Patel *et al.*, 2019). This is in agreement with the low removal rates obtained for compounds such as bisoprolol and tamsulosin, with average removals of 46% ($\pm 33\%$) and 49% ($\pm 21\%$), and 45% ($\pm 32\%$) and 40% ($\pm 22\%$), for the rural and urban sites, respectively. The log p -values for these two substances were 2.21 and 2.14, respectively. However, as observed by the high standard deviations calculated, their removal rates vary widely between samples collected across the year. Moreover, negative removal rates (i.e. an apparent increase in concentration or frequency) were also observed for certain compounds, such as acetamiprid, carbamazepine, nordiazepam and sulfamethoxazole, across both sites. This is due to higher concentrations of certain compounds being found in effluent samples than in influent samples, or even compounds detected in effluent samples that were not detected at all in influent samples. Further research would be needed to assess these specific compounds and understand why this was the case.

Within the sampling timeframe, removal rates were not consistent. There were some compounds that in some months had positive removal rates, but in other months negative removal rates were determined. However, calculations of removal rates are only

indicative because of a lack of information on the type of hydraulic retention times and loads.

2.5 Environmental Risk Assessment

The potential impact of pharmaceuticals on the aquatic environment was investigated by performing an environmental risk assessment (ERA). All compounds detected in surface waters and effluent wastewater samples were considered. All compounds detected had the potential to pose a hazard to the aquatic environment, and therefore RQs were calculated using the European Medicines Agency (EMA) risk assessment tier approach (EMA, 2006). On completion of preliminary phase I analysis, shown in the risk classifications in Figure 2.4, higher risks are more often seen in effluent wastewater samples. The point where effluent is released is considered the worst-case scenario, as the highest concentrations are present before the compounds are diluted by surface waters. As shown in the pie charts in Figure 2.4, 58% of compounds or more detected presented insignificant risk for all matrices and sites tested. Higher risks in surface waters were associated with one compound, E2, at both sites. Only one compound presented a medium risk for both sites: 17 α -ethynylestradiol (EE2). Overall, the rural site was determined to have a lower overall risk, with more compounds assessed as

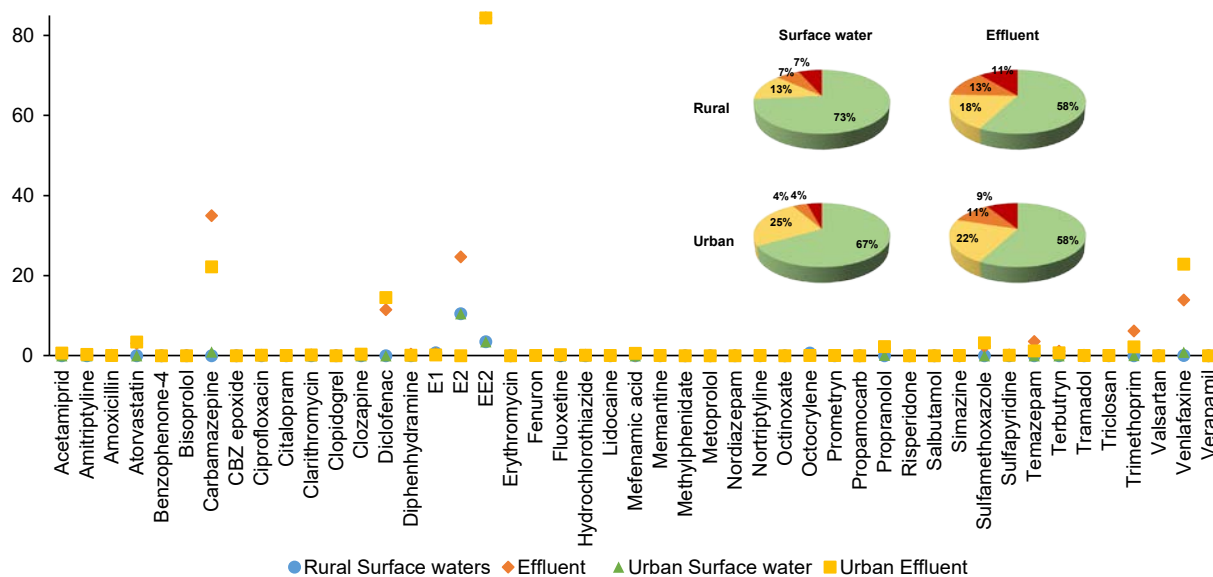


Figure 2.4. RQs of CECs in wastewater effluent and surface waters at both sites (rural and urban) and their risk classification. The pie charts illustrate the risk classifications for compounds detected at both sites tested for surface and effluent samples, where green indicates insignificant risk, yellow indicates low risk, orange indicates medium risk and red indicates high risk.

posing an insignificant risk. This is due to compounds either not being detected or being quantified at lower concentrations. E1 and octocrylene were the only two compounds determined to pose a low risk in both effluent wastewater samples and surface water in the rural site; they were also determined to be of low risk for the two equivalent urban site samples, along with carbamazepine, fenuron, propranolol and venlafaxine. Consequently, the urban site, overall, presented more compounds at higher concentrations, resulting in an increased number of compounds in the low-risk category.

In effluent samples in both sites, an insignificant level of risk was also found for the majority of compounds (26 compounds; $\leq 58\%$), as illustrated in Figure 2.4. Overall, half of all CECs in rural effluent samples and one-third of all CECs in urban effluent samples presented low risks (RQ between 0.1 and 1.0). A number of compounds presented similar risks in both sites. Ciprofloxacin, clozapine, fluoxetine and mefenamic acid were determined to pose a low risk in the urban site only, while diphenhydramine, hydrochlorothiazide and tramadol were calculated to represent a low risk in the rural site only. There was a high degree of commonality among specific CECs presenting a medium/high risk at both sites, including acetamiprid, atorvastatin and carbamazepine, with the addition of terbutryn, a WFD priority substance herbicide, in the rural site due to the higher MEC obtained. On average, in effluent samples from both sites, the top four CECs with high risk were EE2 (RQ = 27.9), venlafaxine (RQ = 18.4), diclofenac (RQ = 13.0) and carbamazepine (RQ = 11.5), and the rural site had an extra substance with high risk, namely E2. These high-risk CECs accounted for 11% and 9% of the total CECs in the rural site and urban site, respectively. The highest RQs were obtained for EE2. All compounds showed dilution between effluent and surface waters, which was expected, and this reduced the RQ value, as they were either not detected or quantified at a lower concentration in surface waters. RQs are typically only calculated in surface waters; they are calculated in effluent here only to allow comparison between sites. It is important to note that WWTPs are not designed to remove these compounds but that different treatment types (primary, secondary or tertiary) will have an impact on their levels in effluent. Nevertheless, WWTPs reduced the concentrations of a number of compounds, indicating

that, if influent wastewater was discharged into water bodies without any treatment, higher RQs would be obtained due to the possibly higher MECs.

2.5.1 Potential risk per site

When all compounds are taken into account, an overall potential risk can be determined for the site investigated. This is important because contaminants are present as mixtures in the aquatic environment, not as a single compound. Most research conducted has been carried out for a single compound at a time; however, these compounds are not isolated in the aquatic environment and cumulative CECs could have a higher impact (Vasquez *et al.*, 2014). The EMA guidelines (EMA, 2006) consider risk assessments on a substance-by-substance basis, but cumulative values can be studied to estimate the overall potential risk of the chemicals detected at a site. This was calculated for both sampling sites, using ΣRQ_{site} . Both sites and all matrices had values ≥ 10 , representing a very high risk. The rural site showed ΣRQ_{rural} values of 15 and 190 for surface water and effluent samples, respectively. As shown in Figure 2.4, different analytes contributed to the total risk, depending on the matrix. For surface waters, the main contributors were E2 (68%) and EE2 (22%), while, for effluent samples, EE2 (44%) and carbamazepine (18%) were the main contributors. The urban site showed ΣRQ_{urban} values of 17 and 160 for surface waters and effluent samples, respectively. For surface waters, two compounds were the main contributors, namely E2 (62%) and EE2 (20%). However, effluent samples were characterised by EE2 (53%), carbamazepine (14%) and venlafaxine (14%).

2.6 Conclusions

The temporal and spatial occurrence of more than 100 CECs were monitored in the aquatic environment and in two WWTPs over a period of 1 year in Ireland. Across all samples, 58 compounds were detected and 39, 32 and 4 were quantified at the ng L^{-1} level in wastewater influent, effluent and surface waters, respectively. The maximum concentrations obtained were 134 ng L^{-1} (propranolol), 1067 ng L^{-1} (hydrochlorothiazide) and 8273 ng L^{-1} (venlafaxine) (i.e. all pharmaceuticals). Contaminants decreased in concentration both after treatment and after they entered the natural aquatic environment, but the

level of decrease varied by compound. Seasonal and geographical variations were not significant for the majority of the substance use categories studied. Contaminants showed a clear decrease in concentration on entering surface waters. An ERA was performed, where CECs in wastewater effluent presented higher cumulative RQs derived from the

following compounds: E2, EE2, carbamazepine, diclofenac, atorvastatin and venlafaxine. Compounds making higher contributions in surface waters included E2, EE2 and E1. Overall, however, in surface waters, Σ RQ was an order of magnitude lower and the majority of compounds were in the low-risk category, suggesting a clear dilution effect in the environment.

3 Year-long Study of Pesticide Occurrence in Irish Wastewater Treatment Plants

3.1 Objectives

Although pesticides not listed as WFD priority substances or EU Watch List substances have been investigated extensively in the surface waters of other countries, there is a distinct lack of literature relating to their occurrence and fate in WWTP influents, effluents and receiving waters in Ireland. The pesticide class of contaminants is of particular interest in Ireland, as the majority of the land mass is dedicated to agricultural activities, and there is extensive use of several of these compounds (López-Ballesteros *et al.*, 2022). The aim of this work was to examine the fate of selected groups of pesticides in Irish WWTPs. The objectives were to obtain information on the occurrence and removal of these pesticides by studying two Irish sites, one in a rural location and one in an urban location, and to calculate RQ values for effluent and receiving water samples to provide an indication of the level of risk posed by the compounds detected.

3.2 Sample Analysis

Grab samples of 1 litre of influent and effluent wastewater and downstream surface water were collected monthly, from October 2018 to September 2019, from two WWTPs managed by Irish Water, as detailed in Chapter 2. This chapter explores pesticides in more detail. A solid phase extraction methodology was developed and implemented to target the extraction, preconcentration and analysis of pesticides. The 25 compounds analysed in this chapter were 2,4-D (2,4-dichlorophenoxyacetic acid), MCPA (2-methyl-4-chlorophenoxyacetic acid), mecoprop, acetamiprid, clothianidin, imidacloprid, thiacloprid, thiamethoxam, bifenthrin, cypermethrin, deltamethrin, esfenvalerate, permethrin, fluconazole, clotrimazole, imazalil, ipconazole, metconazole, miconazole, penconazole, prochloraz, tebuconazole, tetraconazole, glyphosate and aminomethylphosphonic acid (AMPA). Substances were classified based on EU Surface Water Watch List designations; indications in the 2017 draft river basin management plan; recent literature

highlighting substances as potential CECs for influent or effluent European urban WWTPs or associated receiving waters; and negotiations with the EPA on the contract award.

3.3 Results and Discussion

3.3.1 Occurrence of pesticides in wastewater treatment plant influent

Influent samples had the most analytes detected across all three matrices studied, with 19 out of 25 compounds detected. Overall, there were more positive detections in the rural site than in the urban, with the rural site having 109 total detections and the urban site having 100.

Frequently occurring analytes, found in over 50% of influent samples across both sites, were found to be the azole compounds tetraconazole, tebuconazole, miconazole, imazalil and clotrimazole, the pyrethroid permethrin and the neonicotinoid clothianidin. Figure 3.1 shows the frequency of occurrence of these compounds in influent samples across both sites.

Tetraconazole, an azole fungicide, was found in 100% of rural and 92% of urban influent samples. This compound was also detected in both effluent and receiving water samples at the two sites investigated in this study. Concentrations detected in influent ranged from less than LOQ to 150 ngL⁻¹, with the maximum detected concentration found in the rural site in June 2019. This maximum concentration is in agreement with anticipated higher concentrations in the summer months for many analytes in this study, owing to the increase in agricultural practices typically seen during this period and the number of compounds used in agricultural management systems. However, a number of compounds analysed in this study are not used in agricultural practices. One example of a compound with both pharmaceutical and agricultural uses is clotrimazole, a clinical and veterinary antifungal medicine, which was also found at a high frequency at both sites, occurring in 100% of rural site samples

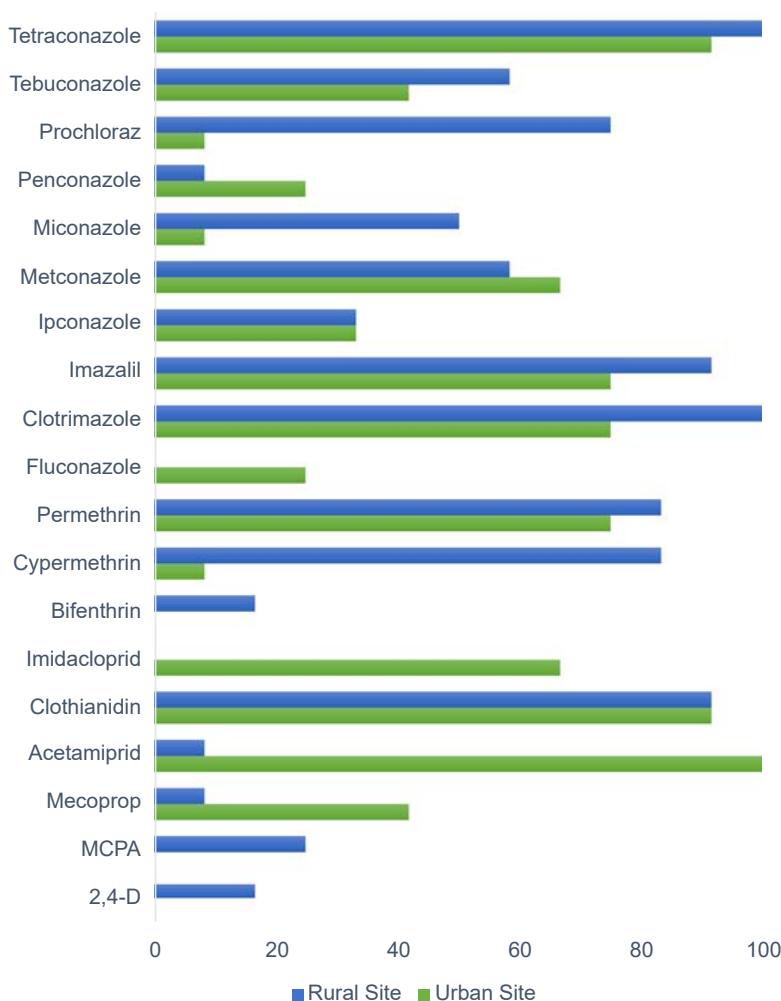


Figure 3.1. Frequency of occurrence of pesticide contaminants in Irish influent samples over a calendar year, from October 2018 to September 2019.

and 75% of urban site samples. The maximum concentration detected was 140 ng L^{-1} . Fluconazole was found at less than LOQ in only 25% of urban influent samples. Permethrin was detected at the highest concentrations in the influent samples, with a maximum concentration of $42,657 \text{ ng L}^{-1}$ ($42.66 \mu\text{g L}^{-1}$) found in April in the rural site sample. Clothianidin was found at the same frequency at both sites, occurring in 91% of samples; however, it was generally below the method LOQ. Occurrences above the LOQ were found in only rural influent samples, with a maximum concentration of 14.8 ng L^{-1} in February 2019.

Of the three acid herbicides (2,4-D, MCPA and mecoprop), only mecoprop was found in the urban site, whereas all three were found in the rural site. All acid herbicide occurrences were found between the months of May and September, coinciding with periods of increased agricultural activity and the

application period of these substances. Concentrations in influent samples for this group of compounds were generally low (less than 6 ng L^{-1}) across both sites. Three pyrethroids (bifenthrin, deltamethrin and esfenvalerate), two neonicotinoids (thiacloprid and thiamethoxam) and the herbicide glyphosate and its primary metabolite AMPA were not detected in any influent samples over the 12 months. However, for glyphosate and AMPA, the LODs were in the $\mu\text{g L}^{-1}$ range, and not the ng L^{-1} range seen for the other analytes. This limitation arose primarily because of the use of direct injection without sample preconcentration in preference to derivatisation. Preconcentration was not viable because of the extremely polar nature of the analytes, making them unable to be retained by the typical Oasis HLB solid-phase extraction cartridges (Waters, Dublin, Ireland) used for pesticide extraction, and the limited sample volume available not permitting multiple extractions of the same sample.

3.3.2 Occurrence of pesticides in wastewater treatment plant effluent

The majority of analytes found in influent samples were also found in the WWTP effluents, with 17 analytes found in effluent samples across both sites. Only three analytes were detected in influent but not in effluent: penconazole, ipconazole and bifenthrin. Individual effluent concentrations were generally lower than influent concentrations and were often below LOQs, with a few analytes showing the opposite tendency (i.e. higher effluent concentrations), specifically MCPA, mecoprop and clothianidin.

Occurrence frequencies previously observed for certain analytes in influent samples were also observed for WWTP effluent samples (Figure 3.2). Tetraconazole was again the analyte with the highest occurrence frequency across both sites, being detected in 100% of samples at each location. The concentrations detected, however, were considerably lower in effluent than in influent, indicating at least partial removal by WWTP treatment. Effluent samples revealed a difference between the two sites that could be observed in the overall analyte occurrence frequencies. The rural site had only four compounds

in over 50% of samples: tetraconazole, clotrimazole, cypermethrin and MCPA. By contrast, tebuconazole, imazalil, tetraconazole, clotrimazole, cypermethrin, permethrin and imidacloprid were all found to occur in less than 50% of urban effluent samples. Imazalil, imidacloprid and permethrin were found in 100% of urban effluent samples. Tebuconazole was found in 92% of urban effluent samples, albeit at comparatively low levels. It should be noted that the treatment type of both WWTPs is 3P – Tertiary P removal, and that work to upgrade sludge treatment was completed at the urban site in the year of study.

3.3.3 Occurrence of pesticides in wastewater treatment plant receiving waters

As expected, receiving waters had the lowest number of overall analytes detected of the three studied matrices, illustrated in Figure 3.3. Twelve of the 25 compounds were detected in surface waters over the course of the study. Seven analytes were detected at both sites: tetraconazole, miconazole, fluconazole, acetamiprid, 2,4-D, MCPA and mecoprop. In the urban site, miconazole, acetamiprid and mecoprop were found more frequently, whereas tetraconazole

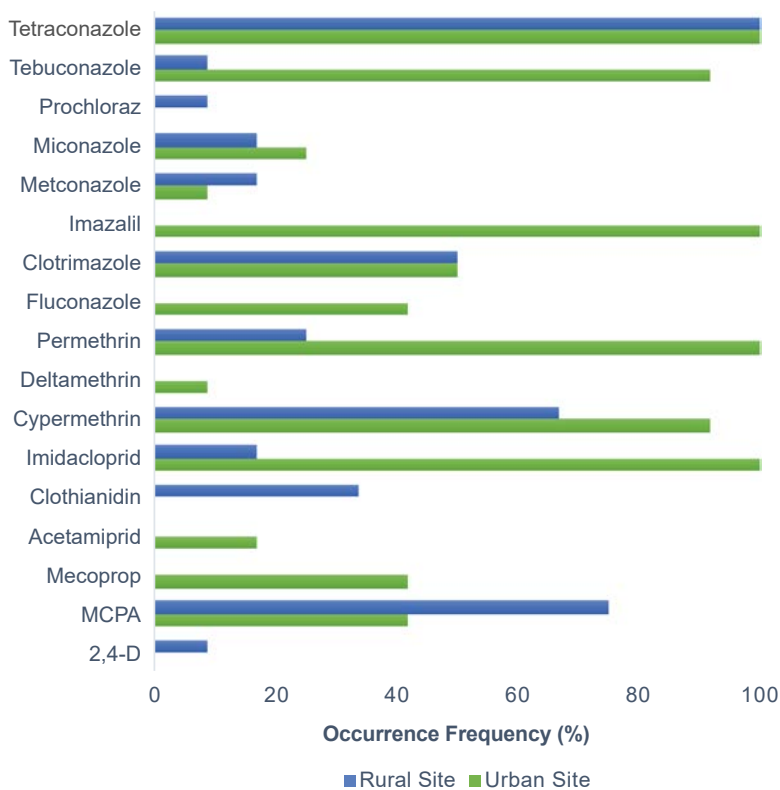


Figure 3.2. Frequency of occurrence of pesticide contaminants in Irish effluent samples over a calendar year, from October 2018 to September 2019.

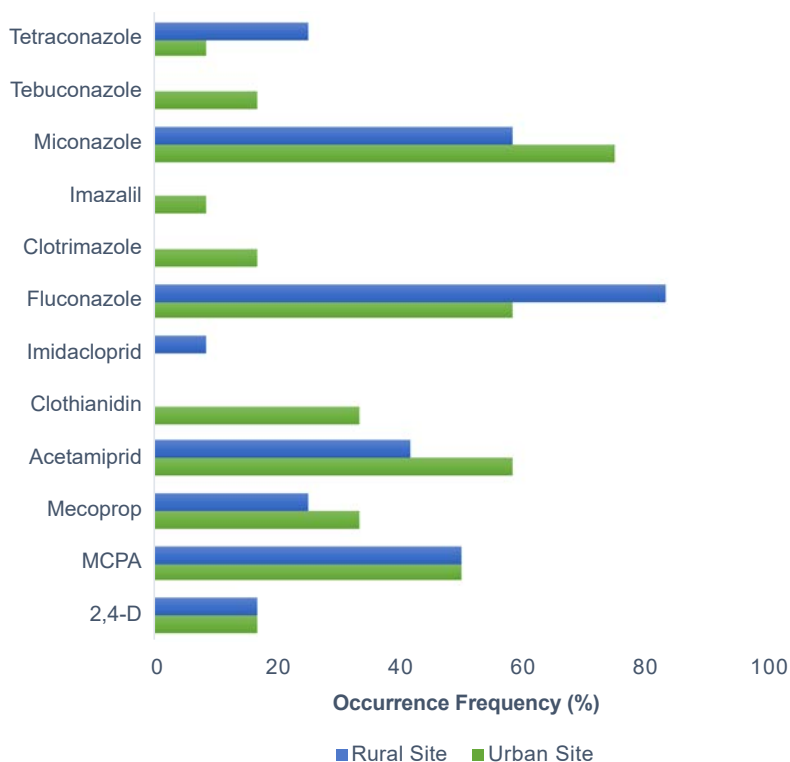


Figure 3.3. Frequency of occurrence of pesticide contaminants in Irish receiving water samples over a calendar year, from October 2018 to September 2019.

and fluconazole were found more frequently in the rural site. The frequency of occurrence was the same across both sites for two analytes: 2,4-D and MCPA.

Tebuconazole, imazalil, clotrimazole and clothianidin were all found in the urban site, but not in the rural site. Imidacloprid was the only analyte found in the rural site that was not also found in the urban site.

Concentrations of all analytes were below LOQs, apart from the acid herbicides on multiple occasions and one-off detections of miconazole (urban site in March) and imidacloprid (rural site in February), as shown in Figure 3.3.

3.3.4 *Relative composition of pesticide occurrences in Irish samples: spatial and temporal variation*

To examine spatiotemporal differences in pesticide occurrence, the samples were grouped into four seasons for each site studied: spring (March–May), summer (June–August), autumn (September–November) and winter (December–February). Cumulative concentrations (in ng L^{-1}) were calculated for each analyte at each site, which were then used to

determine the percentage of total pesticide occurrence contributed by each compound. For concentrations less than the LOQ, half of the method LOQ was used to give an indication of the aquatic environmental concentration for that compound and its influence on sample composition. Concentrations below the LOD were set to zero. This was performed for each water matrix, specifically influent, effluent and receiving waters.

Influent

Total cumulative pesticide concentrations by season can be seen in Figure 3.4. There was a stark difference in total pesticide concentrations between the two sites all year round. The rural site showed significantly higher total concentrations than the urban site. The spring period coincided with the highest total pesticide loads in the rural site overall, with a cumulative $109,623 \text{ ng L}^{-1}$ ($109.6 \mu\text{g L}^{-1}$) of pesticides quantified over this period. In the urban site, the summer season had the highest cumulative concentration, at 6090 ng L^{-1} ($6.1 \mu\text{g L}^{-1}$).

Influent pesticide detections from both sites were dominated by the pyrethroid compound permethrin,

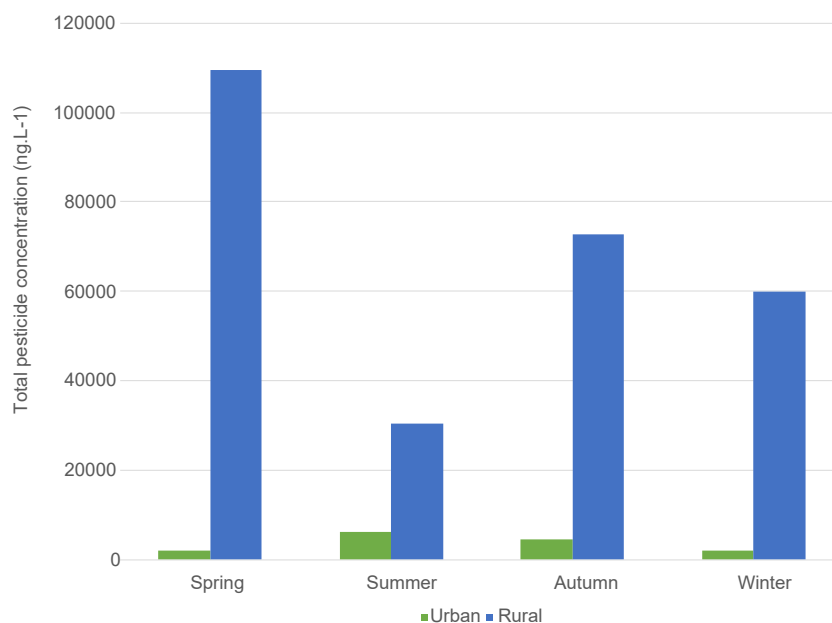


Figure 3.4. Total pesticide concentration in influent samples in each season for the rural and urban sites.

which accounted for >87% and >94% of the year's cumulative pesticide contamination detected in the rural and urban influent samples, respectively. This was followed by the other pyrethroids cypermethrin (5% of yearly total detections at both sites) and, to a lesser extent, bifenthrin, which was found only in spring at the rural site. Occurrences of these analytes in influent was in the high ng L⁻¹ to µg L⁻¹ range. Owing to the dominance of the pyrethroid compounds in influent samples, visualisation of the proportions of other compounds detected was difficult. To examine the distribution of the remaining compounds, the pyrethroid compounds were excluded and the total pesticide occurrence in influent samples was recalculated without these analytes. The distribution from this recalculation can be seen in Figure 3.5.

Some key differences were seen in the total yearly distribution of the remaining compounds between the two sites. Metconazole accounted for over 48% of urban influent concentrations and 29% of rural influent concentrations. A compound that accounted for a very small proportion in the urban site but a significant proportion in the rural site was imazalil, contributing 1.4% and 12.2% of the total urban pesticide loads, respectively. This was also seen for clotrimazole, which had an even larger difference between sites: 0.79% in the urban site versus 16.1% in the rural site. Tetraconazole accounted for 25% of the total contaminant concentrations at both sites, reflecting the similar occurrence frequencies seen for this compound.

When examining pesticide contribution by season, permethrin was in most samples the pesticide found at the highest concentration, accounting for between 89% and 98% across both sites in all seasons. The exception to this was the spring influent sample in the urban site, where permethrin was only 38% of the total concentration, with 37% attributable to cypermethrin and 24% to other compounds. In contrast, the equivalent rural spring samples consisted of 96% permethrin, 3% cypermethrin and 1% other compounds.

As the spring samples were the only ones in which permethrin did not dominate detections, these influents were investigated in more detail. The rural site had a more varied analyte composition than the urban site (in which 91% of the total concentration came from just from two analytes). Metconazole made up a large proportion of the total concentration in each site: 41% and 64% in the rural and urban site, respectively. Tetraconazole accounted for 27% and 21% of the spring samples in urban and rural sites, respectively, while the remaining analytes generally contributed less than 2% each. In the rural site, during the spring period, other significant analytes detected were tebuconazole, clotrimazole and imazalil, at 9%, 14% and 9%, respectively.

Effluent

Similar to the influent samples, effluent samples across the entire year and at both sites were dominated by pyrethroids. A highly relevant factor influencing effluent sample compositions is the removal rates of CECs at

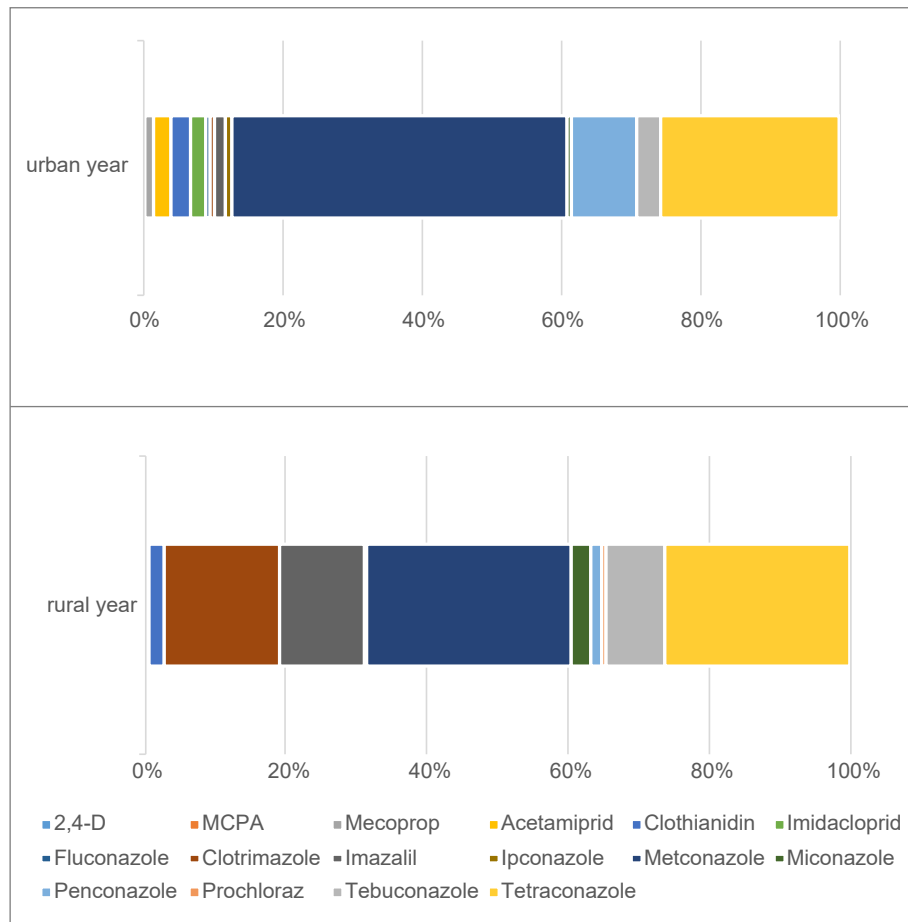


Figure 3.5. Relative concentration of pesticides detected in influent samples in the rural and urban sites over a calendar year, excluding pyrethroid compounds.

each WWTP. Total cumulative pesticide concentrations varied greatly both by season and by site, shown in Figure 3.6. The highest pesticide loads were found, interestingly, in winter samples for both sites. Over 4000 ng L^{-1} of measured pesticide contaminants were found at each site during the winter season. Spring saw the greatest difference in total concentrations between sites, with the urban site again having over 4000 ng L^{-1} of pesticide contamination, whereas the rural site had just under 650 ng L^{-1} .

In these samples, the most dominant compound changed from permethrin to cypermethrin. Cypermethrin made up 93% of the total yearly effluent composition at the rural site and 74% at the urban site. When coupled with the other pyrethroids detected, this analyte group accounted for between 94% and 98% of yearly effluent pesticide loads.

To examine the composition of the remaining 2–6% of yearly effluent sample detections, the pyrethroid group was excluded and totals were recalculated (Figure 3.7). There was variation in sample

compositions between the two sites. The urban site had a more varied distribution of analytes than the rural site. In the urban site, imidacloprid constituted a large proportion of the remaining effluent composition, with roughly equal proportions of MCPA, mecoprop, clotrimazole, imazalil and tetraconazole, and slightly smaller contributions of fluconazole and tebuconazole. In the rural site, MCPA, clothianidin, clotrimazole and tetraconazole accounted for the majority of the remaining yearly effluent compositions.

Examination of seasonal differences in effluent samples showed similar trends to the influent samples, in which pyrethroids were main contributors year round. The season showing the greatest difference between the two sites was autumn. In the urban site, the three pyrethroids detected were seen in more equal proportions than in any other season. The remaining autumn urban effluent samples comprised tebuconazole, tetraconazole and imazalil. By contrast, in the rural site, distribution was limited mainly to cypermethrin, tetraconazole and metconazole.

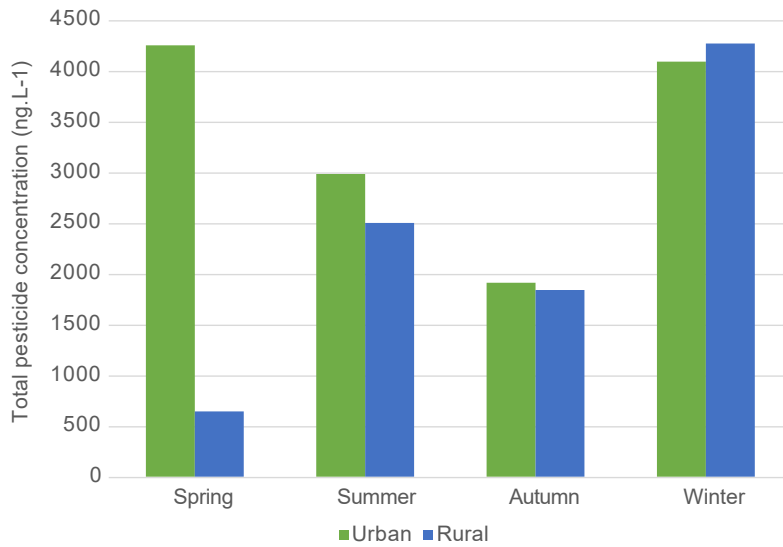


Figure 3.6. Total pesticide concentration in effluent samples in each season for the rural and urban sites.

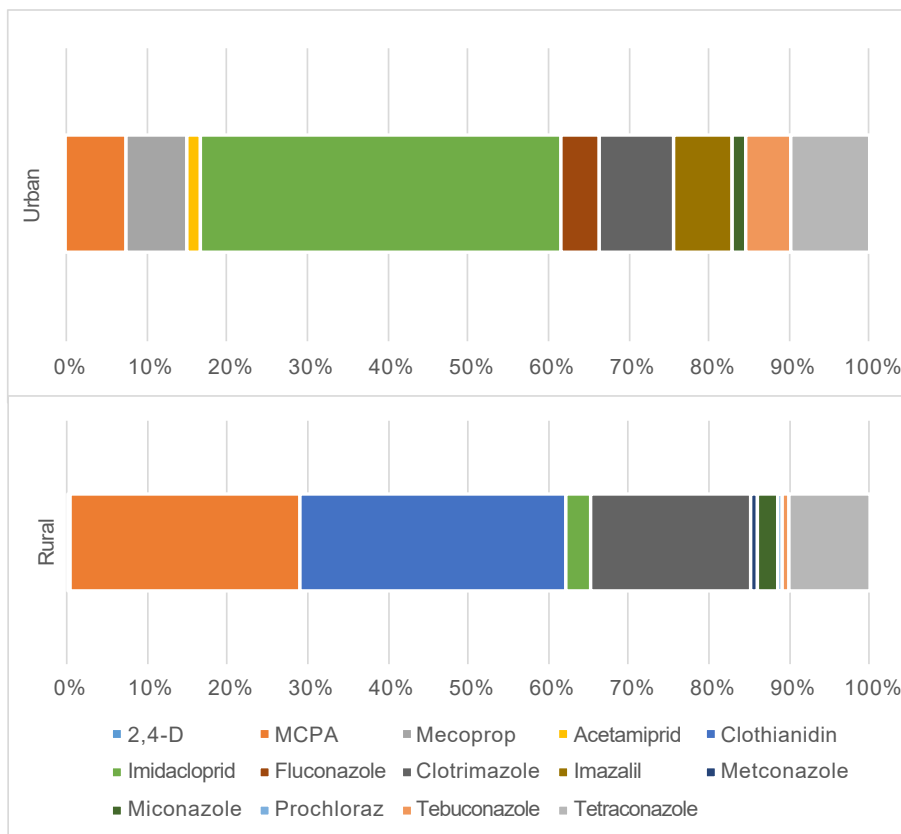


Figure 3.7. Relative concentration of pesticides detected in effluent samples in the rural and urban sites over a calendar year, excluding pyrethroid compounds.

Receiving waters

Total receiving water pesticide loads were significantly lower than those of both influent and effluent samples. Cumulative concentrations over the 12-month study did not exceed 270 ng L⁻¹ at either site, and were

overall similar for both sites (269 ng L⁻¹ and 265 ng L⁻¹ in the urban site and rural site, respectively). The highest concentrations were found during the summer in the rural site and during the autumn in the urban site. Concentrations were lowest for both sites in winter. Seasonal variation between total pesticide

loads were greatest at the rural site, ranging from 23 ng L⁻¹ in winter to 96 ng L⁻¹ in summer. The urban site had a smaller seasonal change, ranging from 53 ng L⁻¹ in winter to 80 ng L⁻¹ in autumn. Seasonal changes in cumulative concentrations can be seen in Figure 3.8.

Analyte composition in receiving waters varied greatly from that seen in the influent and effluent samples. Acid herbicides, which accounted for only a low proportion of the cumulative pesticide concentrations in the other two matrices, were considerable presences in receiving water samples. MCPA made up 46% of the yearly total urban detections and 72% of the yearly total rural detections, although it should also be noted that fewer compounds were detected in receiving waters. The relative yearly concentrations

of pesticides in receiving waters can be seen in Figure 3.9.

Pesticide compositions varied greatly both by season and by studied site. In the urban site, MCPA was the highest contributing analyte in summer and winter, accounting for 77% and 75% of the total pesticide composition, respectively. However, in spring and autumn, distribution was much more varied. Higher proportions of 2,4-D and the azole antifungal miconazole were observed in spring than in any other season. Autumn was the season with most analyte variation. Key contributory analytes were MCPA, clothianidin and mecoprop. In the rural site, the greatest difference in analyte composition was observed in the winter season. From spring through to autumn, MCPA contributed between 66% and 94% of

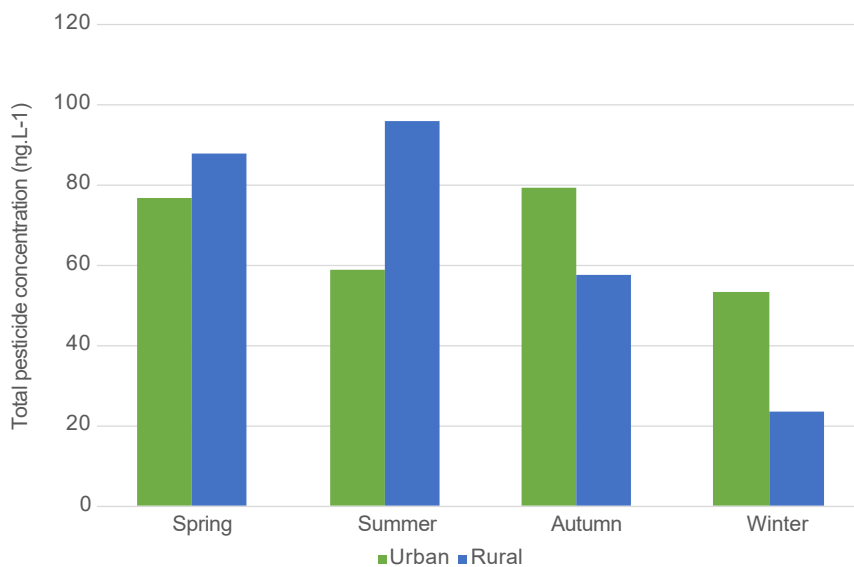


Figure 3.8. Total pesticide concentration in receiving water samples in each season for the rural and urban sites.

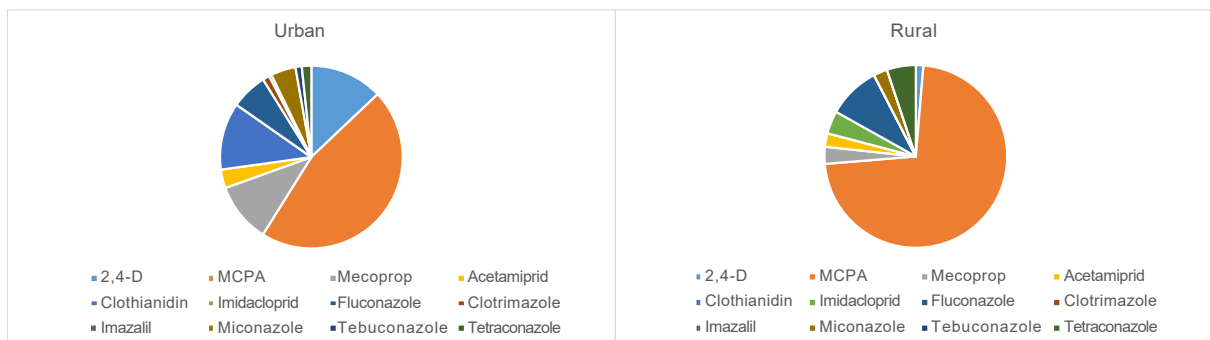


Figure 3.9. Relative concentration of pesticides detected in receiving water samples in the urban (left) and rural (right) sites over a calendar year.

the total cumulative concentration. However in winter, it was not detected at all. The analytes contributing to winter detections were imidacloprid, fluconazole, tetraconazole, miconazole and acetamiprid.

3.4 Determination of Risk

To assess the level of risk posed to the aquatic environment, RQ values were determined for occurrences in both receiving waters and effluent samples. RQ values were not calculated for influent samples, as the concentrations found in these samples are not expected to enter the wider environment. To examine the relative risk between sites, the highest MEC for each substance was used for each site. It should be noted that this is the most conservative approach, utilising the highest MEC instead of the average or median. The PNEC values utilised for RQ determination were those of the NORMAN network (using the lowest PNEC search function), apart from neonicotinoids, for which the substantially lower EU Watch List values were utilised. To enable a direct comparison with the work of Solaun *et al.* (2021), the RQs were classified into three risk levels: (1) RQ values less than 0.1 indicate a low risk; (2) RQ values between 0.1 and 1 indicate a medium risk; and (3) RQ values greater than 1 indicate a high risk. The RQ was estimated as the ratio between the MEC and the PNEC values (Sousa *et al.*, 2019), as shown in equation 3.1:

$$RQ = MEC/PEC \quad (3.1)$$

The majority of pesticides detected in receiving waters were determined to be a low risk to both studied sites. Only four analytes were identified as a moderate or high risk in surface waters: one acid herbicide and three neonicotinoids. MCPA was identified as being a moderate risk to the rural site due to a maximum measured environmental concentration of 83 ng L⁻¹ in June 2019. In the urban site, MCPA was considered a low risk.

Of the neonicotinoids, acetamiprid was found to be a moderate risk to both sites, with RQ values in the range of 0.1–0.15. Clothianidin was found in only the urban site, in October 2018, with an MEC of 16 ng L⁻¹, resulting in an RQ value of 1.9, and therefore was classified as a high risk. Conversely, imidacloprid was found in only the rural site, in February 2019, with a

MEC of 11 ng L⁻¹, leading to an RQ value of 1.3 and consequently a high risk classification.

RQ values were also determined for effluent samples, as WWTP effluents are released directly into the aquatic environment, allowing any contaminants present in the effluent to potentially pose a risk to aquatic life, although it should be noted that these calculations do not consider the impact of dilution. As anticipated, there were more moderate- or high-risk RQ values found for WWTP effluent, as concentrations are expected to be higher, and the overall number of analytes found was also larger than in receiving waters. MCPA was, again, found in both sites; however, based on effluent sample values, it was determined to be a low risk in both, with RQ values ranging from 0.005 to 0.008 across both sites. This is in contrast to the values directly calculated in receiving waters, where the rural RQ for MCPA was determined to be of moderate risk. The other acid herbicides were also determined to be of low risk when detected, with only the rural site showing presence of 2,4-D and only the urban site showing presence of mecoprop.

Similarly to the receiving waters, occurrences of neonicotinoids were identified as a moderate or high risk to the aquatic environment. Acetamiprid was, again, identified as a moderate risk, and imidacloprid and clothianidin identified as a high risk. The RQ values for high-risk analytes were higher than those of the receiving water, ranging from 3.6 (clothianidin) to 6.4 (imidacloprid), although, as has been noted previously, these calculations do not include dilution factors.

The azole compounds found in effluent samples were also determined to be low risk, except for clotrimazole. It was determined to be of moderate risk, with RQ values ranging from 0.2 to 0.3 across both sites. All other detected azoles were classed as low risk, with metconazole, miconazole, tebuconazole and tetraconazole found at both sites, fluconazole and imazalil found only at the urban site, and prochloraz found only at the rural site.

The pyrethroid pesticides cypermethrin, permethrin and deltamethrin were detected at considerable concentrations in the effluent. Deltamethrin was found in only one sample, less than the LOQ, at the urban site in October 2018. However, given the extremely low PNEC values for the entire pyrethroid group, the single detection of deltamethrin indicates a very

high risk to the urban site where it was detected. The MECs of the other two pyrethroids, cypermethrin and permethrin, also produced RQ values indicating extremely high risk. Permethrin had RQ values ranging from 505 to 2370 across both sites. Cypermethrin had the highest RQ values: an occurrence in the urban site of 2437 ngL^{-1} in March 2019 resulted in an RQ of 30,463, and an occurrence in the rural site of 1910 ngL^{-1} in January 2019 resulted in an RQ of 23,875. It should be noted, however, that neither of these compounds was detected in the receiving waters.

3.5 Conclusions

This chapter presents a comprehensive study of CECs in two Irish WWTPs. Total pesticide loads in both WWTP influents and effluents were predominantly composed of the pyrethroid compounds permethrin and cypermethrin all year round. Permethrin was removed (either fully or partially, depending on the site) through treatment processes; however, cypermethrin was not, leading to this compound contributing the highest proportion of the total effluent pesticide concentrations. These analytes were not detected in receiving waters at either sample location. Acid herbicides accounted for the majority of cumulative pesticide concentrations in receiving waters. However, these analytes were either not detected at all or were not significant contributors to influent or effluent pesticide concentrations, and so their concentrations increased between effluent and receiving water. This

indicates an alternative source for these compounds in the receiving waters, rather than the WWTPs investigated.

Removal rates were found to vary hugely between analytes, treatment plants and the time of sampling. Only three compounds were found to be consistently removed efficiently (greater than 60% removal) across both sites: metconazole, penconazole and tebuconazole. Permethrin was very effectively removed by the rural site, but rates varied in the urban site, with an average removal of 48% and a very large standard deviation.

A number of compounds were found to have negative removal rates, i.e. a higher concentration in WWTP effluent samples than in influent samples. This was seen most notably with the azole compound clotrimazole. Two analytes, imazalil and mecoprop, were found to be partially removed by the rural WWTP but were not removed by the urban site.

The pyrethroid pesticides cypermethrin and permethrin were identified as being of extremely high risk to the sites studied, because they had the highest MECs in wastewater effluent samples. Owing to the paucity of deltamethrin detections, it was difficult to assess the potential risk it poses. The azole antifungal compound clotrimazole was found to be a moderate risk to both sites from WWTP effluent. The acid herbicide MCPA was found to be of moderate risk to rural receiving waters, alongside the neonicotinoid pesticides acetamiprid and imidacloprid.

4 A Combined Approach to Pesticide Monitoring in Surface Water Catchments

4.1 Objectives

Passive sampling is a tool of increasing interest to the water quality monitoring community owing to its ability to absorb ultra-trace levels of micropollutants from the water body and capture spikes in pollution that may be missed in grab samples as time-weighted averages (TWAs). Results determined in investigations in this project (Chapters 2 and 3) showed that pesticide occurrence in Irish surface waters is widespread, and that many of these compounds are not entirely removed through treatment. The objective of the study described in this chapter was to investigate the use of a combined sampling approach to catchment monitoring for pesticide pollutants. This was an independent study that did not involve sampling of Irish Water WWTPs. Two areas in Ireland were selected for

study of surface waters, five sites in County Donegal (rural land use) and three in County Kildare (urban land use), as shown in Figure 4.1. These sites were selected for monitoring pesticide contamination by taking into account the local catchment land uses and possible point source pressures. Sampling was conducted during the summer season of 2021, and the occurrence and frequency of pesticides were investigated. The compounds analysed were acetamiprid, clothianidin, imidacloprid, thiacloprid, thiamethoxam, 2,4-D, MCPA, mecoprop, glyphosate, AMPA, clotrimazole, miconazole, fluconazole, imazalil, ipconazole, metconazole, prochloraz, penconazole, tebuconazole, tetraconazole, bifenthrin, cypermethrin, deltamethrin, esfenvalerate and permethrin.

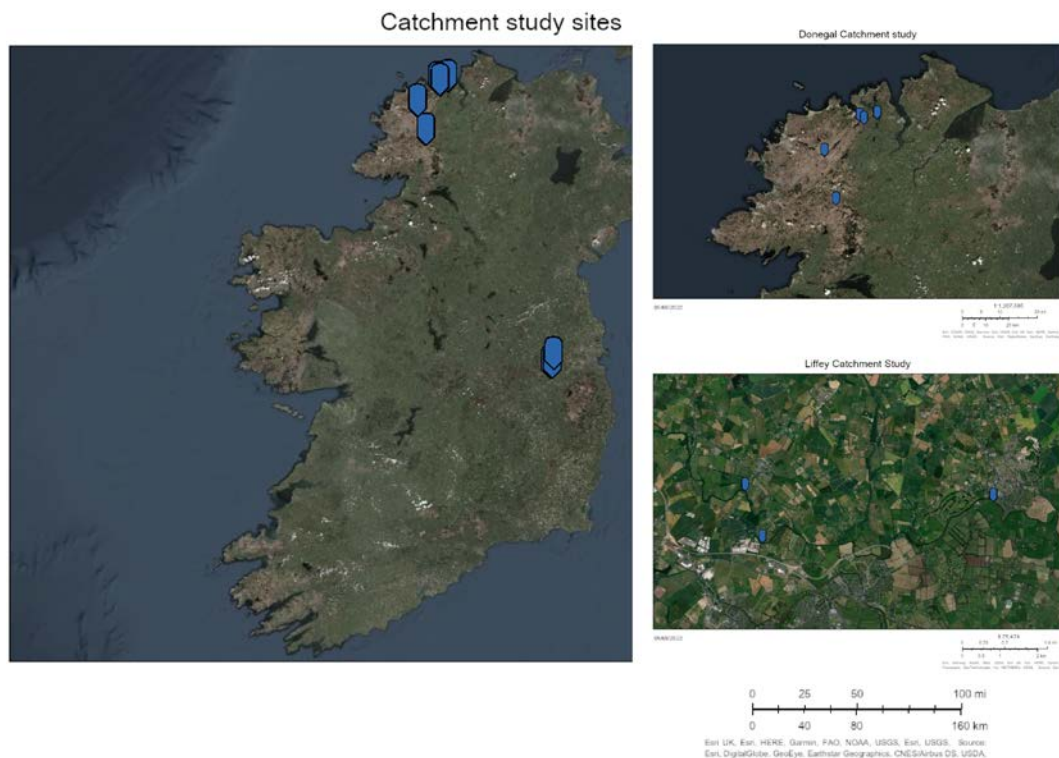


Figure 4.1. Map of sampling sites selected for study. The top right panel shows the five sites selected for study in the County Donegal area: Glendowan (Clogher), Glenveagh National Park, Glen A, Glen B and Cranford (Big Burn). The bottom right panel shows the three sites along the River Liffey in County Kildare: Liffey upstream, Liffey midstream and Liffey downstream.

4.2 Sample Collection

Two different configurations of Chemcatcher passive samplers were deployed in summer 2021 at five sites distributed in different rivers in County Donegal and at three sites along the River Liffey in County Kildare. Non-polar analyte targeted discs were deployed in the rural area (C18 chemistry disc) for 5 weeks and acidic analyte targeted discs (anion exchange chemistry disc) were deployed in the urban area for 2 weeks. The different disc chemistries, and associated deployment times, were chosen because of the different land practices associated with these regions and the pesticides expected to be present. Additional grab samples were taken to accompany the passive samplers in June, July and August 2021 in the rural site, and in June and July 2021 in the urban site, and were processed using solid-phase extraction. Passive sampler data were expressed as TWA concentrations using the approach previously described by Vrana *et al.* (2006). Values for uptake rate (R_s) were taken from the literature (Ahrens *et al.*, 2015; Townsend *et al.*, 2018), or, where information for uptake of a particular compound was not available, R_s values based on previously studied analytes with similar $\log K_{ow}$ values were used, as described by Moschet *et al.* (2014). Direct literature values for the uptake of the three acidic herbicides on anion exchange discs and the azole compounds imazalil, penconazole and prochloraz on C18 discs were available (Ahrens *et al.*, 2015; Townsend *et al.*, 2018). Owing to the increased level of uncertainty associated with the use of estimated values, the TWA concentrations presented

in this study for these analytes are considered semi-quantitative and are indicative of the relative concentrations found.

4.3 Results and Discussion

4.3.1 Occurrence of pesticides in grab samples

Grab samples showed the presence of 13 pesticides in Irish surface water catchments (Figure 4.2). All 13 compounds were found in Donegal, whereas only nine were found in the River Liffey. The top three most frequently occurring compounds were all azoles used for their antifungal properties, namely clotrimazole, fluconazole and miconazole. Clotrimazole was detected in 100% of grab samples; however, concentrations were always below the LOQ. Fluconazole was similarly found below the method LOQ in all grab samples. However, miconazole was detected above the LOQ on two occasions, once in the River Liffey catchment at the midstream (MS) point in July 2021, and once in Donegal at the Cranford (Big Burn) location in August. Both detections were at very low levels (3 ng L^{-1}). These results are similar to those presented in Chapter 3, in which the azole compounds were among the most frequently found in surface waters but at very low concentrations. This is also consistent with the literature, in which these compounds are frequently found in surface waters (Chen and Ying, 2015). The RQ values for these analytes, determined in Chapter 3, showed low risk at these levels, which can be extended to the results

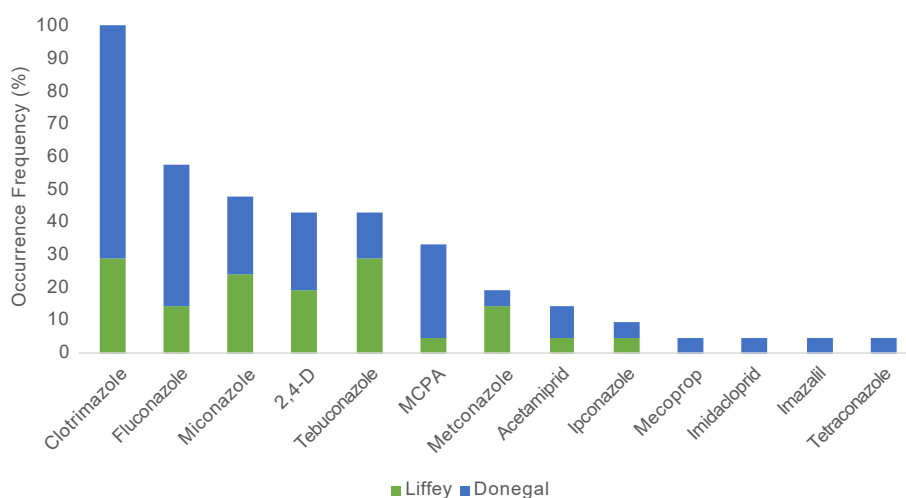


Figure 4.2. Bar chart showing frequency of occurrence of analytes found in surface water grab samples during the sampling campaign of summer 2021 for the combined catchment monitoring study ($n=21$).

found in grab samples in this study. Several analytes were undetected in the grab samples, including all five pyrethroids, three neonicotinoids and two azoles. This is similar to the results for receiving waters (see Chapter 3), where many of the same analytes were not found, although there were some differences, particularly with regard to neonicotinoid detections. Nonetheless, the implications of the findings overall are that these analytes are not a significant presence in Ireland, or they are occurring at concentrations too low to be detected in the grab samples. In the case of the latter, it should be considered that pyrethroids have particularly low PNECs and pose significant analytical challenges.

Cumulative pesticide concentrations were, by a significant margin, highest in grab samples from the Cranford site (Figure 4.3), with nearly 250 ngL⁻¹ found at this location. The acid herbicide MCPA was the most common pesticide, being detected at levels above the LOQ at every sampling event. MCPA was also detected at levels above the LOQ at both sites along the Glen river. Acid herbicides, predominantly MCPA, were also found to make up a significant proportion of river water cumulative pesticide concentrations (see Chapter 3, section 3.3), with 72% of the yearly total cumulative concentration in the rural site coming from this group. From the results presented in this chapter, this compound remains a significant presence in the Irish receiving waters sampled. This is in line with the literature, in which MCPA concentrations and loads of

up to 5.8 µg L⁻¹ and 106 kg y⁻¹ were measured (Cassidy *et al.*, 2022).

The results from receiving water samples reported in Chapter 3 showed maximum MCPA concentrations of over 80 ng L⁻¹ in June 2019 in the rural site. The grab samples in this study contained MCPA concentrations of over 117 ng L⁻¹ in July 2021 in Donegal, which is also rural. These results show a large increase in the maximum MCPA concentrations determined in samples during this project, confirming the observation by the EPA in 2017 (EPA, 2017). Unfortunately, owing to COVID-19 restrictions, samples from the summer of 2020 were not available for the examination of this compound, and so a definitive trend over the years could not be established.

Although a very rural area, Donegal has not historically been linked with intensive herbicide use because the land use in this area is dominated by sheep farming and forestry, which may account for the pyrethroid compounds previously detected here (Regan *et al.*, 2018). The results found in grab samples here indicate that acid herbicides, including MCPA, are more of a presence in this area than initially thought and further monitoring of such herbicides would be beneficial.

The Glenveagh National Park and Glendowan (Clogher) sites were the least contaminated areas studied, where no quantifiable levels of analytes were determined in grab samples (Table 4.1). Some detections below the LOQ were seen for 2,4-D and

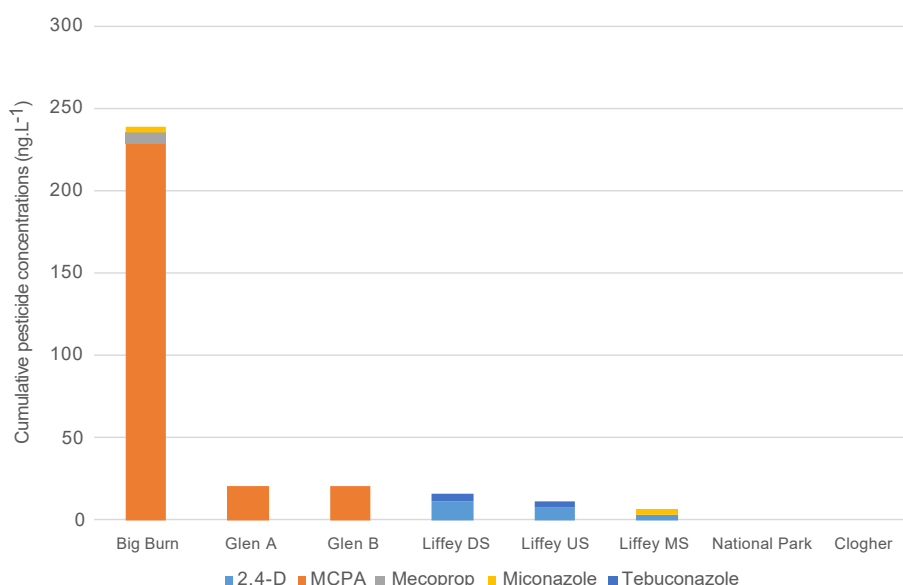


Figure 4.3. Bar chart showing cumulative pesticide concentrations in grab samples for each of the sites studied in the combined catchment study. DS, downstream; MS, midstream; US, upstream.

Table 4.1. TWA concentrations (ng L⁻¹) of pesticides determined from passive sampling during summer 2021 at sites in the River Liffey and Donegal

Pesticide	Liffey			Donegal			
	Upstream	Midstream	Downstream	Glen A	Glen B	Glendowan (Clogher)	Cranford (Big Burn)
2,4-D	2923.4±501.5	4144.5±559.6	1842.7	n/d	n/d	n/d	n/d
MCPA	280.2±33	427.4±129.8	302.3	n/d	n/d	n/d	n/d
Mecoprop	15.04±6.4	15.2±7.02	38.94	n/d	n/d	n/d	n/d
Bifenthrin ^a	n/d	n/d	n/d	3830.7±429	3575.6	n/d	n/d
Cypermethrin ^a	n/d	n/d	n/d	34,947.3	50,519.8	20,048.9	n/d
Deltamethrin ^a	n/d	n/d	n/d	2156.4±493.8	n/d	n/d	n/d
Permethrin ^a	n/d	n/d	n/d	25,165.5	45,259.5	n/d	n/d
Imazalil	n/d	n/d	n/d	41.3±23.7	n/d	26.6±11.4	12.6±7.8
Ipconazole ^a	n/d	n/d	n/d	6.5±2.2	n/d	n/d	n/d
Metconazole ^a	n/d	n/d	n/d	207.6±155.01	n/d	n/d	35
Miconazole ^a	n/d	n/d	n/d	235.7	n/d	131.4±85.3	198.5±60
Penconazole	n/d	n/d	n/d	13.7±1.3	n/d	n/d	n/d
Tebuconazole ^a	n/d	n/d	n/d	217.1±37.7	339.5	115.1±87.2	111.6±82.8
Tetraconazole ^a	n/d	n/d	n/d	59.3±3.9	n/d	n/d	68.2±3.2

^aDenotes semi-quantitative results only.

n/d, not detected.

some azole compounds; however, occurrences at these concentrations are unlikely to be associated with significant risk, as was seen in Chapter 3.

4.3.2 Occurrence of pesticides in passive samplers

Several pesticides were detected in passive sampling devices but were not detected in grab samples. Full details of TWA passive sample results for the analytes detected can be found in Table 4.1.

In this study, all three acidic herbicides included in the method were found at every point along the River Liffey using the anion exchange Chemcatcher configuration. The highest TWA concentration was found for 2,4-D, which was present in the low $\mu\text{g L}^{-1}$ range. The highest levels of 2,4-D were found at the midstream point in the Liffey catchment, between the upstream and midstream sampling locations. This trend was also seen for MCPA, where the levels reached 427.4 ng L^{-1} . This is an interesting observation, as the results in Chapter 3 indicated that the acid herbicide pollution in the receiving waters was likely to be from a source other than the WWTPs studied, because of the increase in their concentration between effluent and receiving waters,

further demonstrating the variety of potential point and diffuse sources of river pollution. Successful utilisation of passive sampling for detecting acidic herbicides has been reported in the literature in recent years (Taylor *et al.*, 2020; Townsend *et al.*, 2018). A study published in 2020 by Khan *et al.* examined two catchments in Wexford in south-east Ireland, and this work, which utilised Chemcatcher passive samplers, detected acidic herbicides in surface waters throughout the year. Khan *et al.* (2020) found TWA levels comparable to those found in this Liffey study of up to 262.9 ng L^{-1} of MCPA in the summer months. Interestingly, the concentration of 2,4-D was significantly lower in the Wexford study than those found in the Liffey. 2,4-D is known to have broad applications in both agricultural and non-agricultural settings. In the USA, the compound is reported to be the most widely used herbicide in non-agricultural settings (Freisthler *et al.*, 2022). Therefore, its higher presence in the Liffey catchment could be related to other anthropogenic activities conducted in this area, such as amenity horticulture.

In contrast to the other two acid herbicides, passive sampling found mecoprop at higher concentrations at the downstream site, implying a pollution source for this analyte that was further downstream than

the WWTP and a children's farm. A large golf course (Millicent Golf Club) is located less than 1 km upstream of the downstream site. Golf courses and the associated lawn care, as indicated in the previous paragraph, are known to be sources of acid herbicide pollution and so are a likely explanation for this observation (EPA, 2019).

As mentioned in section 4.3.1, pyrethroid pesticides have previously been found in the Donegal area (Regan *et al.*, 2018). Passive sampling in that study used polydimethylsiloxane and semipermeable membrane devices and found levels of cypermethrin between 0.06 and 70 ng L⁻¹ in the months of April/May in 2014/15. Passive sampling at these same sites a number of years later showed that these compounds continued to be present in the µg L⁻¹ range (Table 4.1). In recent years there have been efforts to phase out the use of pyrethroid pesticides, including cypermethrin, by restricting its use to a few applications, although no restrictions are in place for forest applications. It is therefore not surprising that, as has been demonstrated both throughout this research and in other studies (Affum *et al.*, 2018; Miller *et al.*, 2019), occurrences of controlled substances in environmental matrices are still a frequent finding. This indicated increase in concentration could be due to several factors in addition to changes in usage, including the time of year studied and the type of passive sampling device used. For example, semipermeable membrane devices have been known to be susceptible to biofouling, which in turn decreases the sampling rate and therefore uptake onto the disc (Lissalde *et al.*, 2016). Owing to the design of the Chemcatcher, fouling on the actual disc is less likely because of the use of an overlaid low-density polyethylene membrane. In addition, another potential factor is variation in the flow velocity of these rivers over time. Flow velocity has been noted in previous studies to have a significant impact on the sampling rates of the C18 Chemcatcher configuration, in which a higher flow corresponded to an increase in sampling rates (Kingston *et al.*, 2000; Vrana *et al.*, 2006). It is therefore possible that the Chemcatcher device was able to sequester more of the analyte onto the disc in our study than in previous studies conducted in the area.

Within the Donegal study, the Glen A site showed most pesticide contamination, with 11 analytes detected. The Glen B and Glendowan (Clogher) sites

showed the least pesticide presence, with only four analytes found at each, including cypermethrin and tebuconazole at both sites. Tebuconazole was the only analyte found in all passive samplers in the Donegal area, with indicative TWA concentrations in the 100–400 ng L⁻¹ range. Tebuconazole was found infrequently in the grab samples and always below the LOQ, again demonstrating the benefit of including passive sampling in catchment monitoring. Tebuconazole has been previously found frequently in passive sampling campaigns in the UK using a Chemcatcher fitted with the HLB-L sorbent (Taylor *et al.*, 2021).

4.3.3 Evaluation of a combined sampling approach to catchment assessment

There are some very evident benefits of using passive sampling technologies for catchment monitoring. The detection of several pesticides in passive sampling discs that were not found in the accompanying grab samples is clear evidence of this. The ability to detect pyrethroid pesticides that were undetected in the grab samples, as well as in the receiving waters, as reported in the previous chapter, is of great benefit. The use of these devices can help bridge the gap between analytical method detection limits and the required EQS values for monitoring these substances, which has for years presented a challenge (although it should be noted that this will not be sufficient for WFD compliance assessment, as passive sampling does not monitor the whole water column (just the dissolved phase)). The EQS value for cypermethrin is 0.08 ng L⁻¹, which has been shown to be exceedingly difficult to detect with most analytical methods. In a previous study by Vorkamp *et al.* (2014), in which 12 litres of water was extracted, the LOD was above this EQS. Using passive sampling devices in conjunction with the analytical methods developed for these compounds offers a promising direction for future monitoring due to its applicability to a broader range of analytes. Although some of the results presented in this study were semi-quantitative, qualitative data alone can provide insightful information about the chemical status of a water body. Indeed, much of water quality monitoring is moving towards non-targeted analysis as a tool for assessment (McCord *et al.*, 2022). Therefore, passive sampling could be a welcome addition to this approach, particularly for compounds that have lower method LODs.

However, passive sampling does present its own unique challenges, including vandalism and the labour required for sampler preparation, deployment and collection. The most significant drawback of this approach was demonstrated by the total loss of the Glenveagh set of samplers. It is likely that a member of the public or concerned citizen removed these devices from the river, thinking that they were litter. In addition, on final retrieval of the Clogher discs, the cage was found on the river bank, evidently removed and left there by an unknown person.

Interference with passive sampling discs at this site caused issues with producing standard deviations for all analytes, as some compounds appeared to be lost/degraded by removal from the river. This tampering must have occurred during the latter half of deployment, as the devices were still in place at the sampling mid-point when grab samples were collected. A similar issue occurred with one of the replicates at the Glen B site, when one of the discs was damaged beyond repair, therefore not allowing standard deviations to be calculated.

Use of plastic sheets, rather than cages, resulted in them being frequently tampered with or damaged, and so it is recommended that cages be used for future campaigns wherever possible. Although every effort was made to place and label these devices appropriately to avoid interference from passers-by, this is not totally avoidable, as was seen by the removal of the cage at the Clogher site. Previous studies using passive sampling have also experienced

issues with sampler interference, loss or damage (Grabic *et al.*, 2010; Lacorte *et al.*, 2022).

4.4 Conclusions

This study investigated the implementation and suitability of a combined sampling approach to surface water monitoring. Two areas of Ireland were selected for monitoring pesticide contamination by considering the local catchment land uses and possible point pressures. Sampling was conducted during the summer season of 2021 to coincide with the period when pesticide contamination is most likely to be a risk to local water bodies.

Pesticide contamination was found at all sites in both grab and passive samples, aside from the Glenveagh site, where the passive samplers were lost before retrieval. One of the recommendations arising from this study is that the use of only one sampling approach is insufficient for creating a detailed picture of water quality in a catchment. As is evident from these results, the use of grab samples alone would mean that many ultra-trace-level compounds or pollution events would be missed. However, the use of passive sampling alone is a risk because of the ease with which these devices can be lost or tampered with. There are clear benefits of employing a combined approach to catchment monitoring, and therefore the use of both passive and grab sampling is recommended, where possible, in future surface water monitoring campaigns.

5 Links Between Pesticides, Invertebrate Fauna and Ecological Status

5.1 Objectives

The objective of the study described in this chapter was to investigate the impacts of pesticides on invertebrate communities in Irish rivers. This was done by comparing the pesticide grab sampling data obtained in Chapter 3 and grab sampling and passive sampling data obtained in Chapter 4 with existing EQSs, documented thresholds of biological effects and EPA invertebrate bioindicator data available for the study areas.

5.2 Data

5.2.1 IMPACT project data

Pesticide data were collected in two sampling campaigns. The first monitored the receiving waters of two WWTPs, one rural and one urban, using grab samples taken once a month for 1 year (from October 2018 to September 2019), as described in Chapter 3. The second campaign used grab sampling and passive samplers deployed in summer 2021, as

described in Chapter 4 (Table 5.1). It was not possible to match passive sampling data with established ecotoxicological reference values and toxicity data, and thus passive sampler data are treated semi-quantitatively to denote pesticide presence and their relative concentrations at the sites. The dataset consists of three acid herbicides, five neonicotinoid insecticides, five pyrethroid insecticides and 10 azole fungicides.

5.2.2 National monitoring data

Pesticide data were available from the EPA website (EPA, 2022) for some water bodies corresponding to the IMPACT (Innovative Monitoring to Prioritise Contaminants of Emerging Concern (CECs) for Ireland) study sites. The EPA monitors invertebrate communities as a key determinant of ecological water quality in rivers. This is done using a “Q-value” index, which ranges from 1 to 5 (from “poor” to “high” quality, respectively) (Toner *et al.*, 2005). This is determined once in each 3-year cycle from a subset of

Table 5.1. IMPACT sampling sites and regimes

Sampling site	Sampling regime
Rural samples	
Rural WWTP	Grab (once a month from October 2018 to September 2019)
Donegal sites	
Cranford (Big Burn)	PS (5 weeks) and grab (July, August and September 2021)
Glen A	PS (5 weeks) and grab (July, August and September 2021)
Glen B	PS (5 weeks) and grab (July, August and September 2021)
Glendowan (Clogher)	PS (5 weeks) and grab (July, August and September 2021)
Glenveagh National Park	PS (5 weeks) and grab (July, August and September 2021) ^a
Urban samples	
Urban WWTP	Grab (once a month from October 2018 to September 2019)
Kildare sites	
Liffey upstream	PS (2 weeks) and grab (June and July 2021)
Liffey midstream	PS (2 weeks) and grab (June and July 2021)
Liffey downstream	PS (2 weeks) and grab (June and July 2021)

^aPassive sampler was lost.

PS, passive sampling.

approximately 200 sites (Feeley *et al.*, 2020). These data were also retrieved from the EPA website.

5.2.3 Environmental quality standards

Annual average environmental quality standards (AA-EQS) and maximum allowable concentration environmental quality standards (MAC-EQS) are set for WFD priority substances as ecotoxicological thresholds based on their adverse biological impacts in the aquatic environment. For the pesticides examined in this study, such values are currently set in Ireland only for cypermethrin, as a priority substance under the WFD (S.I. No. 386 of 2015). For acid herbicides, EQS values set by the Scottish Environment Protection Agency were used as surrogates (SEPA, 2020). For other pyrethroids and neonicotinoids, draft EQS values recommended by the European Commission Scientific Committee on Health, Environmental and Emerging Risks (SCHEER, 2022) were taken as surrogates.

5.3 Pesticides

5.3.1 Acid herbicides

LODs and LOQs among acid herbicides ranged from 1.8 to 6.1 ngL⁻¹ and from 5.3 to 18.6 ngL⁻¹, respectively. These values were below the surrogate EQSs (SEPA, 2020) and thus the data seem adequate to investigate ecological impacts (if the LOD exceeds the EQS, one might fail to detect damaging impacts). All three acid herbicides, 2,4-D, MCPA and mecoprop, were recorded quantitatively in the study area and the results are presented in detail below.

2,4-D

2,4-D was detected at both urban and rural sites. In urban sites, it was recorded at all three Liffey sites, with the maximum concentration of 31.9 ngL⁻¹ in grab samples. In the rural sites in Donegal, it was recorded at five out of six sites but below the LOQ in grab samples. The recorded concentrations were much below the surrogate AA-EQS and MAC-EQS of 0.3 µg L⁻¹ and 1.3 µg L⁻¹, respectively (SEPA, 2020). 2,4-D toxicity in the aquatic environment depends on its form; 2,4-D acid and its salts affect plants most strongly, in line with its designed purpose, whereas 2,4-D esters tend to affect fish most strongly (EA,

2007). Among plants, the lowest estimate of toxicity is a 60-day NOEC of 3.3 µg L⁻¹ for the aquatic plant *Myriophyllum sibiricum* (EA, 2007). Among freshwater invertebrates, the lowest estimate of acute toxicity is a 48-h EC₅₀ (effective (sub-lethal) concentration 50%) of 390 µg L⁻¹ for the true fly *Chironomus plumosus*, whereas the lowest estimate of chronic toxicity is a 21-day NOEC of 200 µg L⁻¹ for the water flea *Daphnia magna* (EA, 2007; Mayer and Eilersieck, 1986; both cases in the ester form). Based on this information, the concentrations recorded in this study are unlikely to impact invertebrate communities or freshwater ecosystems more generally.

MCPA

MCPA was recorded at both rural and urban sites. In the urban sites, it was recorded at all three sites, with a maximum concentration of 26.2 ngL⁻¹ in grab samples. In the rural sites, it was recorded at four out of the six sites, with the maximum concentration of 82.6 ngL⁻¹ in grab samples (Table 4.1). The EPA recorded 25 ngL⁻¹ of MCPA in the “Clogher (Finn)_10” water body in County Donegal, in the vicinity of the Glendowan IMPACT site. All of these concentrations were much below the surrogate AA-EQS and MAC-EQS of 12 µg L⁻¹ (below pH 7) and 80 µg L⁻¹ (above pH 7) and 120 µg L⁻¹ (below pH 7) and 800 µg L⁻¹ (above pH 7), respectively (SEPA, 2020). MCPA in the aquatic environment is most toxic to plants, with the lowest (14-day) EC₅₀ of 152 µg L⁻¹ for the duckweed *Lemna gibba* (Morton *et al.*, 2019). Among freshwater invertebrates, the lowest estimate of acute toxicity is a 48-h EC₅₀ of greater than 190 mg L⁻¹ for *D. magna*, whereas the lowest estimate of chronic toxicity is a 21-day NOEC of 50 mg L⁻¹ for the same species (Morton *et al.*, 2019). Based on this information, the concentrations recorded in this study are unlikely to impact invertebrate communities or freshwater ecosystems more generally.

Mecoprop

Mecoprop was recorded in all sites at least once. In the urban sites, it was recorded at all three sites, with a maximum concentration of 13 ngL⁻¹ in grab samples. In the rural site, it was recorded at two of the six sites, with just a single quantified concentration of 7.2 ngL⁻¹ in grab samples. The recorded mecoprop concentrations were much lower than the surrogate

AA-EQS and MAC-EQS of $18 \mu\text{g L}^{-1}$ and $187 \mu\text{g L}^{-1}$, respectively (SEPA, 2020). Mecoprop in the aquatic environment is most toxic to plants, with the lowest (7-day) NOEC of $180 \mu\text{g L}^{-1}$ for the duckweed *Lemna minor* (EA, 2010). Among freshwater invertebrates, the lowest estimate of acute toxicity is a 48-h EC_{50} of greater than $100,000 \mu\text{g L}^{-1}$ for the water flea *D. magna* (EA, 2010), whereas the lowest estimate of chronic toxicity is a 28-day NOEC of $22,200 \mu\text{g L}^{-1}$ for the same species (EA, 2010). Based on this information, the concentrations recorded in this study are unlikely to impact invertebrate communities or freshwater ecosystems more generally.

Macroinvertebrate bioindicators

In the rural sites, MCPA concentrations of up to 82.6 ng L^{-1} have been quantitatively recorded from four sites: the WWTP site reported on in Chapter 3 and three sites in County Donegal reported on in Chapter 4: Glen A and Glen B, and Cranford (Big Burn); the last also had the single quantitative mecoprop record in Donegal of 7.2 ng L^{-1} . Among them, the WWTP site was classed by the EPA as “poor” (Q3) in 1990, but no data have been available since then. The three Donegal sites have ranged from “poor” (Q3) to “good” (Q4) since 2018. Notably, two adjacent sites were classed as Q3/0 or Q3–4/0 prior to that, where 0 typically denotes toxic pollution levels (EPA, 2022; Toner *et al.*, 2005). In the urban sites, 2,4-D concentrations of up to 31.9 ng L^{-1} have been quantitatively recorded from all three sites. Among them, the WWTP site from Chapter 3 also recorded MCPA and mecoprop concentrations of up to 26.2 ng L^{-1} and 13 ng L^{-1} , respectively. The EPA classed the Liffey upstream site as “high” (Q4–5) in 1990, but no data have been available since then (EPA, 2022). The other Liffey sections were classed as “good” (Q4) in 2019.

5.3.2 Neonicotinoid insecticides

LODs and LOQs among neonicotinoid insecticides ranged from 0.8 to 4.7 ng L^{-1} and from 2.4 to 7.7 ng L^{-1} , respectively. The LOD and LOQ for imidacloprid exceeded the proposed (i.e. not yet finalised) MAC-EQS (SCHEER, 2022), whereas, for clothianidin, they were only marginally below it, and so these data may not be adequate for investigating ecological impacts. The LODs and LOQs for acetamiprid, thiacloprid and thiamethoxam were well below the proposed PNECs

and thus these data seem adequate for investigating ecological impacts.

Clothianidin and imidacloprid were recorded quantitatively in this study and their results are presented below. Acetamiprid was only recorded below the LOQ in grab samples in the Liffey, whereas thiacloprid and thiamethoxam were not recorded.

Clothianidin

Clothianidin was recorded at only one site in the urban areas, with just a single quantified concentration of 15.7 ng L^{-1} in grab samples. It was not detected in the rural sites. The concentration recorded exceeded the draft AA-EQS under discussion of 10 ng L^{-1} but was below the MAC-EQS also under discussion of 340 ng L^{-1} (SCHEER, 2022). The toxicity of clothianidin varies among aquatic invertebrate species by several orders of magnitude (Miles *et al.*, 2017). Insects are the most sensitive aquatic organisms to nicotinoids in general (Morrissey *et al.*, 2015; Raby *et al.*, 2018). Among them, Diptera and Coleoptera appear to be the most sensitive and Odonata the least sensitive to clothianidin (Miles *et al.*, 2017; Raby *et al.*, 2018). Among freshwater invertebrates, the lowest estimate of acute toxicity, based on current EU discussions, is a 96-h EC_{50} of 3400 ng L^{-1} for the true fly *Chironomus dilutus*, whereas the lowest estimate of chronic toxicity is 28-day EC_{10} (effective (sub-lethal) concentration 10%) of 100 ng L^{-1} for the snail *Planorbella pilsbryi* (Prosser *et al.*, 2016; Raby *et al.*, 2018; SCHEER, 2022). EC_{50} and EC_{10} are the concentrations required to obtain a 50% and 10% effect, respectively. Based on this information, the concentrations recorded in this study are unlikely to impact freshwater invertebrate communities.

Imidacloprid

Imidacloprid was recorded at only two sites in the rural areas, with just a single quantified concentration of 10.7 ng L^{-1} in grab samples. It was not detected in the urban areas. The concentration recorded exceeded the draft AA-EQS of 2.4 ng L^{-1} but was below the recommended MAC-EQS of 65 ng L^{-1} (SCHEER, 2021).

Insects are generally the aquatic organisms most sensitive to neonicotinoids (Morrissey *et al.*, 2015; Raby *et al.*, 2018). Among them, Ephemeroptera and

Diptera appear to be most sensitive to imidacloprid (Morrissey *et al.*, 2015; Raby *et al.*, 2018). Among freshwater invertebrates, the lowest estimate of acute toxicity is a 96-h LC₅₀ (lethal concentration 50%) of 650 ng L⁻¹ for the mayfly *Epeorus longimanus*, whereas the lowest estimate of chronic toxicity is a 28-day EC₁₀ of 24 ng L⁻¹ for the mayfly *Caenis horaria* (Alexander *et al.*, 2007; Roessink *et al.*, 2013; SCHEER, 2021). Based on this information, the concentrations recorded in this study are unlikely to impact freshwater invertebrate communities.

Macroinvertebrate bioindicators

A single quantified clothianidin concentration of 15.7 ng L⁻¹ was recorded at the urban WWTP discharge point, as part of the year-long study. The nearby EPA riverine monitoring station (Castlekeely Ford) was classed as “good” (Q4) in 2019. A single quantified imidacloprid concentration of 10.7 ng L⁻¹ was recorded at the rural WWTP discharge point. The nearby EPA site was classed as “poor” (Q3) in 1990, but no data have been available since then (EPA, 2022).

5.3.3 Pyrethroid insecticides

LODs and LOQs for the pyrethroid insecticides ranged from 141.4 to 640.2 ng L⁻¹ and from 428.5 to 2849.1 ng L⁻¹, respectively. The values for cypermethrin and permethrin greatly exceeded the draft EQSs (SCHEER, 2021) and thus the data seem inadequate for investigating ecological impacts, as potentially harmful concentrations may have been undetected.

None of the five pyrethroids was detected in the grab samples. Bifenthrin, cypermethrin, deltamethrin and permethrin were detected below the LOQ or semi-quantitatively from passive samplers in County Donegal, but were not detected in the urban site. Esfenvalerate was not detected in this study.

Cypermethrin

The EPA recorded concentrations of 0.021 ng L⁻¹ and 0.022 ng L⁻¹ of cypermethrin in sites in the “Clogher (Finn)_10” and “Glen (Lackagh)_10” river water bodies in the vicinity of the Glendowan and Glen A IMPACT sites, respectively. These values are below the AA-EQS of 0.08 ng L⁻¹ and the MAC-EQS of 0.6 ng L⁻¹ (S.I. No. 386 of 2015).

Insects and crustaceans are the aquatic organisms most sensitive to cypermethrin (EC, 2011). Among freshwater invertebrates, the lowest estimate of acute toxicity is a 96-h LC₅₀ of 1.3 ng L⁻¹ for the crustacean *Gammarus pulex*, whereas the lowest estimate of chronic toxicity is a 21-day NOEC of 9 ng L⁻¹ for *D. magna* (EC, 2011). Based on this information, the concentrations recorded by the EPA in the study area are unlikely to impact invertebrate communities or freshwater ecosystems more generally.

Macroinvertebrate bioindicators

The two quantified cypermethrin concentrations of 0.021 ng L⁻¹ and 0.022 ng L⁻¹ were recorded at EPA sites “Br Sw Letterkillew” and “Bridge W. of Glen” in Donegal. The former was classed by the EPA as “moderate” (Q3–4) in 2019, whereas the latter was classed as “moderate” (Q3–4) in 2021 and “good” (Q4) in 2018. However, both of these sites were classed as Q3/0 prior to that (Table 4.1; EPA, 2022; Toner *et al.*, 2005).

5.3.4 Azole fungicides

LODs and LOQs among azole fungicides ranged from 0.6 to 3 ng L⁻¹ and from 1.9 to 9 ng L⁻¹, respectively. At the time of writing of this report, there were no known EQSs or suitable proxies for azole fungicides to guide the investigation of their ecological impacts.

Miconazole and tebuconazole were recorded quantitatively in this study and their results are presented below. Fluconazole, clotrimazole, imazalil, ipconazole, metconazole, tebuconazole and tetraconazole were only recorded below the LOQ from grab samples or semi-quantitatively from passive samplers in both counties, penconazole was only recorded semi-quantitatively from passive samplers in the rural site, and prochloraz was not detected in this study (Tables 2.3 and 3.3).

Miconazole

Miconazole was detected in all urban sites, with a maximum concentration of 4.4 ng L⁻¹ in the grab samples. In the rural sites, miconazole was detected at all but one of the sites, with just a single quantified concentration of 3.3 ng L⁻¹ in the grab samples.

Fungicides have been shown to affect aquatic plants and fish (de Alkimin *et al.*, 2020; Bhagat *et al.*, 2021; Matthiessen and Weltje, 2015; Richter *et al.*, 2016), but toxicity data for aquatic fungi are scarce (Ittner *et al.*, 2018). Similarly, there is very little information on miconazole's toxicity to aquatic invertebrates. A 48-h EC_{50} of 0.3 mg L^{-1} and a 21-day lowest-observed-effect concentration of 0.022 mg L^{-1} have been reported for *D. magna* (Furuhagen *et al.*, 2014). The concentrations recorded in the current study are several orders of magnitude smaller than these toxicity estimates, and so they seem unlikely to impact freshwater invertebrate communities, but the limited toxicity data curtail conclusions.

Tebuconazole

Tebuconazole was detected in all urban sites, with a maximum concentration of 4.1 ng L^{-1} in the grab samples. In the rural sites, tebuconazole was detected at half of the sites, but only below the LOQ in grab samples or semi-quantitatively from passive samplers.

Fungicides have been shown to affect aquatic plants and fish (de Alkimin *et al.*, 2020; Bhagat *et al.*, 2021; Matthiessen and Weltje, 2015; Richter *et al.*, 2016), but toxicity data for aquatic fungi are scarce (Ittner *et al.*, 2018). Similarly, there is very little information on tebuconazole's toxicity to aquatic invertebrates. A 48-h LC_{50} of 2.9 ng L^{-1} has been reported for *D. magna* (US EPA, 2007), whereas a 21-day exposure to 0.4 ng L^{-1} impaired its growth and reproduction (Sancho *et al.*, 2016). The concentrations recorded in the current study are several orders of magnitude smaller than these toxicity estimates, and so they seem unlikely to impact freshwater invertebrate communities, but the limited toxicity data curtail conclusions.

Macroinvertebrate bioindicators

In the rural sites, a single quantified miconazole concentration of 3.3 ng L^{-1} was recorded at the Cranford (Big Burn) site. This site was classed by the EPA as "poor" (Q3) in 2021 and as "moderate" (Q3–4) in 2018. However, it was classed as Q3/0 in 2012 and Q3–4/0 in 2015 (EPA, 2022; Toner *et al.*, 2005).

In the urban sites, the two quantified miconazole concentrations of up to 4.5 ng L^{-1} were recorded at the WWTP, where the nearby EPA site was classed as "good" (Q4) in 2019.

The two quantified miconazole concentrations of up to 4.1 ng L^{-1} were recorded 1 km upstream and 10 km downstream of the urban WWTP site. The EPA site located at the upstream site was classed as "high" (Q4–5) in 1991, but has not been sampled since, whereas a site located 2 km further downstream has been classed as "good" (Q4). The EPA site located downstream of the urban WWTP IMPACT site was classed as "good" (Q4) in 2019 (EPA, 2022).

5.4 Conclusions

No clear pattern emerged between the pesticide concentrations and risks determined in Chapters 3 and 4, and national invertebrate indicators. Two sites with the largest number of pesticides detected in this study had been suspected of having toxic pollution levels in the past, according to the EPA invertebrate monitoring. Conversely, the site with the highest invertebrate score had the smallest number of pesticides detected. However, beyond this, the Q-value score varied within the narrow range of 3–4 on a scale of 1–5, offering no tangible relationship with the pesticide concentrations and risks evaluated earlier in this report. Nonetheless, the study reported in this chapter informed some further research priorities.

Acid herbicides were the most commonly detected pesticides in this study and were found in one-third of the samples examined. Although they are generally thought to have low toxicity to animals, they target plants specifically, and can affect stream productivity (Rumschlag *et al.*, 2020). Given that nutrient enrichment is another common problem in Irish freshwaters, herbicide pollution could temporarily mask its manifestation by suppressing plant and algal productivity. It would be interesting to investigate how nutrients and herbicides interact in terms of stream productivity and stream ecosystems as a whole.

Although the recorded clothianidin and imidacloprid concentrations were below those known to affect aquatic organisms, they both exceeded the MAC-EQS (but not the AA-EQS), which are under discussion within the EU, with the aim of safeguarding aquatic ecosystems from acute toxicological events. Therefore, more data are needed to detect their peak and average concentrations in Ireland. Despite their widespread use, high solubility in water and thus potential for run-off, and well-documented ecological impacts (Morrisey *et al.*, 2015; Sánchez-Bayo *et al.*,

2016), neonicotinoids are not currently included in WFD monitoring in Ireland, apart from EU Watch List monitoring. In particular, state-owned commercial forestry business Coillte has replaced cypermethrin with acetamiprid for controlling pine weevil in forestry, which may also affect water quality.

Cypermethrin has been partially phased out as an agricultural pesticide in Ireland, with only limited use still permitted in “wood preservatives (PT08)” and private forestry, and limited use of the similarly acting alpha-cypermethrin still permitted in “insecticides, acaricides and products to control other arthropods (PT18)” (DAFM, 2022). Miller *et al.* (2019) found that 7 out of the 10 banned pesticides included in their study of several UK river catchments were still present in biota, which was tentatively attributed to their persistence in sediments, but illicit use is also possible. Given that cypermethrin is generally classed as non-persistent (University of Hertfordshire: Pesticide Properties DataBase²), any further detections should be investigated to ascertain their provenance. For example, potential sources of cypermethrin can be identified by analysing their isomeric composition.

Azole fungicides can be toxic to animals, but there is insufficient information to investigate the effects on

freshwater invertebrates. This is an urgent knowledge gap, given their widespread use and poor degradation in wastewater treatment processes (Kahle *et al.*, 2008).

In this study, between 3 and 13 pesticides were detected per site (see Chapter 3), with a median of 8. Most detections were below the LOQ or (where available) EQS. However, while EQSs are set to safeguard the aquatic environment, the standard ecotoxicological tests that they are based on may miss some of the more nuanced biological effects that occur at the sub-organism level or take a long time to manifest. Furthermore, such tests are not set up to investigate the cumulative effects of multiple simultaneously acting pesticides and other concomitant stressors that may add to or even multiply their individual biological impacts (Lemm *et al.*, 2021; Piggott *et al.*, 2015). Thus, efforts should be stepped up to regulate the use of pesticides, noting that not all the pesticides evaluated here are used in agricultural management systems, and, where possible, to prevent discharges into non-target environments from agricultural spray drift and surface run-off and from sewage overflows and effluent.

2 <http://sitem.herts.ac.uk/aeru/ppdb/en/> (accessed 2 October 2023).

6 International Comparison of Endocrine-disrupting Compounds in River Waters

6.1 Objectives

Endocrine-disrupting compounds (EDCs) are a class of CECs that are a major concern and, consequently, were selected for monitoring in this study, which aimed to compare the occurrence and frequency of these

compounds in Irish waters with those in the UK and Spain (as shown in Figure 6.1). A total of 26 analytes (including steroids, flame retardants, plasticisers and preservatives; Table 6.1) were monitored in three major rivers: the Liffey (Ireland), the Thames (UK)

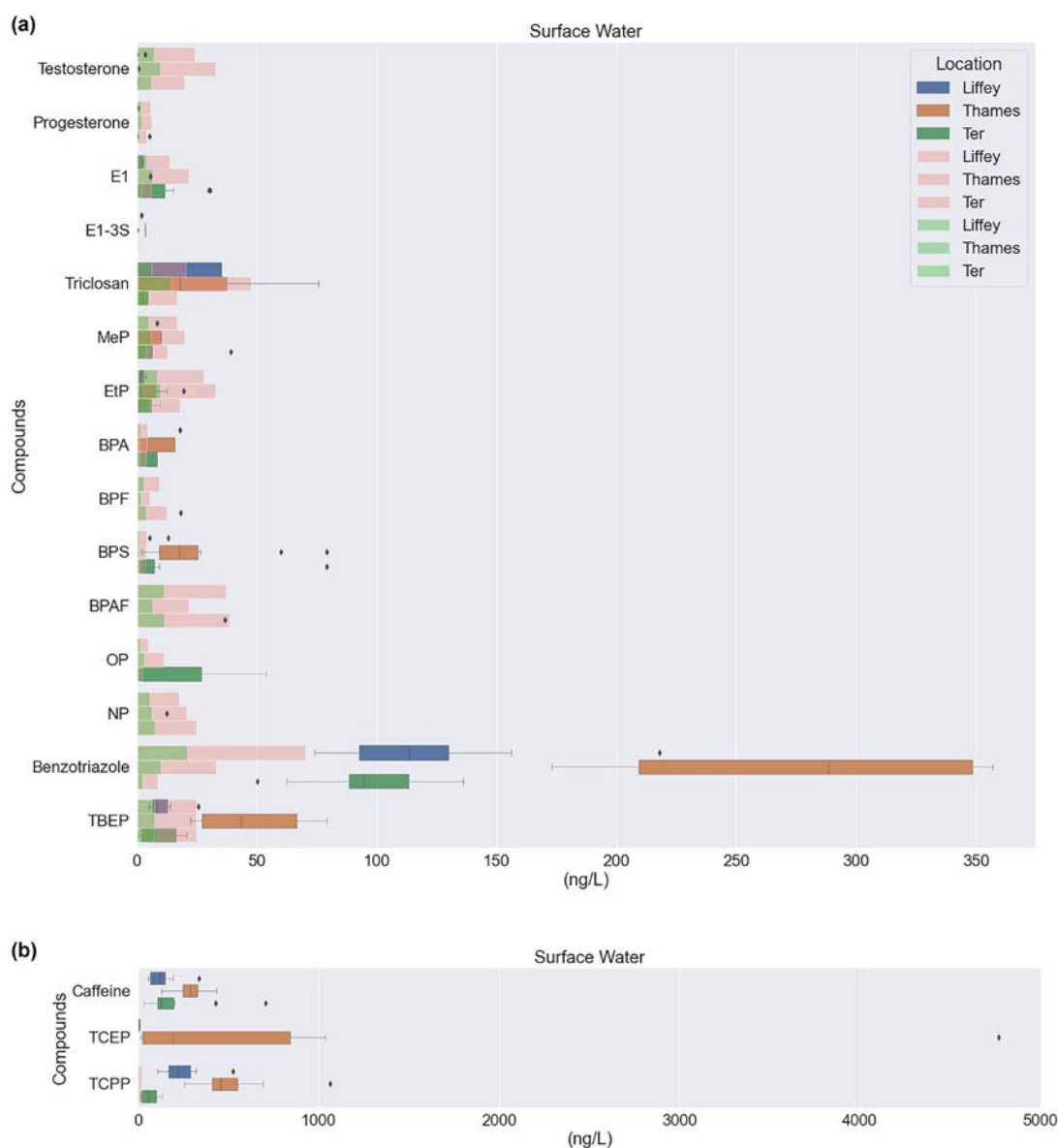


Figure 6.1. Concentration of selected EDCs in surface waters for all compounds detected ($n = 10$, weeks analysed) for the three areas investigated: Liffey (blue), Thames (orange) and Ter (green). (a) Concentrations up to 375 ng L^{-1} and (b) concentrations detected up to 5000 ng L^{-1} . Boxes represent the interquartile range (IQR), whiskers extend to points that lie within 1.5 IQRs of the lower and upper quartile, and dots represent outliers. LODs and LOQs are represented by chart bars in light green and light pink, respectively.

Table 6.1. Classification of EDCs and related compounds analysed in this study

Family	Compounds	CAS number
Steroids	17 β -Estradiol (E2)	50-28-2
(Natural and synthetic human estrogens and conjugates)	Estriol (E3)	50-27-1
	17 α -Ethinylestradiol (EE2)	57-63-6
	Estriol 3-sulfate (E3-3S)	481-95-8
	Estrone 3-sulfate (E1-3S)	438-67-5
	Estrone (E1)	53-16-7
	Testosterone	58-22-0
	Progesterone	57-83-0
Antimicrobials/disinfectants	Triclosan	3380-34-5
Preservatives	Methylparaben (MeP)	99-76-3
	Ethylparaben (EtP)	120-47-8
	Propylparaben (PrP)	94-13-3
	Benzylparaben (BeP)	94-18-8
Plasticiser	Bisphenol A (BPA)	80-05-7
(Industrial production of polycarbonates and epoxy resins)	Bisphenol B (BPB)	77-40-7
	Bisphenol F (BPF)	620-92-8
	Bisphenol S (BPS)	80-09-1
	Bisphenol AF (BPAF)	1478-61-1
Alkylphenols	Nonylphenol (NP)	25154-52-3
(Manufacture of household and industrial products)	Octylphenol (OP)	140-66-9
Anticorrosive	1H-benzotriazole (BT)	95-14-7
Organo-phosphorus and brominated-based flame retardants	Tris(butoxyethyl) phosphate (TBEP)	78-51-3
	Tris(chloroisopropyl) phosphate (TCPP)	13674-87-8
	Tris(2-chloroethyl) phosphate (TCEP)	115-96-8
	Tetrabromobisphenol A (TBBPA)	79-94-7
Chemical marker	Caffeine	58-08-2

CAS, Chemical Abstracts Service.

and the Ter (Spain). Occurrence and frequency were investigated across all locations. Caffeine is included as an EDC in this study, although it is noted that it is also a useful chemical marker.

6.2 Sample Collection and Preparation

River samples were collected from three European cities for international comparison purposes. The River Thames was chosen because London is the largest city in the UK. Samples were collected from Gabriel's Pier in London and from the River Liffey at O'Connell Bridge in Dublin. In Spain, water samples were collected from the River Ter, approximately 1250 metres downstream of a WWTP discharge, which serves the entire city of Girona and surroundings. Grab samples of river water were collected weekly at the three locations during a 10-week period from October 2020 to January 2021 for an international comparison. All participants collected the samples following the same protocol, with all samples collected in 500-mL Nalgene bottles (Fisher Scientific, UK) between 9:00 and 11:00 am. Prior to sampling, the bottles were pre-rinsed twice with methanol and then ultrapure water, separately. Then, the bottles were further rinsed with river water before the collection of grab samples in duplicate, with the bottles being filled to the top (no headspace or preservative present).

Once samples were collected, they were transported to laboratories in cool boxes. On arrival, the samples were filtered and then stored at -20°C prior to transport or analysis. The samples collected in Dublin and London were frozen and shipped to the Girona

laboratory within 24–48 hours, where they were kept frozen until analysis. Details of the full quantitative analysis can be found in Rapp-Wright *et al.* (2023b).

6.3 Results and Discussion

6.3.1 Occurrence and frequency

The occurrence of the EDCs detected in the three locations is presented in Figure 6.1, with LODs and LOQs. Of a total of 26 compounds analysed, 14 were detected in the rivers Liffey and Thames, and 15 in the Ter. The frequency of detection of most of the compounds was 0% across the three sites, owing to concentrations below the LOD (LODs were not taken into account for frequency data calculations), as observed in Figure 6.2.

Five, six and four compounds were detected with 100% frequency in the rivers Liffey, Thames and Ter, respectively. The concentrations of EDCs ranged from less than the LOD to 524 ng L^{-1} (tris-(2-chloroisopropyl) phosphate), less than the LOD to 4767 ng L^{-1} (tris(2-chloroethyl) phosphate) and less than the LOD to 705 ng L^{-1} (caffeine) for the Liffey, Thames and Ter, respectively. However, only 8, 9 and 10 compounds were able to be quantified for the Liffey, Thames and Ter, respectively. Compounds such as propylparaben, benzylparaben and bisphenol B were not detected at any location throughout the sampling campaign, and compounds such as caffeine and triclosan were detected at all sites at similar frequencies.

Overall, cumulative values showed that higher concentrations were detected in the River Thames

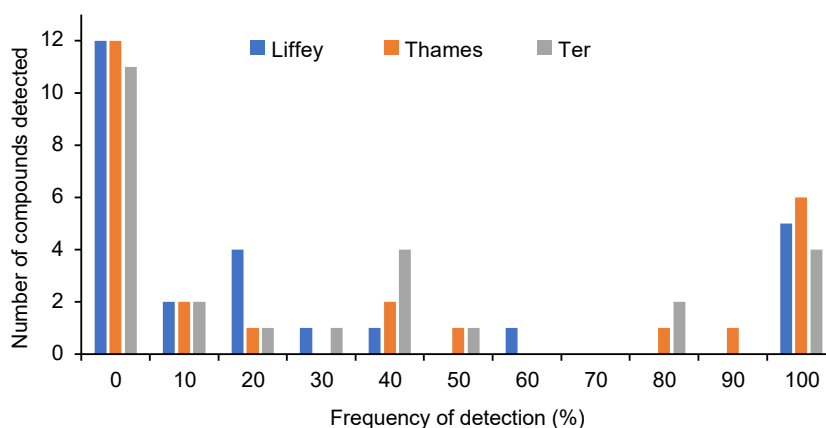


Figure 6.2. Number of compounds per frequency of detection in the three rivers tested during the 10-week sampling campaign.

due to higher levels detected in the flame retardants class, resulting in values up to almost 20,000 ng L⁻¹ (20 µg L⁻¹) for all compounds detected (Figure 6.3). Lower cumulative values were obtained for the River Liffey (5410 ng L⁻¹) and for the River Ter (4356 ng L⁻¹). These values follow those expected for high-density populated areas, i.e. London, Dublin and Girona.

Steroid hormones

Only three hormones (testosterone, progesterone and E1) were detected at quantifiable concentrations across all sites from the eight hormones studied. Estrone-3-sulfate (E1-3S) was also detected, but concentrations were always below the LOQ. The natural estrogen E1 was quantified at the highest concentration of all compounds in the category, at 31 ng L⁻¹ in the River Ter. Therefore, a contribution of only 2% of the total concentrations of all compounds detected was attributable to the steroids category in the Ter samples, as shown in Figure 6.3. None of the compounds quantified in the Thames samples belonged to the steroids category, where the highest concentration (for E1-3S) was less than 7.2 ng L⁻¹ (i.e. less than the LOQ). The same compound was found at the highest concentration in the Liffey (less than 3.9 ng L⁻¹, i.e. less than the LOQ).

Chemical markers

Caffeine was consistently quantifiable in all samples and locations, with averages of 131 ± 86 ng L⁻¹, 213 ± 203 ng L⁻¹ and 277 ± 93 ng L⁻¹ for the rivers Liffey, Ter and Thames, respectively. This is unsurprising, as

it is found in a variety of foods, drugs and beverages, and is the most consumed psychoactive substance in the world, with detection of high levels linked to large populations (Edwards *et al.*, 2015; Silva *et al.*, 2014). Caffeine has shown some endocrine-disrupting activity in fish, suggesting it as a potential xenoestrogen (Godoi *et al.*, 2020; Li *et al.*, 2012). It has a half-life of approximately 1.5 days in water; however, due to its constant discharge, it can act as a persistent chemical, creating a dynamic equilibrium (Moore *et al.*, 2008). The highest concentrations were found in the River Ter, in one sample, in week 2 of the sampling campaign. Concentrations in the River Thames were, in most cases, higher than in the River Liffey.

Antimicrobial/disinfectants

In this study, the maximum concentration of 76 ng L⁻¹ was quantified for triclosan in the River Thames. For the River Liffey, similar concentrations could have been detected due to the high LOQ achieved (70 ng L⁻¹); however, lower LOQs would be necessary to confirm this. On the other hand, samples quantified from the River Ter were less than the LOQ of 9 ng L⁻¹ obtained. Consequently, the antimicrobial category contributed 0% of the total concentrations of EDCs in the Ter, compared with a contribution of 2% and 1% for the Liffey and Thames, respectively, as shown in Figure 6.4. Regarding frequency data, the values obtained were really similar across all locations: 60%, 50% and 50% for the Liffey, Thames and Ter, respectively.

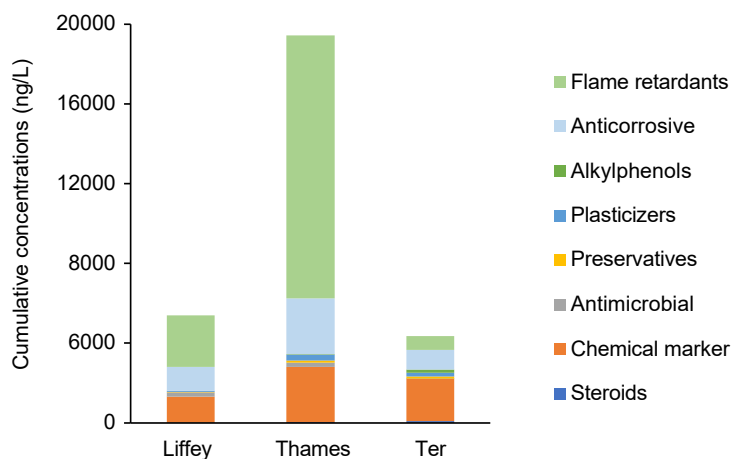


Figure 6.3. Cumulative concentrations of all EDCs detected during the 10-week sampling campaign in the three rivers investigated.

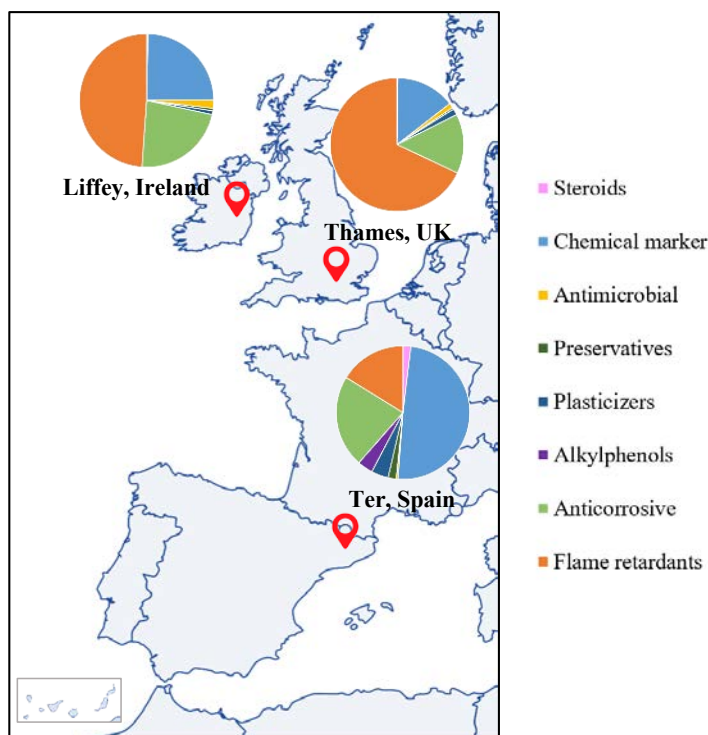


Figure 6.4. Compound classification of EDCs identified in the rivers Liffey, Thames and Ter. Weekly average cumulative values are shown for each location.

Preservatives

Only methylparaben and ethylparaben were detected across all locations, while propylparaben and benzylparaben were not detected in any samples. Methylparaben had the maximum concentration of all compounds in this category, at 39 ng L^{-1} in the River Thames, with 40% detection frequency. The remaining concentrations were quantified at less than LOQ concentrations, noting that the LOQs obtained were 17 and 13 ng L^{-1} , with 10% and 40% frequencies, for the rivers Liffey and Ter, respectively. The maximum concentration of ethylparaben was 20 ng L^{-1} in the River Thames. Higher frequency values were obtained when compared with methylparaben: 100%, 90% and 80% for the Liffey, Thames and Ter, respectively (Figure 6.4). Total contributions of concentration for the preservative category were 1%, 0% and 2% for the Liffey, Thames and Ter, respectively, as seen in Figure 6.4, owing to the majority of samples being detected at less than LOD concentrations.

Plasticisers

Four of the five bisphenol compounds investigated in the plasticisers category were detected across all three locations, of which two (i.e. bisphenol A

and bisphenol F) presented in concentrations less than the LOQs. This is as a result of the inability to achieve a suitably low LOQ: $\leq 36 \text{ ng L}^{-1}$ (Liffey matrix) and $\leq 61 \text{ ng L}^{-1}$ (Thames matrix) for bisphenol A and bisphenol F, respectively. Only bisphenol S and bisphenol AF had concentrations above their quantification limits – $\leq 0.2 \text{ ng L}^{-1}$ and $\leq 0.9 \text{ ng L}^{-1}$ (both Liffey matrix), respectively – significantly lower than the other two compounds. Maximum concentrations were 79 ng L^{-1} for bisphenol S in both the River Ter and the River Thames and 37 ng L^{-1} for bisphenol AF in the River Ter.

Frequencies varied depending on the specific compound and matrix, with bisphenol S found at 100% frequency in the Thames, 80% in the Ter and only 20% in the Liffey. Bisphenol AF and bisphenol F were detected only once (10%) in the Ter, while bisphenol A had higher detection frequencies, ranging from 20% (Liffey) to 40% (Thames and Ter).

Alkylphenols

In this study, nonylphenol was detected in the River Thames only, with a frequency of just 10% (i.e. one sample) and a concentration less than the LOQ ($< 21 \text{ ng L}^{-1}$). 4-Octylphenol was also detected in

only one location, the River Ter, with concentrations ranging from 27 to 54 ng L⁻¹ and a 40% frequency. It should be noted, however, that the MAC-EQS of nonylphenol is 2.1 µg L⁻¹, i.e. 10-fold lower than the LOQ, although the AA-EQS for 4-octylphenol is below our LOQ. Therefore, the total contributions based on concentrations were 0% for the Thames and the Liffey and only 4% for the Ter (Figure 6.4).

Anticorrosives

Benzotriazole was detected with a 100% frequency in all three locations, with concentrations ranging between 74 and 218 ng L⁻¹, 173 and 357 ng L⁻¹ and 50 and 136 ng L⁻¹ for the rivers Liffey, Thames and Ter, respectively, as observed in Figure 6.5. The high concentrations detected in the River Ter could be attributed to the discharge of the WWTP. Although only one compound was studied in this category, high levels of contribution were found in all rivers: 23%, 14% and 22% for the Liffey, Thames and Ter, respectively (Figure 6.4).

Flame retardants

Four flame-retardant compounds were studied in this category. Only three compounds were detected in the samples tested (i.e. tetrabromobisphenol A was not detected at any sample). Tris(chloroisopropyl) phosphate and tris(butoxyethyl) phosphate were quantifiable in all detected samples (greater than the LOQ). However, tris(2-chloroethyl) phosphate was not detected (frequency of 0%) in the River Ter, and concentrations in the Liffey were below the LOQ. This category was the largest contributor to

the total concentrations in the Liffey and Thames, as seen in Figure 6.4, at 49% and 68%, respectively. It contributed only 16% of the total concentration in the Ter, since only two compounds were detected, and at low concentrations. High frequency values were obtained for tris(chloroisopropyl) phosphate and tris(butoxyethyl) phosphate (100%) in all locations.

Tris(2-chloroethyl) phosphate was the flame retardant detected at the highest concentration throughout the study: 4767 ng L⁻¹ in the River Thames. Tris(chloroisopropyl) phosphate was also detected at high concentrations in the River Thames, up to 1065 ng L⁻¹, significantly higher than tris(butoxyethyl) phosphate, which was detected at 79 ng L⁻¹. Owing to these high concentrations, the highest cumulative concentration values of all matrices investigated were found in the River Thames (Figure 6.3).

6.3.2 Geographical variation

Geographical variation between the three locations were examined by comparing the cumulative concentrations in the categories discussed in section 6.3.1. Overall, the higher concentrations in the River Thames resulted in significant differences between locations for plasticisers, caffeine, flame retardants and benzotriazole, as can be observed in Figure 6.6.

6.4 Environmental Risk Assessment

In this study, 26 compounds were selected because of their endocrine-disrupting properties, making them potentially a high risk to aquatic organisms if present.

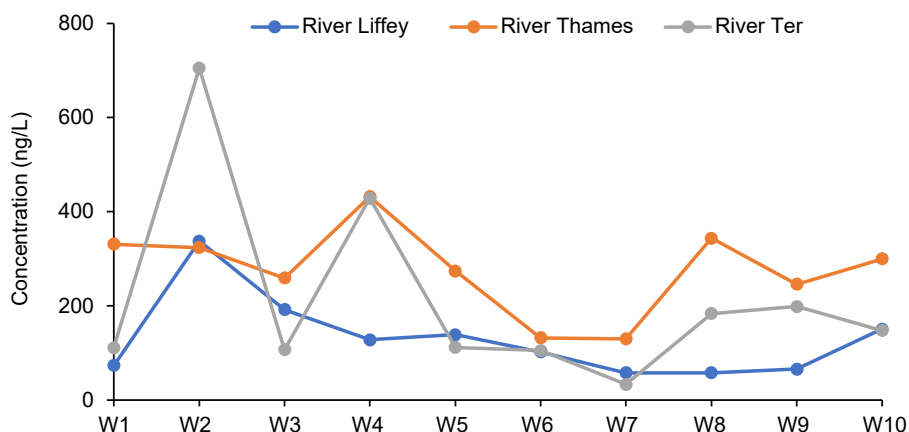


Figure 6.5. Benzotriazole concentrations (ng L⁻¹) in all samples analysed (10-week period) in the rivers Liffey, Thames and Ter. W, week of sampling.

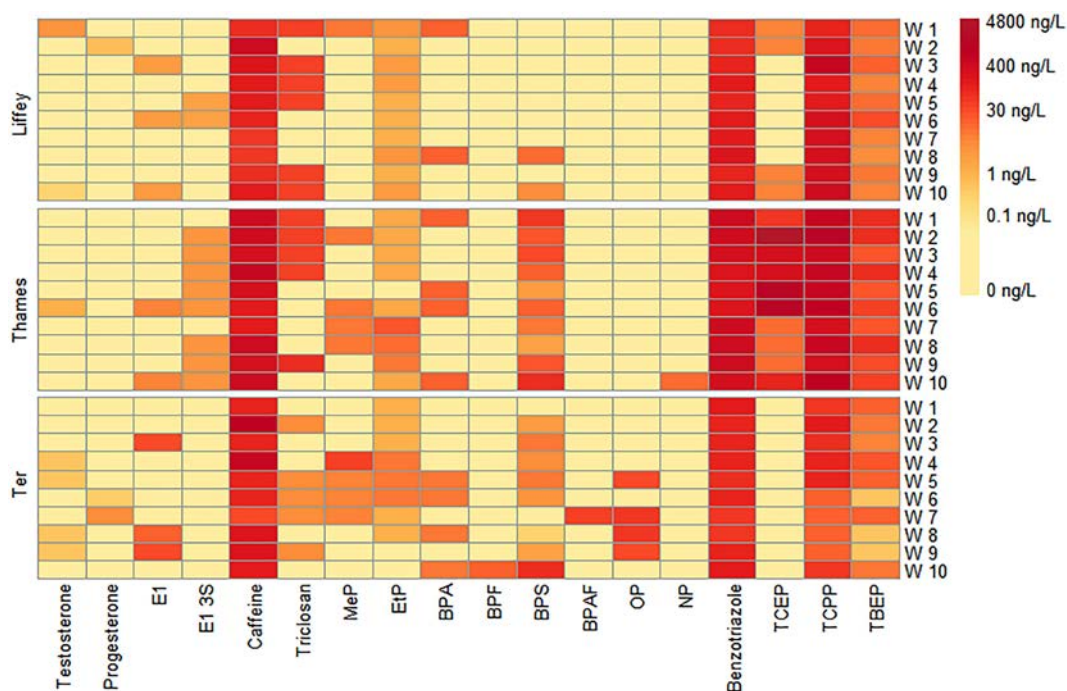


Figure 6.6. Heatmap showing the EDCs detected in the rivers Liffey, Thames and Ter for all weeks sampled and the range of concentrations (ng L^{-1}), where the darker the colour, the higher the concentration detected. W, week of sampling.

Following monitoring in three rivers, an ERA was performed to investigate their impact.

All compounds detected were considered to be of concern, given their endocrine-disrupting properties, and accordingly moved to phase II of the ERA. In this second phase, PNEC values were calculated, utilising ecotoxicity data (mg L^{-1}) obtained from published literature, the ecotoxicological NORMAN database and ECOSAR software, using equation 6.1 (Hoyett *et al.*, 2016):

$$\text{PNEC} = \text{EC}_{50} \text{ or } \text{LC}_{50} / \text{AF} \quad (6.1)$$

Consequently, RQs were then calculated for a total of 18 compounds detected across the three rivers, as described in Chapter 2. The highest RQ value was obtained for caffeine in the three matrices, with 705 the maximum value obtained overall, for the River Thames. Reassuringly, the majority of compounds did not pose significant risks, with 64%, 57% and 53% of the risk classed as “insignificant” for the rivers Liffey, Thames and Ter, respectively, when using freshwater data. This classification applied to nine, eight and eight compounds, respectively (Figure 6.7), including compounds such as progesterone, E1-3S, methylparaben and benzotriazole. Low risks were

determined for 7% of the compounds (i.e. one compound, shown in Figure 6.8) studied in the rivers Liffey and Thames, and 27% (i.e. four compounds) for the River Ter; however, the compounds varied between locations. For example, testosterone was assessed as low risk for the rivers Thames and Ter but medium risk for the Liffey due to the higher concentration found in the last river. Moreover, medium risks were determined for 15%, 22% and 13% of the compounds in the Thames, Ter and Liffey, respectively, which also varied across the sites. Lastly, higher risks were associated with a minority of the compounds, resulting in only a 14% contribution to risk (i.e. two compounds) for the Liffey and Thames and a 7% risk contribution (i.e. one compound) for the Ter. Specifically, caffeine presented high risks in all three sites, with bisphenol A assessed as a high risk for the Liffey and Thames but only a medium risk for the Ter.

6.4.1 Considering combination effects of the chemicals detected in each river

The “cocktail effect” is the result of the combination of contaminants in the aquatic environment. The effects of the combined contaminants are generally classified as synergistic (when the combined effect

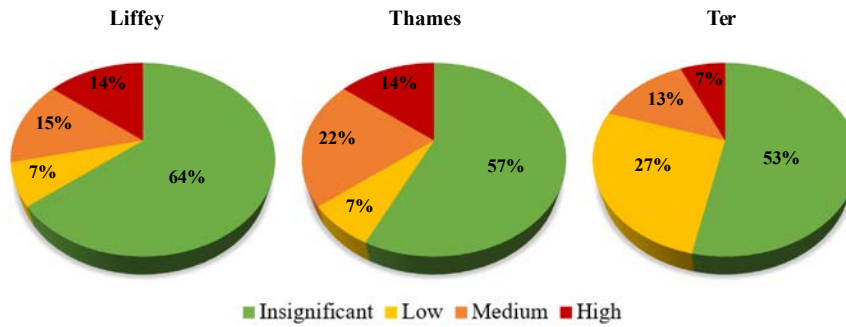


Figure 6.7. Risk classification for compounds detected in the rivers Liffey, Thames and Ter.

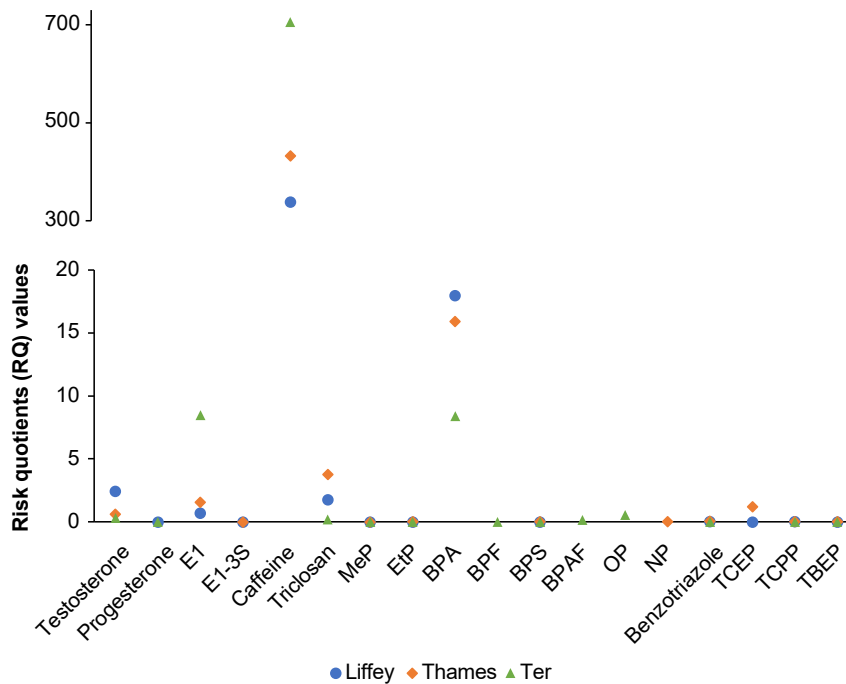


Figure 6.8. RQs of EDCs detected in the rivers Liffey, Thames and Ter.

is greater than the sum of their individual effects), antagonistic (when the combined effect is less than the sum of their individual effects) or additive (when the combined effect is equal to the sum of their individual effects). Typically, an ERA neglects the potential cocktail effect and so can underestimate the cumulative compound risk. Consequently, the site risk was calculated for all compounds detected per river location. To assess the potential risk of the entire site, total risks and relative risks were calculated (ΣRQ_{site} and ΣrRQ_{site}) for the rivers Ter, Thames and Liffey, where the same risk categories were used. The estimated contribution of each compound to the site was also calculated, dividing the RQ of the compound by the total risk of the investigated area. All sites had a

very high risk overall, mainly associated with the high concentrations of caffeine (a chemical marker) in all rivers, contributing to 94%, 95% and 97% of the total risk for the rivers Liffey, Thames and Ter, respectively. The EDC contributing the highest potential risk, again for all rivers, was bisphenol A, with 5%, 3% and 1% for the rivers Liffey, Thames and Ter, respectively. Lastly, 1% contributions were found for testosterone, triclosan and E1. The remaining compounds had extremely low contributions to the total site risk.

These results highlighted caffeine, bisphenol A and E1 as important contributors to total site risk for the River Ter, caffeine, bisphenol A and triclosan for the River Thames, and caffeine, bisphenol A and testosterone for the River Liffey.

6.5 Conclusions

A total of 14 compounds were detected in the rivers Liffey and Thames and 15 in the Ter, where concentrations were up to 524 ng L⁻¹ (tris(chloroisopropyl) phosphate), 4767 ng L⁻¹ (tris(2-chloroethyl) phosphate) and 705 ng L⁻¹ (caffeine), respectively. Concentrations varied across the different rivers, ranging from less than the LOD to 524 ng L⁻¹ (tris(chloroisopropyl) phosphate), less than the LOD to 4767 ng L⁻¹ (tris(2-chloroethyl) phosphate) and less than the LOD to 705 ng L⁻¹ (caffeine) for the rivers Liffey, Thames and Ter, respectively. Overall, higher concentrations were found in the Thames, where cumulative concentration values of up to 20,000 ng L⁻¹ were detected. Caffeine was obtained at the highest concentration in the Ter, despite the population of Girona being much smaller than the other cities, probably due to the proximity of a WWTP effluent downstream of the collection point. Variations according to geographical location were

studied for all compounds detected across the three sites; however, only four use categories presented significant differences between locations: plasticisers, caffeine, flame retardants and benzotriazole. An ERA was performed, and high risks were associated with two compounds for the rivers Liffey and Thames and one compound for the Ter. The highest RQ was calculated for caffeine in the River Ter (RQ=705), and this compound generally explained most of the combined RQs in all samples across sites, along with bisphenol A. Consequently, these compounds should be prioritised in defining future policy to protect and enhance water quality across different geographical locations. Substance prioritisation was determined by location, with the following EDCs identified: caffeine, bisphenol A and E1 for the River Ter; caffeine, bisphenol A and triclosan for the River Thames; and caffeine, bisphenol A and testosterone for the River Liffey. This highlighted caffeine and bisphenol A as priorities independently of the location.

7 Recommendations

Based on the ERAs performed in Chapters 2, 3 and 6 for effluents and surface waters, a list of compounds has been identified for prioritisation in the Irish context (Table 7.1). It is recommended that these compounds are investigated further, in a study that incorporates the ERA recommendations below.

A series of recommendations is targeted at future ERAs of CECs:

- The RQs of CECs determined in this study were calculated using the MECs detected. However, this study considered only two locations, one rural and one urban. While the sites were chosen by the EPA as potential “worst-case scenario” sites, based on previous work carried out, two sites cannot accurately reflect the potential risk of CECs in water bodies nationally. To determine the risks posed by CECs in Ireland, a more comprehensive spatial analysis should be carried out.
- Risk assessment has been performed using only the aqueous phase; however, this does not represent the whole environment. Compounds with logP values greater than 5, such as

octinoxate (a UV filter often found in sunscreens) and triclosan (an antibacterial and antifungal agent), which were evaluated in this study, tend to be retained in organic matter. Therefore, it is expected that the concentrations found in this study are an underrepresentation of their presence, and potential risk, in the environment. It is recommended that, in addition to water samples, sediments and/or suspended particulate matter are also evaluated for compounds with these physicochemical properties.

- The risk assessments carried out in this study were based on determined WFD EQSs and PNEC values from databases such as NORMAN, and on a literature review, particularly where gaps in databases were identified. However, available data are sometimes limited for certain compounds. Prediction software can be used to obtain these values; however, this can result in over- or underestimation of final RQs. It is recommended, therefore, that more ecotoxicity research compliant with international best practice (Klimisch *et al.*, 1997; Moermond *et al.*, 2016) is conducted to provide an expanded database of PNEC values and, as a result, enable more accurate risk assessments to be carried out.

Table 7.1. CECs recommended for prioritisation

Matrix	Compound
Surface waters	E1
	E2
	EE2
	Testosterone
	Bisphenol A
	Propranolol
	MCPA
WWTP effluents	Carbamazepine
	Diclofenac
	E2
	EE2
	MCPA
	Propranolol
	Sulfamethoxazole
	Venlafaxine
	Permethrin
	Cypermethrin

A second series of recommendations is targeted at pesticides:

- As reported in Chapter 5, pesticides used both in agricultural settings and in clinical and veterinary settings were investigated in the aquatic environment, with between 3 and 13 pesticides detected per site in this study. The pesticides detected in the water bodies analysed were suspected to result in large part from agricultural run-off, amenity horticulture and veterinary use. Therefore, the presence of acid herbicides such as MCPA is not unexpected. The extent to which it has been detected in County Donegal, in an area previously associated with very low herbicide use, is concerning, and further research into its use there is recommended, as MCPA was found to be of moderate risk to rural receiving waters.

- The neonicotinoid pesticides acetamiprid and imidacloprid were also determined to be of moderate risk to rural receiving waters. Given the potential impact of these compounds on insects, including pollinators, it is recommended that the use of these compounds in rural areas is researched further, both to explore the sources of neonicotinoid pesticides in rural receiving waters and to investigate whether agricultural practices can be refined to reduce the environmental risk. In particular, the impact of the Coillte decision to replace cypermethrin with the EU Watch List substance acetamiprid for controlling pine weevil in forestry should be investigated further to determine the extent of potential environmental risk that acetamiprid poses.

Lastly, this study was concerned with the identification of CECs in water bodies that are likely to pose the

greatest environmental risk in an Irish context. By their very definition, however, CECs are compounds of which our knowledge is limited, as they are not listed for routine aquatic monitoring and assessment. It is estimated that, of the approximately 100,000 chemicals in use in our world, we have reliable data for less than 5%. There is significant uncertainty about the presence of many of these compounds in our environment and even more about the levels that could harm the environment and/or human health via the environment. In tandem with analysis of individual compounds, therefore, effect-based monitoring approaches should also be developed to assess the potential risk associated with the “cocktail” of CECs in water bodies. These approaches should be incorporated into investigative monitoring strategies to identify areas where heightened risk exists and areas that should be prioritised for a more detailed analysis and risk assessment.

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Abbreviations

2,4-D	2,4-Dichlorophenoxyacetic acid
AA-EQS	Annual average environmental quality standards
AF	Assessment factor
AMPA	Aminomethylphosphonic acid
CEC	Contaminant of emerging concern
E1	Estrone
E1-3S	Estrone 3-sulfate
E2	17 β -Estradiol
EC₁₀	Effective (sub-lethal) concentration 10%
EC₅₀	Effective (sub-lethal) concentration 50%
ECOSAR	Ecological Structure Activity Relationships
EDC	Endocrine-disrupting compound
EE2	17 α -Ethinylestradiol
EMEA	European Medicines Evaluation Agency
EPA	Environmental Protection Agency
EQS	Environmental quality standard
ERA	Environmental risk assessment
IMPACT	Innovative Monitoring to Prioritise Contaminants of Emerging Concern (CECs) for Ireland
LC₅₀	Median lethal concentration
LOD	Limit of detection
LOQ	Limit of quantification
MAC-EQS	Maximum allowable concentration environmental quality standards
MCPA	2-Methyl-4-chlorophenoxyacetic acid
MEC	Maximum environmental concentration
NOEC	No-observed-effect concentration
PCP	Personal care product
PNEC	Predicted no-effect concentration
PS	Passive sampling
RQ	Risk quotient
TWA	Time-weighted average
UV	Ultraviolet
WFD	Water Framework Directive
WWTP	Wastewater treatment plant

An Gníomhaireacht Um Chaomhnú Comhshaoil

Tá an GCC freagrach as an gcomhshaoil a chosaint agus a fheabhsú, mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaoil a chosaint ar thionchar díobhálach na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialáil: Rialáil agus córais chomhlíonta comhshaoil éifeachtacha a chur i bhfeidhm, chun dea-thorthaí comhshaoil a bhaint amach agus díriú orthu siúd nach mbíonn ag cloí leo.

Eolas: Sonraí, eolas agus measúnú ardchaighdeán, spriocdhírthe agus tráthúil a chur ar fáil i leith an chomhshaoil chun bonn eolais a chur faoin gcinnteoireacht.

Abhcóideacht: Ag obair le daoine eile ar son timpeallachta glaine, táirgiúla agus dea-chosanta agus ar son cleachtas inbhuanaithe i dtaobh an chomhshaoil.

I measc ár gcuid freagrachtaí tá:

Ceadúnú

- > Gníomhaíochtaí tionscail, dramhaíola agus stórála peitрил ar scála mór;
- > Sceitheadh fuíolluisce uirbhig;
- > Úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe;
- > Foinsí radaíochta ianúcháin;
- > Astaíochtaí gás ceaptha teasa ó thionscal agus ón eitlíocht trí Scéim an AE um Thrádáil Astaíochtaí.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- > Iniúchadh agus cigireacht ar shaoráidí a bhfuil ceadúnas acu ón GCC;
- > Cur i bhfeidhm an dea-chleachtais a stiúradh i ngníomhaíochtaí agus i saoráidí rialáilte;
- > Maoirseacht a dhéanamh ar fhreagrachtaí an údaráis áitiúil as cosaint an chomhshaoil;
- > Caighdeán an uisce óil phoiblí a rialáil agus údaruithe um sceitheadh fuíolluisce uirbhig a fhorfheidhmiú
- > Caighdeán an uisce óil phoiblí agus phríobháidigh a mheasúnú agus tuairisciú air;
- > Comhordú a dhéanamh ar líonra d'eagraíochtaí seirbhíse poiblí chun tacú le gníomhú i gcoinne coireachta comhshaoil;
- > An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaoil.

Bainistíocht Dramhaíola agus Ceimiceáin sa Chomhshaoil

- > Rialacháin dramhaíola a chur i bhfeidhm agus a fhorfheidhmiú lena n-áirítear saincheisteanna forfheidhmithe náisiúnta;
- > Staitisticí dramhaíola náisiúnta a ullmhú agus a fhoilsiú chomh maith leis an bPlean Náisiúnta um Bainistíocht Dramhaíola Guaisí;
- > An Clár Náisiúnta um Chosc Dramhaíola a fhorbairt agus a chur i bhfeidhm;
- > Reachtaíocht ar rialú ceimiceáin sa timpeallacht a chur i bhfeidhm agus tuairisciú ar an reachtaíocht sin.

Bainistíocht Uisce

- > Plé le struchtúir náisiúnta agus réigiúnacha rialachais agus oibriúcháin chun an Chreat-treoir Uisce a chur i bhfeidhm;
- > Monatóireacht, measúnú agus tuairisciú a dhéanamh ar chaighdeán aibhneacha, lochanna, uiscí idirchreasa agus cósta, uiscí snámha agus screamhuisce chomh maith le tomhas ar leibhéal uisce agus sreabhadh abhann.

Eolaíocht Aeráide & Athrú Aeráide

- > Fardail agus réamh-mheastacháin a fhoilsiú um astaíochtaí gás ceaptha teasa na hÉireann;
- > Rúnaíocht a chur ar fáil don Chomhairle Chomhairleach ar Athrú Aeráide agus tacaíocht a thabhairt don Idirphlé Náisiúnta ar Gníomhú ar son na hAeráide;

- > Tacú le gníomhaíochtaí forbartha Náisiúnta, AE agus NA um Eolaíocht agus Beartas Aeráide.

Monatóireacht & Measúnú ar an gComhshaoil

- > Córais náisiúnta um monatóireacht an chomhshaoil a cheapadh agus a chur i bhfeidhm: teicneolaíocht, bainistíocht sonraí, anailís agus réamhaisnéisiú;
- > Tuairiscí ar Staid Thimpeallacht na hÉireann agus ar Tháscairí a chur ar fáil;
- > Monatóireacht a dhéanamh ar chaighdeán an aeir agus Treoir an AE i leith Aeir Ghlain don Eoraip a chur i bhfeidhm chomh maith leis an gCoinbhinsiún ar Aerthruailliú Fadraoin Trasteorann, agus an Treoir i leith na Teorann Náisiúnta Astaíochtaí;
- > Maoirseacht a dhéanamh ar chur i bhfeidhm na Treorach i leith Torainn Timpeallachta;
- > Measúnú a dhéanamh ar thionchar pleananna agus clár beartaithe ar chomhshaoil na hÉireann.

Taighde agus Forbairt Comhshaoil

- > Comhordú a dhéanamh ar ghníomhaíochtaí taighde comhshaoil agus iad a mhaoiniú chun brú a aithint, bonn eolais a chur faoin mbeartas agus réitigh a chur ar fáil;
- > Comhoibriú le gníomhaíocht náisiúnta agus AE um thaighde comhshaoil.

Cosaint Raideolaíoch

- > Monatóireacht a dhéanamh ar leibhéal radaíochta agus nochtadh an phobail do radaíocht ianúcháin agus do réimsí leictreamaighnéadacha a mheas;
- > Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as tasmí núicléacha;
- > Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta;
- > Sainseirbhísí um chosaint ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Ardú Feasachta agus Faisnéis Inrochtana

- > Tuairisciú, comhairle agus treoir neamhspleách, fianaise-bhunaithe a chur ar fáil don Rialtas, don tionscal agus don phobal ar ábhair maidir le cosaint comhshaoil agus raideolaíoch;
- > An nasc idir sláinte agus folláine, an geilleagar agus timpeallacht ghlan a chur chun cinn;
- > Feasacht comhshaoil a chur chun cinn lena n-áirítear tacú le hiompraíocht um éifeachtúlacht acmhainní agus aistriú aeráide;
- > Tástáil radóin a chur chun cinn i dtithe agus in ionaid oibre agus feabhsúchán a mholadh áit is gá.

Comhpháirtíocht agus Líonrú

- > Oibriú le gníomhaireachtaí idirnáisiúnta agus náisiúnta, údaráis réigiúnacha agus áitiúla, eagraíochtaí neamhrialtais, comhlachtaí ionadaíochta agus ranna rialtais chun cosaint comhshaoil agus raideolaíoch a chur ar fáil, chomh maith le taighde, comhordú agus cinnteoireacht bunaithe ar an eolaíocht.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an GCC á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóir. Déantar an obair ar fud cúig cinn d'Oifigí:

1. An Oifig um Inbhuanaitheacht i leith Cúrsaí Comhshaoil
2. An Oifig Forfheidhmithe i leith Cúrsaí Comhshaoil
3. An Oifig um Fhianaise agus Measúnú
4. An Oifig um Chosaint ar Radaíocht agus Monatóireacht Comhshaoil
5. An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tugann coistí comhairleacha cabhair don Gníomhaireacht agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair inmí agus le comhairle a chur ar an mBord.

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