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PestMan: Pesticide Management for Better Water Quality

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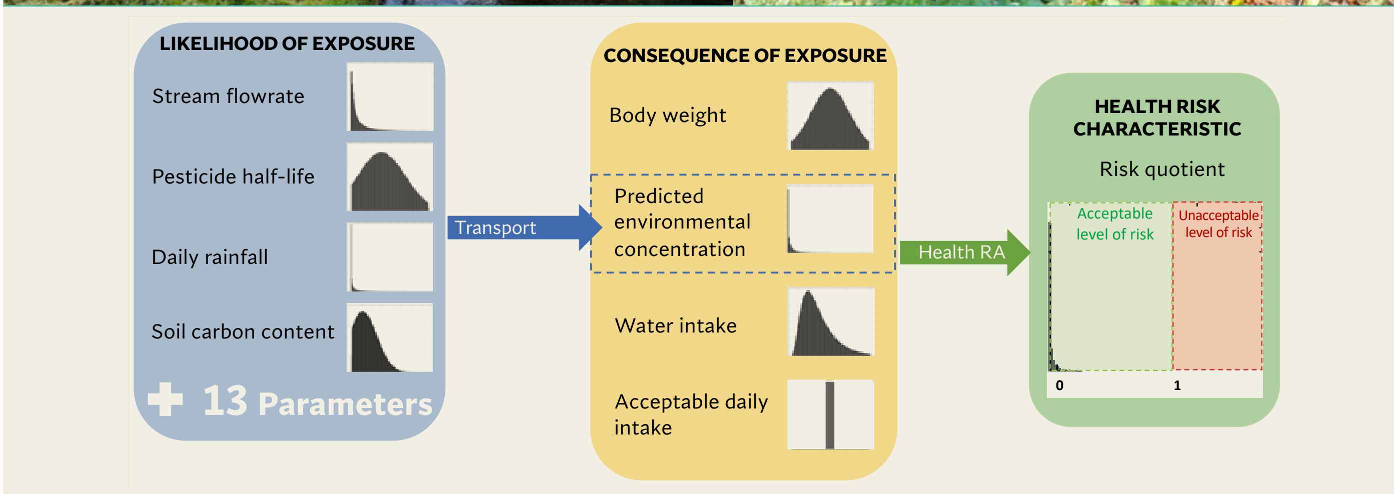

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Rialtas na hÉireann
Government of Ireland

Environmental Protection Agency

The EPA is responsible for protecting and improving the environment as a valuable asset for the people of Ireland. We are committed to protecting people and the environment from the harmful effects of radiation and pollution.

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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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Lead organisations: University of Galway, University College Cork and Teagasc Environmental Research Centre

Identifying pressures

An increasing world population means that the demand for food will inevitably increase. To address this, agriculture has intensified, which, in turn, has led to an increased use of pesticides. Although their use is strictly controlled, it is estimated that only up to 10% of pesticides reach target organisms. Consequently, pesticides are present in soil, groundwater and surface water, potentially adversely impacting waterways, ecosystems and human health. The assessment of potential pesticide transmission risk to waterways, based on soil texture and pesticide properties, is required, as is the development of remediation methods to break the pathway of loss from source to receptor. Furthermore, as the majority of human health risk models are often deterministic in nature, and do not reflect the inherent uncertainties and variabilities in pesticide transmission, it is necessary to develop robust probabilistic models to account for these uncertainties. Together, these will inform the implementation of risk mitigation approaches.

Informing policy

Pesticides are used as part of farm intensification strategies, either to bring marginal land into production or to maintain competitively high crop yields. Guidelines have been put in place by governments to regulate pesticide use and address the risks they pose. These guidelines lay out a framework for pesticide regulation consisting of limits on the amount of pesticides used, risk screening and detailed risk assessment to reduce harm to ecosystems, the environment and human health. Despite this, pesticides have been detected in surface water and groundwater at levels exceeding the drinking water parametric value of 100 ng l^{-1}.

Developing solutions

A screening tool was developed to allow farmers to determine the potential pesticide transmission risk. Intervention measures, conducted at field scale, to break the pathway between source and receptor showed that coconut-based activated carbon, when placed in filter pipes, was an effective adsorption medium for pesticides. Other "at source" intervention methods, such as "split" applications of pesticides, where the yearly application of pesticides is split into two equal doses, were effective in preventing surface run-off and leaching of pesticides. A semi-quantitative risk scoring method was developed to allow users to identify high-risk pesticides and examine how they may contribute to the health risks of a population on a regional or national scale. A probabilistic assessment of health risk levels arising from exposure to the modelled concentrations found very low levels of risk under current climatic and land use conditions. This model may be combined with alternative human health risk models and assessments or environmental risk models to provide a better understanding of the impact of pesticides on drinking water resources and to further quantify the risks posed to consumers and non-target organisms.

EPA RESEARCH PROGRAMME 2014–2020

PestMan: Pesticide Management for Better Water Quality

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EPA Research Report

Prepared for the Environmental Protection Agency

by

University of Galway, University College Cork and Teagasc Environmental Research Centre

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This report is based on research carried out/data from February 2020 to September 2023. 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

Pesticide use is associated with the mass production of foodstuffs to cater for global demand. However, pesticides released unintentionally from both the agricultural and urban sectors have the potential to enter non-target ecosystems. To reduce the amounts of pesticides being used and make food systems more environmentally friendly in the European Union, the Farm to Fork Strategy proposes reducing the overall use of chemical pesticides by 50%. However, legacy pesticides, some of which have not been approved since the last century, are still being detected in European waterways, with many levels detected being over the parametric value for drinking water, of 100 ng l^{-1}. Modelling the health risks of these legacy pesticides and identifying effective remediation methods for dealing with them are therefore of interest.

The overarching aim of this research was to use a multidisciplinary approach merging knowledge of soil processes, molecular biology, engineering and quantitative risk assessment methodologies to (1) gain an understanding of the drivers of and pressures caused by the use of pesticides in the environment; (2) examine the fate and persistence of pesticides; (3) evaluate any potential impact on and risks to the environment and human health from pesticides; and (4) develop a low-cost, passive, *in situ* remediation method, to mitigate the problems caused by pesticides in the environment.

A screening tool to assess the potential risk of pesticide transmission to waterways was developed. The tool is based on soil texture and various pesticide properties, including water solubility, soil permeability and soil half-life. This screening tool can afford farmers the opportunity to determine if a pesticide is environmentally friendly or if its use could pose a threat to waterways. A modelling framework was also developed to facilitate a probabilistic assessment of pesticide transport into water resources via surface run-off and leaching, with the inclusion of information on additional and influential site conditions and in-stream processes. This was used to assess pesticide concentrations in surface water and groundwater, and the risk of regulatory threshold exceedances. The analysis indicated that triclopyr and 4-chloro-2-methylphenoxyacetic acid (MCPA) occur in greater concentrations in both surface water and groundwater than any of the other pesticides analysed. The model also found that surface water supplies were at greater risk overall of pesticide pollution than groundwater supplies. The concentrations predicted from this quantitative assessment were then used to analyse potential human health risks. It was found that the pesticides examined using the modelling framework posed a very low risk to humans via drinking water supplies based on study site conditions, current agricultural practices and climate conditions.

Batch adsorption and kinetic studies were undertaken to assess the potential of several raw and pyrolysed low-cost industrial and agricultural materials as pesticide adsorbents for the removal of commonly used herbicides in Ireland. Based on the outcome of these studies, filters containing coconut-based activated carbon (CAC) were placed in streams in two agricultural catchments and one urban area for a period of 7 months. Two different configurations of intervention were investigated: one used filter bags containing 16 kg of sieved CAC, while the second used the same filter bags but filled with 12 kg of sieved CAC and fitted into a polyethylene pipe so that they filled the full diameter of the centre section of the pipe. The field study demonstrated that the filter pipes reduced herbicide concentrations more efficiently than the filter bags. Where the water flow was slow and when the water was not able to flow around or over either the filter bags or pipe, then significant reductions ($p \leq 0.05$) in herbicide concentrations in the streams and drains were observed.

Based on the findings of this project, further work on the design of the intervention systems, including modifying the size of the filter bags and the shape of the pipe, is recommended. Rather than targeting pesticides alone, chemicals of emerging concern, such as pharmaceuticals, antibiotics, personal care products and veterinary products, could also be investigated. In an effort to reduce costs and the system's carbon footprint, the possibility of using Irish agricultural waste materials as the activated carbon adsorbent instead of CAC should be explored, as CAC must be imported to Ireland. One waste material that could be used for this purpose is slurry, a by-product of the dairy and beef industries.

1 Introduction

Pesticides are defined as substances that are used to suppress, eradicate or prevent the spread of organisms that are considered harmful to crops or a nuisance. They include biocidal products and plant protection products (EU, 2021). Once released into the environment, pesticides can move through soil or surface water to streams and groundwater, where they can have unintended ecological effects; for instance, they can accumulate in aquatic organisms and cause the loss of ecosystem biodiversity (Stehle and Schulz, 2015; Arisekar *et al*., 2019).

The detection of legacy pesticides in water samples has been mainly attributed to their desorption from the soils or sediments where they may have accumulated during previous pesticide applications (Pizzini *et al.*, 2021; Postigo *et al*., 2021). Legacy pesticides in the environment arise from a four-step process: (1) the application of pesticides to land, (2) run-off to streams and rivers, (3) partitioning to sediments and (4) desorption/resuspension from sediments several years after their initial application. Depending on their properties (e.g. polarity, octanol–water partition coefficient), pesticides can be adsorbed onto soil or sediment particles, with hydrophobic pesticides being adsorbed at particularly high levels (Khanzada *et al*., 2020). Pesticide pollutants can also be desorbed/resuspended during the disturbance, handling or disposal of contaminated sediment, or during hydromorphological modification, such as that caused by dredging, channelisation, land drainage and hard infrastructure, such as dams (Pizzini *et al*., 2021; Mishra *et al*., 2022).

In addition to posing a threat to the environment, low but repeated exposure to pesticides has been linked to several human health disorders (Yin *et al*., 2020; El-Nahhal and El-Nahhal, 2021a). As a result, governmental bodies use legislation to regulate the approval of pesticides for use on the European market, to promote their sustainable use and to reduce risks posed to the environment and consumers (EU, 1991, 2009a,b). Pesticide risk can be evaluated and classified through incremental stages, including data collection, priority setting, risk assessment and risk reduction, before official registration for use. Over the last 30 years, risk-ranking methodologies have progressed and they now use criteria such as mobility and persistence in the environment, ecotoxicological effects on non-target organisms, toxic effects on the human population or a combination of these criteria to rank pesticides according to risk. While such methods may be considered useful, various limitations, such as reliance on pesticide physico-chemical properties to assess mobility, the use of animal health indicators to represent human health risk and the general exclusion of metabolites, reduce their effectiveness and reliability for ranking and comparing pesticides according to risk. This limits their ability to properly inform future pesticide-monitoring programmes.

Several physical and chemical treatment approaches, including adsorption, membrane filtration and advanced oxidation processes, as well as biological approaches, such as bioremediation, activated sludge processes and phytoremediation, have been employed to remove pesticides from aqueous solutions (Mojiri *et al*., 2020). Each method has its own benefits and drawbacks in terms of both technical and economic aspects (Saleh *et al*., 2020). One of the most extensively used pesticide remediation methods is adsorption onto low-cost materials (Mojiri *et al*., 2020). This is simple and cost-effective. However, the issues of incomplete removal of pesticides and the generation of toxic side products are the main disadvantages of this method (Mojiri *et al*., 2020; Shahid *et al*., 2021).

1.1 Objectives

The objectives of the Pesticide Management for Better Water Quality (PestMan) project were to:

- undertake a review of pesticide use in Europe, examine the issue of legacy pesticides (including their exceedance of drinking water standards and their persistence in the environment) and quantify the efficacy of existing and emerging methods of pesticide mitigation;
- rank key pesticides by risk of transmission through soil to waterways, taking into account physico-chemical properties of the pesticides,

soil permeability and the relationship between the adsorption of pesticides and soil texture;
- quantify the efficacy of raw and pyrolysed waste materials for adsorbing herbicides and examine the efficiency of low-cost intervention systems, placed in streams and tributaries, for herbicide removal;
- develop an easy-to-use risk-screening tool to identify high-risk pesticides in catchments and apply a probabilistic approach to modelling the transport of pesticides into drinking water and the resulting health risk.

2 The Impact of Historical Legacy Pesticides on Achieving Legislative Goals in Europe

2.1 Overview

In this review, the current knowledge regarding pesticide use in Europe, as well as pathways of pesticide movement to waterways, are investigated. The issues of legacy pesticides, including exceedances, are examined, and existing and emerging methods for pesticide remediation, particularly of legacy pesticides, are discussed. The fact that some legacy pesticides can be detected in water samples more than 25 years after not being approved highlights the need for improved EU strategies and policies aimed at targeting legacy pesticides so that future targets can be met. This chapter is an abridged version of McGinley *et al*. (2023), used in accordance with licence CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/), with minor changes made for consistency and in line with EPA style.

2.2 Pesticide Usage and Pathways of Loss

The sale of pesticides used within the EU-27 over the 10-year period 2011–2020 fluctuated from 356 kt in 2011 to 350 kt in 2020, with the highest sales, of 368 kt, recorded in 2018 (Eurostat, 2022a). Fungicides and herbicides were the dominant pesticides used in the EU-27 from 2011 to 2020, accounting for 40–44% and 30–36%, respectively, of total pesticide sales. A smaller proportion (9–16%) of the pesticides used were insecticides, with the remainder being a mixture of plant growth regulators, anti-sprouting agents and molluscicides. The variation in pesticide usage per hectare (kg ha^{-1}) of agricultural land for 2020 was considerable between countries within the EU-27, from Ireland with 0.6 kg ha^{-1} to > 11 kg ha^{-1} for Malta (Eurostat, 2022a,b). Although 16 countries in the EU-27 applied less than 2 kg ha^{-1} of pesticides, the overall amount of pesticides being applied across the EU-27 continues to rise. The recent EU strategy on sustainable food production, implemented in 2020, proposes to cut overall pesticide use in the EU-27 by 50% by 2030, as well as to reduce nutrient losses (especially nitrogen and phosphorus) by 50% and fertiliser use by 20% (EU, 2020). One possible way of achieving the reduction in both nutrient loss and fertiliser use would be to transition from a grassland-dominated system to a more arable crop-based system. While this could achieve the required reduction in nutrient loss, it could also lead to an increase in pesticide usage, particularly herbicides, which are required for arable and vegetable crops.

A significant percentage of pesticides applied in agricultural practices never reach their target organism (Ali *et al*., 2019), with Schulz (2004) estimating that 10% of applied pesticides reach non-target areas. As a result, and because of the widespread use of pesticides in agricultural and urban areas, pesticides can migrate to various surface water resources by several pathways, including surface run-off (Cosgrove *et al*., 2022), leaching (Cosgrove *et al*., 2019), spray drift (Ravier *et al*., 2005), groundwater inflow (Gzyl *et al*., 2014) and subsurface drainage systems (Halbach *et al*., 2021). Surface run-off is the predominant pathway, mainly through heavy rainfall events and snowmelt, particularly in saturated fields, fields with hilly slopes or fields with a high water table (Jing *et al*., 2021). The input of pesticides to surface water is particularly high during the main application period of spring and summer, and also increases during rainfall events (Szöcs *et al*., 2017).

The main factors influencing the transport of pesticides to receptors are adsorption and desorption to and from soil particles (Paszko and Jankowska, 2018), pesticide half-life and the physico-chemical properties of soil (Boivin *et al*., 2005). Adsorption is predominantly influenced by the properties and chemical composition of the soil, which is a complex mixture of inorganic materials and organic matter (Leovac *et al*., 2015), and the physico-chemical properties of the pesticide (Kodešová *et al*., 2011). The adsorption of pesticides onto the soil surface determines how pesticides are either transported or degraded, which will, ultimately, determine the concentration of pesticides in both soil and soil solutions (Gondar *et al*., 2013).

2.3 Legacy Issues

Many toxic pesticides have not been approved for use by the EU, although some have persisted in the environment for decades after initial application (Ccanccapa-Cartagena *et al.*, 2019). In 2022, 452 active substances were approved for use as plant protection products in the EU-27, while 937 active substances were not approved (EU, 2022). Of the active substances that were on the market before 1993, 70% have since been withdrawn (EU, 2017). Figure 2.1 shows the top 12 herbicides, fungicides and insecticides that were detected in surface waters across the EU-27 after they were no longer approved by the EU, with several being detected many years after approval had been withdrawn. The legislation that defines the maximum allowable concentration of pesticides in drinking water in the EU, of 100 ng l^{-1}, has been described as the most stringent in the world (Knauer, 2016). Because of this stringency, many pesticides that are not approved continue to be detected in Europe at levels exceeding legal limits in both surface water and groundwater. In total, pesticides that are no longer approved for use in the EU have been detected on 233 occasions in EU waterways since their approval was withdrawn, including some that were not approved in the last century, although not all were detected at above the maximum permissible concentration, of 100 ng l^{-1}, for drinking water.

2.4 Mitigation Options

Conventional methods to remove pollutants, including pesticides, from the environment include adsorption, sedimentation, advanced oxidation processes and membrane technologies (Mojiri *et al.*, 2020; Jatoi *et al.*, 2021; Shahid *et al.*, 2021). Although these methods are commonly used, they can involve high operating costs, can generate toxic side products and do not completely remove the pollutants (Mon *et al.*, 2018). The development of more efficient and safer removal systems is necessary. A list of these systems, along with relevant references, is given in McGinley *et al.* (2023). Among several emerging mitigation methods for the removal of pesticides from water, metal organic frameworks are among the most promising, owing to their well-defined pore structure and large surface areas. One disadvantage that all adsorbent materials have is that it can be difficult to remove the pesticides from the adsorbents, and the interactions of the cleaning materials with the pesticides requires further exploration. The most cost-effective method is the use of vegetated buffer strips to protect streams and other wetland habitats, as well as improving water quality.

2.5 Management Implications Across Europe

Following the introduction of the EU Directive on the Sustainable Use of Pesticides in 2009 (EU, 2009a),

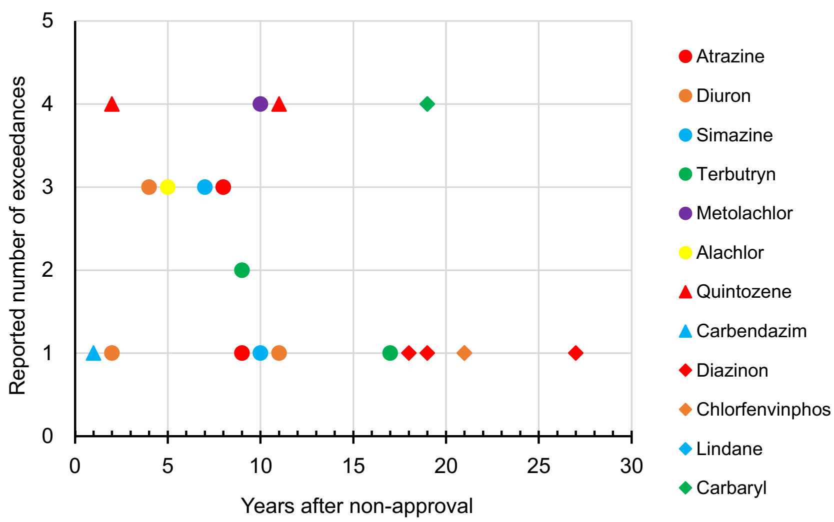


Figure 2.1. Timeline of reported parametric value exceedances of some selected pesticides that are not approved. Herbicides are denoted by circles, fungicides by triangles and insecticides by diamonds. Reproduced from McGinley *et al.* (2023); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

many papers have been published regarding measures for reducing pesticide use. A recent review focused on the effectiveness of public policy instruments in reducing pesticide use by farmers in Europe (Lee *et al*., 2019). Bans, zoning, monitoring and penalties were placed in the regulatory domain, while instruments involving certification, and training and advisory services were in the informative domain. While the review determined that no specific instrument was guaranteed to reduce pesticide use, it suggested that measures were frequently identified as ineffective if based on the sole use of regulatory-based instruments, namely bans and prescriptions (maximum doses or pesticide levels). On the other hand, prescriptions and subsidies, prescriptions and advisory services, and prescriptions, taxes, training, monitoring and advisory services were seen as most beneficial for pesticide reduction.

The latest Farm to Fork Strategy (EU, 2020) aims to cut chemical pesticide use across the EU-27 by 50% in 2030. To achieve this, the Commission intends to revise the Sustainable Use of Pesticides Directive (EU, 2009a), enhance provisions on integrated pest management and promote greater use of safe alternative ways of protecting harvests from pests and diseases (EU, 2020). Integrated pest management will be one of the main tools in reducing the use and dependence on chemical pesticides. One approach that is intended to achieve this goal is the placing of pesticides containing biologically active substances on the market. In a recent EU factsheet, it was noted that, although Member States had made progress implementing the Sustainable Use of Pesticides Directive, fewer than one in three states had completed the review of their national action plan by the 5-year legal deadline (EU, 2021a).

2.6 Conclusions

The EU strategy to make food production environmentally friendly by reducing the overall use of chemical pesticides by 50% by 2030 may be too ambitious, given that usage has remained relatively constant since 2011. The potential attainment of this target could have implications for the number of pesticide detections in water bodies across the EU-27. The omission of legacy pesticides from the current EU Farm to Fork Strategy, and the requirement of a maximum allowable concentration of pesticides in soils or sediments, may be a serious omission.

3 Assessment of Potential Pesticide Transmission, Considering Soil Texture and Pesticide Properties

3.1 Introduction

The main factors influencing the transport of pesticides to receptors are soil half-life (Fantke *et al*., 2014), adsorption and desorption to and from soil particles (Paszko and Jankowska, 2018), and physico-chemical properties of soil (Boivin *et al*., 2005). The adsorption of pesticides onto the soil surface determines how pesticides are either transported or degraded, which ultimately determines the concentration of pesticides in both soil and soil solutions (Gondar *et al*., 2013). Although many soil factors have been investigated with regard to pesticide adsorption, including pH (Gondar *et al*., 2013), organic content (Conde-Cid *et al*., 2019), pore size (Siek and Paszko, 2019) and cation exchange capacity (Kodešová *et al*., 2011), to date no study has conducted a meta-analysis of the literature that investigates the relationship between pesticide adsorption and soil texture.

The aim of this chapter is to describe a meta-analysis of literature that has assessed pesticide adsorption and soil texture data, and integrate this with pesticide properties such as soil half-life and solubility, to determine if a relationship exists that could guide future modelling and decision-making protocols regarding the safe use of pesticides. This chapter is an abridged version of McGinley *et al*. (2022a), used in accordance with licence CC BY-NC-ND 4.0 (https://creativecommons.org/licenses/by-nc-nd/4.0/), with minor formatting changes made in line with EPA style.

3.2 Materials and Methods

A detailed literature search was undertaken by searching key words including: pesticide, soil, adsorption, sorption, adsorption isotherm, and soil texture triangle. The search was limited to peer-reviewed papers published, in English, since 2000 that included data on adsorption isotherm parameters and soil texture. No geographical limitations were employed. Search engines used included databases such as Scopus, as well as publisher-specific search engines including ScienceDirect, the American Chemical Society, and the Royal Society of Chemistry. A total of 1212 articles and a small number of book chapters and reports were reviewed. Following this, the pesticides were ranked according to the number of studies in which they were investigated and they also had to be currently approved for use by the EU. This resulted in a short-list of 54 publications, reporting on the 28 most commonly studied pesticides, which are still available for use and are approved in the EU or elsewhere. These 28 pesticides were grouped into herbicides, fungicides and insecticides, with no molluscicides, bactericides or rodenticides present in that group.

3.2.1 Adsorption modelling

The manuscripts that fulfilled the selection criteria of this study modelled their experimental data using the Freundlich (1907) adsorption isotherm, with some also reporting the parameters of the Langmuir (1918) adsorption isotherm. To facilitate comparative analysis, only the Freundlich model was used for determination of the adsorption isotherm coefficients. The Freundlich isotherm model is:

$$q_e = K_F C_e^{1/n} \tag{3.1}$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}) and C_e is the concentration of the adsorbate at equilibrium (mg l^{-1}); K_F is the Freundlich sorption capacity coefficient (mg g^{-1}(mg l^{-1})$^{-1/n}$) and the exponent n is the Freundlich exponent (dimensionless) (Lima *et al*., 2015).

3.2.2 Pesticide transport potential ranking

The movement of pesticides from the target crop through the soil and to the water receptor is a function of soil permeability (m s^{-1}), the adsorption capacity of each soil texture for the investigated pesticide (g m^{-3}), soil half-life of the pesticide (days) and the pesticide solubility in water (S_w; mg l^{-1}). In order to establish a soil texture-specific transport potential risk ranking for each of the pesticide groups examined in this study, a ranking system incorporating each of these parameters was developed, with the highest value indicative of the greatest risk of transmission to receiving waters. The permeability of soils was ranked according to soil texture (USDA, 2001). Soil adsorption values were generated from the median value for each pesticide/soil texture association reported in the literature (see McGinley *et al*., 2022a). The water solubility and soil half-life values were obtained from the Pesticide Properties DataBase. Using this rubric, each parameter was independently ranked from 1 to 12, where 12 was considered to be the highest risk for pesticide mobility through soil to surface and groundwater bodies, i.e. high permeability soils, low pesticide adsorption capacity, high soil half-life and high water solubility. In this study, high permeability soils were considered to be most at risk for surface and groundwater pollution. If surface water processes were only considered, low permeability soils, which would have large surface run-off potential relative to surface flow, would be considered to be most at risk. Finally, these independent risk values were combined (with equal weighting) to give a final risk ranking for each pesticide across all soil textures, but also for all of the pesticides within an individual soil texture classification.

3.3 Results and Discussion

Table 3.1 shows the potential pesticide transmission risks as a function of water solubility, soil half-life, adsorption by soil of the pesticide and also soil texture. The potential transmission risk can be quantified either on the basis of soil texture or pesticide type, with the highest score in each case being the most transmissible.

The highest potential transmission risk ranking for each individual pesticide across all herbicides, fungicides and insecticides shows that the soil textures resulting in highest transmission risks are sandy loam and sand, with 19 of the highest rankings being in one of these two soil textures (Table 3.1). These two soil textures have low clay content (<20%), implying that a high clay content is important in the retention of pesticides within the soil, as previously reported (Ren *et al*., 2018; García-Delgado *et al*., 2020).

There are two different ways that the data in Table 3.1 can be interpreted. The data can be viewed from the point of view of the pesticide. Considering the herbicide chlorotoluron, for example, the potential risk ranking varies from 36 in sand to 17 in clay. Therefore, the soil textures most likely to transmit chlorotoluron may be identified. Alternatively, the data may be examined considering only soil texture. Within sandy loam soils, for example, 4-chloro-2-methylphenoxyacetic acid (MCPA), mecoprop-P, bentazone, metamitron and metribuzin are some of the highest risk herbicides, with ranking values of 35, 34, 34, 35 and 34, respectively (Table 3.1). As pendimethalin, also used for the removal of broad-leaved weeds from cereals, has a much lower transmission ranking value in sandy loam soils (24; Table 3.1), it might be more appropriate for selection when applying to this soil texture. In a similar manner, the choice of terbuthylazine (14; Table 3.1) would be appropriate when considering removing broad-leaved weeds and grasses from cereal and vegetable crops in clay soil than any of the other herbicides in this study (16–27; Table 3.1).

3.4 Conclusions

Using soil texture-specific adsorption isotherm data for several groups of pesticides, their solubility in water, soil half-life and soil permeability, a transmission risk ranking was developed in this study. This is designed as a decision-making support tool for agricultural land management, as it allows the agricultural sector to assess, either by soil texture or pesticide type, the risk of loss of pesticides to receptors. Whilst this is a simple decision-making support tool, rather than the more complicated and complex pesticide root zone model (PRZM) modelling approach (PRZM_SW website), it offers a manageable choice for the end user. It is also useful for modelling the loss of pesticides to water and for identification of critical source areas for better land management.

Table 3.1. Pesticide transmission risk rankings

		Sand	Loamy sand	Sandy loam	Sandy clay loam	Loam	Sandy clay	Silt loam	Silt	Clay loam	Silty clay loam	Silty clay	Clay
Herbicides	2,4-D			30		26		25		24	22	22	20
	Bensulfuron-methyl					23					19	17	
	Bentazone			34		32		30		29	27	26	25
	Chlorotoluron	36	28	29	29	29		25		20	19	18	17
	Dimethenamid-P							28					
	Ethofumesate	28	29	29				22					17
	Glyphosate	28	26	27		23		22			18		16
	Isoxaflutole					20		24		22	21	13	
	Lenacil												22
	MCPA			35				33		31			23
	Mecoprop-P			34									
	Metamitron	34	34	35				32					24
	Metribuzin			34									
	Metsulfuron-methyl				35		33			30			27
	Pendimethalin			24		22		19					
	Phenmedipham	21	23	27				17					21
	Terbuthylazine	35	32	30		27		26			24		14
Fungicides	Azoxystrobin	32	29	27		25		22					
	Metalaxyl			38	36	33		26		25			23
	Metalaxyl-M			30	30	25				30			
	Myclobutanil			42									18
	Penconazole	33	33	31	28	28							
	Pyrimethanil							28					
	Tebuconazole	31		29									
	Thiabendazole									25			
Insecticides	Abamectin	21		18			15						9
	α-Cypermethrin							13					
	Deltamethrin		22							15			

Total transmission risk ranking = risk rankings for permeability + adsorbency + solubility + half-life (McGinley *et al.*, 2022a). The higher the score, the higher the risk for transmission through soil to waterways. The colour of the ranking value indicates the likelihood of potential transmission risk, with red being most likely and green being least likely. The maximum score for transmission risk ranking was 48.

2,4-D, 2,4-dichlorophenoxyacetic acid; MCPA, 4-chloro-2-methylphenoxyacetic acid.

4 Batch Adsorption of Herbicides from Aqueous Solution onto Diverse Reusable Materials

4.1 Introduction

Several types of media have been used as absorbents for herbicides (Papazlatani *et al*., 2019; Amoah-Antwi *et al*., 2020), including granulated activated carbon (GAC), which is commonly used in water treatment plants (EPA and HSE, 2019) because of its large surface area (300–2500 $m^2 g^{-1}$) and microporous structure (Jusoh *et al*., 2011). Typical adsorption capacities for the herbicides MCPA and 2,4-dichlorophenoxyacetic acid (2,4-D) on GAC range from 174.2 $mg\,g^{-1}$ to 181.8 $mg\,g^{-1}$ (Salman and Hameed, 2010). Biochar, another porous material rich in carbon, has also been used to adsorb pesticides from soils (Khalid *et al*., 2020) and remove pollutants from water (Kamali *et al*., 2021; Rana *et al*., 2021). However, concerns have been raised about its potential negative effects on soil and the presence of toxic substances (Xiang *et al*., 2021). An alternative approach is to utilise agricultural and industrial waste materials for this purpose.

The aim of this study was to examine the adsorption of five of the most commonly used herbicides in Ireland – namely MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr (DAFM, 2017) – from aqueous solutions onto a range of raw and pyrolysed materials originating from an industrial setting. The study findings are described in detail in McGinley *et al*. (2022b).

4.2 Materials and Methods

4.2.1 *Chemicals and materials used*

The herbicides and chemicals used were MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr. Solutions were prepared, using Milli-Q ultrapure water (18.3 mΩ Milli-Q Element system), at a concentration of 100 $mg\,l^{-1}$ in 0.01 M $CaCl_2$ and were shaken for a minimum of 24 hours.

Twelve different materials identified as potential adsorbents were selected based on criteria such as low cost, bulk availability and potential for local sourcing. These were GAC, peat fibre, bottom ash, fly ash, blast slag, Phoslock, zeolite, alum sludge from a water treatment plant (modified by adjusting the physical characteristics to facilitate hydraulic conductivity without affecting the chemical characteristics of the alum sludge), two spruce biochars (S-BC1 and S-BC2) and two herbal pomace biochars (HP-BC1 and HP-BC2). The processes used for the production and characterisation of all four biochars are described in Siggins *et al*. (2020). All adsorbents were dried at 105°C for 24 hours then crushed or cut to a particle size of 1–2 mm and stored in airtight containers at room temperature.

4.2.2 *Batch adsorption assays*

A preliminary 72-hour batch test was conducted to evaluate the effectiveness of the 12 different materials at adsorbing selected herbicides. The results of this test were used to determine which adsorbents performed best and warranted further investigation. Each batch test was carried out in 40-ml-capacity amber glass vials with an equilibration solution containing 100 $mg\,l^{-1}$ of herbicides and an adsorbent dose of 5 $g\,l^{-1}$. The vials were sealed with polytetrafluoroethylene (PTFE)-lined caps and shaken at 160 rpm for up to 72 hours at 10°C. Control vials without any adsorbent were used to accurately measure adsorption and compensate for herbicide loss through other processes. Once equilibrium was achieved, samples were filtered through a 0.45-μm PTFE syringe filter and analysed immediately. Adsorption kinetics studies, conducted as part of the research, are detailed in McGinley *et al*. (2022b). The findings from these tests were utilised to determine the optimal time for fitting adsorption isotherms to the data.

4.3 Results and Discussion

4.3.1 *Adsorbent selection*

GAC performed the best in terms of adsorption for all five herbicides (> 95% removal). Of the four biochars investigated, S-BC2 performed best at

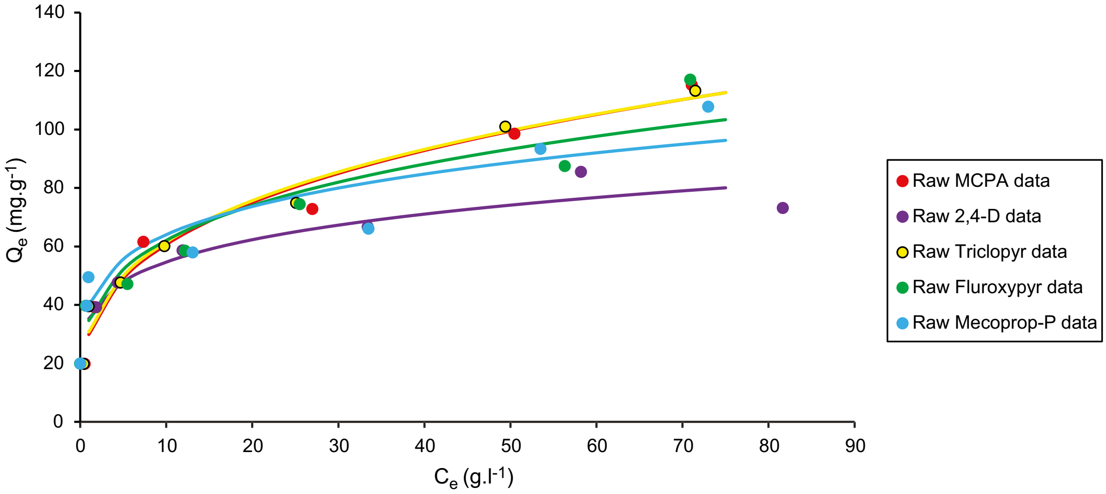


Figure 4.1. Freundlich adsorption isotherms of MCPA, mecoprop-P, 2,4-D, triclopyr and fluroxypyr onto GAC. Modelled data are shown as colour-coded lines. Reproduced from McGinley *et al.* (2022b) with permission from Elsevier.

removing MCPA, triclopyr and fluroxypyr. Based on the adsorption data, it was decided to use GAC for the adsorption of MCPA, mecoprop-P, 2,4-D, triclopyr and fluroxypyr for both the kinetic and isotherm studies.

4.3.2 Adsorption kinetics and isotherms

The adsorption kinetics of each herbicide, namely MCPA, mecoprop-P, 2,4-D, triclopyr and fluroxypyr, were studied using the optimal adsorbent, GAC (Figure 4.1). Maximum adsorption onto GAC occurred within 18 h for all herbicides. MCPA and mecoprop-P exhibited a two-phase adsorption process, consisting of a rapid initial adsorption stage followed by a slower stage, consistent with findings in previous kinetic adsorption research (Ahmad *et al*., 2013).

The adsorptions of all five herbicides were best described by the Freundlich model (Figure 4.1), which indicates that adsorption occurred as mono- and multi-layer adsorption onto a heterogeneous surface. This involves both physisorption and chemisorption, which is in agreement with the pseudo-second-order kinetic model obtained for both MCPA and mecoprop-P (Rizzi *et al*., 2020).

4.4 Conclusions

The materials investigated showed limited capacity for adsorbing herbicides. GAC was found to be the most effective adsorbent for removing the five herbicides investigated, achieving a removal rate of over 95%. Analysis based on adsorption kinetic models and Fourier transform infrared spectroscopy indicated that MCPA and mecoprop-P followed a pseudo-second-order kinetic model, suggesting that chemisorption was the rate-limiting step. Fluroxypyr and triclopyr followed a pseudo-first-order kinetic model, indicating that intraparticle diffusion was the limiting step, while 2,4-D followed a first-order kinetic model, suggesting that the transport of adsorbate to the adsorbent was the rate-limiting step.

5 Field Assessment of Coconut-based Activated Carbon Systems for the Treatment of Herbicide Contamination

5.1 Introduction

In the EU, Council Directive 2020/2184 (EU, 2021) on the quality of water intended for human consumption sets the parametric value for pesticides, either individually or in total, as 100 ng l^{-1} or 500 ng l^{-1}, respectively. However, these values are occasionally exceeded (McGinley *et al*., 2023). Such exceedances are particularly problematic, as conventional water treatment methods are ineffective for the removal of herbicides (Intisar *et al*., 2022; Taylor *et al*., 2022). While some drinking water treatment facilities incorporate powdered carbon or GAC filters to remove herbicides (EPA and HSE, 2019), this is not common practice in many countries because of the prohibitive costs. An alternative approach may involve treatment at the source, i.e. in the field rather than in a treatment plant. This early intervention for the removal of pollutants would positively affect both human and environmental health by reducing herbicide exposure.

Many low-cost media, based on either raw or pyrolysed waste materials coming from an agricultural or industrial origin, have been used as adsorbents for herbicides (Jatoi *et al*., 2021; Taylor *et al*., 2022). In recent years, novel activated carbons, derived from renewable, readily available, low-cost agricultural materials, including canola stalk, orange peel and coconut husk, have been widely researched in batch adsorption studies (Herath *et al*., 2019; Amiri *et al*., 2020). Kodali *et al*. (2021) reported that coconut-based activated carbon (CAC) was a promising adsorbent, mainly owing to its relatively large surface area. However, there is a dearth of field/pilot studies using activated carbon, including CAC, as an adsorbent for herbicides. Such field/pilot studies would be informative in providing information of the configuration of potential intervention devices and their implementation in waterways.

Therefore, the aims of this study were to evaluate the extent of exceedances in two agricultural catchments and one urban catchment in Ireland, and use the data obtained to design, install and assess the efficacy of two low-cost, CAC-based *in situ* remediation systems capable of herbicide removal close to the source of contamination. This chapter is an abridged version of McGinley *et al*. (2024), used in accordance with licence CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/), with minor changes made in line with EPA style.

5.2 Materials and Methods

5.2.1 Study areas

This study examined herbicide exceedances and the efficiency of remediation measures in two agricultural catchments and one urban catchment in Ireland (Figure 5.1). The Corduff catchment (53° 57′ 40″ N, 6° 45′ 22″ W) is located north-west of Carrickmacross in County Monaghan. The site is 578 ha in area, 89% of which is grassland and the remainder of which is used for non-agricultural purposes. The Dunleer catchment (53° 50′ 6″ N, 6° 23′ 46″ W) is situated west of Dunleer in County Louth. It is 948 ha in area, 50% of which is grass and 33% is tillage, and the remainder of which is used for woodland and non-agricultural purposes. The urban site is a drain running through a golf course located in the north-west of Ireland. The golf course is a parkland course, which is 46.5 ha in area. Due to a confidentiality agreement, further details on its location are not disclosed.

5.2.2 Identification of monitoring locations and interventions used

High-risk locations for pollution impact potential were identified at the agricultural catchment sites, based on an online EPA geographical information system (GIS) application that contains information on flow delivery paths and entry points for phosphorus (https://gis.epa.ie/EPAMaps). From these delivery paths and points, optimal locations for the placement of the interventions were selected following visual inspection and taking cognisance of physical accessibility and willingness

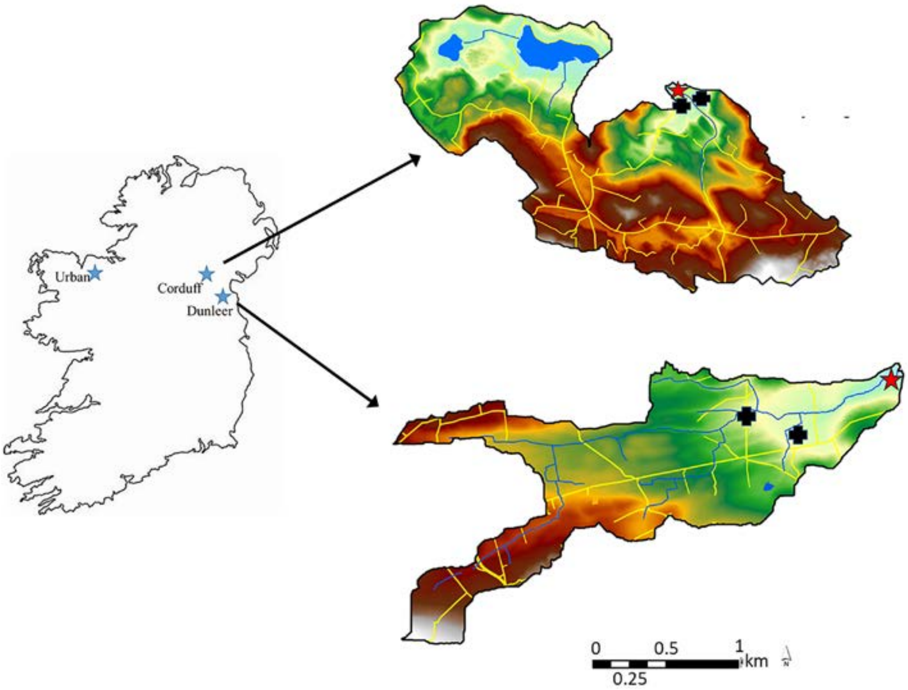


Figure 5.1. Map of Ireland showing the location of the three sampling sites with blue stars. The outlet points at the two agricultural catchments are denoted with red stars, while the locations of the interventions in year 2 are marked with black crosses.

of the farmers to grant access. Two locations were selected for Corduff and Dunleer: in both cases, these locations included a main stream and a tributary upstream (*c*.200 m and *c*.1000 m, respectively) of the outlet. One location within the drain, *c*.10 m upstream of the outlet, was used in the urban site.

Two configurations of interventions were investigated at each study site. Both configurations used CAC (Nova-Q, Ireland), sieved to a particle size of >2 mm. CAC has been demonstrated to have a comparable, or even better, adsorption capacity for herbicides than GAC (John McGinley, University of Galway, unpublished data). One configuration used filter bags (2-mm netted 400-g bags, 100 cm × 40 cm) containing 16 kg of CAC (hereafter referred to as "filter bags"). The second configuration used the same filter bags, but in this case they were filled with 12 kg of sieved CAC and fitted into a polyethylene pipe (0.3 m wide × 0.8 m long) so that they filled the full diameter of the centre section (0.4 m) of the pipe (hereafter referred to as the "filter pipe") (Figure 5.2). At each intervention site, three staggered filter bags were placed perpendicular to the flow of the water,

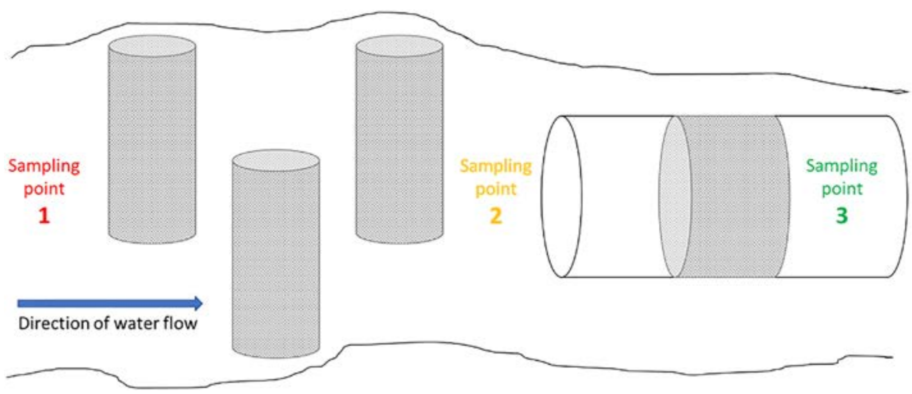


Figure 5.2. Schematic of different configurations of the intervention positioned in the stream. The blue arrow indicates direction of water flow. The three filter bags are upstream from the filter pipe. Sampling points, colour coded, are also indicated on the diagram.

to maximise contact of the media with the water but not cause flooding (Figure 5.2). Just downstream of the filter bags, the filter pipe was placed in line with the flow of the water, so an aliquot of water passed through the filter.

5.2.3 Herbicide sampling and analysis

Herbicide sampling was carried out using Chemcatcher passive sampling devices that were placed in the water, in duplicate, for 2-week periods. For both years 1 (2021) and 2 (2022), monthly herbicide sampling was conducted at the outlet of each of the three sites from April to October. In year 2, additional monthly herbicide sampling was undertaken to assess the efficiency of the two intervention configurations at three sampling locations: (1) immediately (< 1 m) upstream of the filter bag interventions (sampling point 1 (red) in Figure 5.2), (2) between the filter bags and the filter pipe (sampling point 2 (yellow) in Figure 5.2) and (3) within the filter pipe (sampling point 3 (green) in Figure 5.2), downstream of the adsorbent. This allowed for the determination of herbicide removal by each of the intervention configurations independently, where the concentration difference between sampling

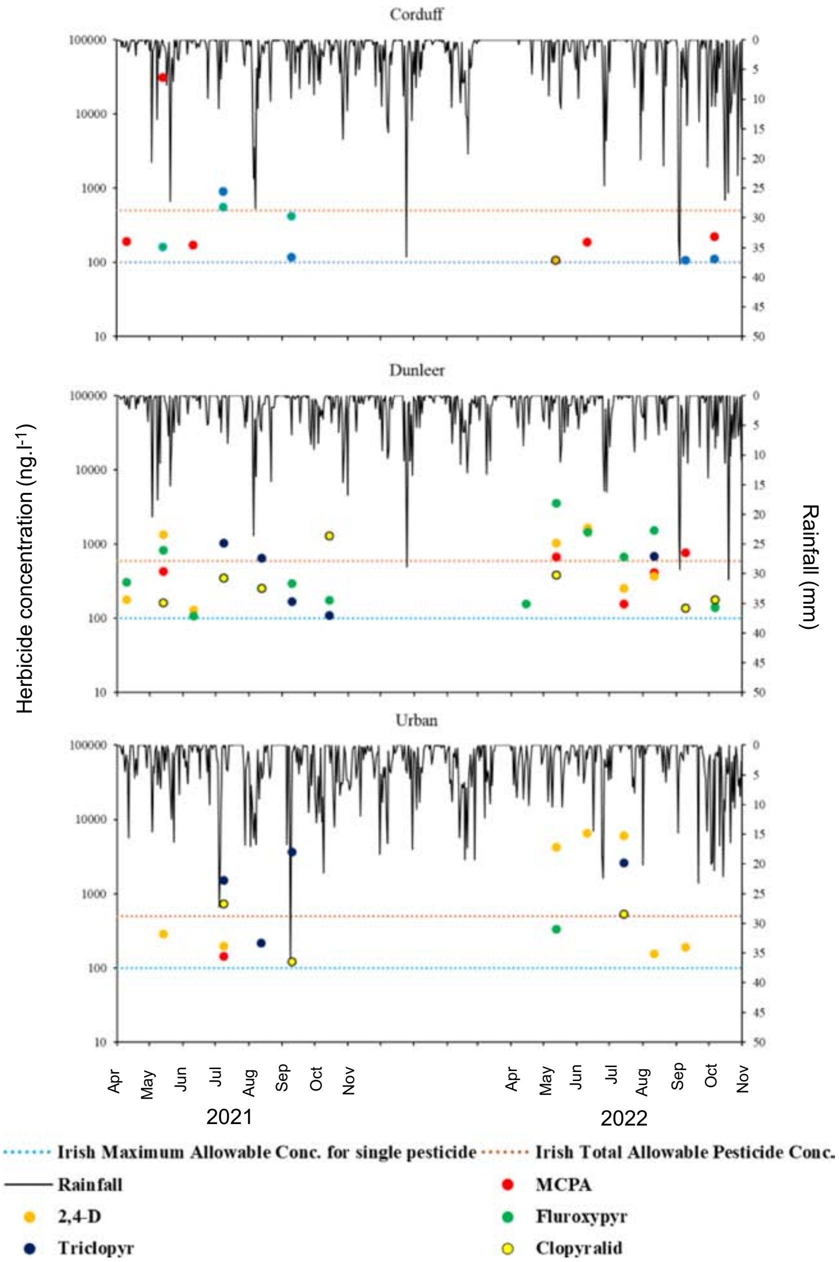


Figure 5.3. Exceedances of herbicides at outlet points in Corduff, Dunleer and urban sampling areas for year 1 (2021) and year 2 (2022) of the study.

points 1 and 2 indicated removal by the filter bags, and the difference between sampling points 2 and 3 indicated removal by the filter pipe.

5.3 Results and Discussion

5.3.1 Outlet monitoring

In total, 298 detections of individual herbicides were recorded across all three outlets, of which 131 were over the parametric value of 100 ng l^{-1} (EU, 2021). The parametric value of 500 ng l^{-1} (EU, 2021) for total cumulative herbicides was exceeded on 38 occasions. At the three sites, the herbicide exceedances at the outlets over both years were, from highest to lowest, fluroxypyr ($n = 34$), 2,4-D ($n = 29$), triclopyr ($n = 27$), MCPA ($n = 24$) and clopyralid ($n = 18$). Figure 5.3 shows the exceedances at the outlets, as well as the rainfall over the 2-year sampling period. The values shown are the averages of the levels recorded by the two devices placed in the water each month at the outlets. The majority of the exceedances occurred during April to June of each year, with several also observed in early autumn (September/October). This corresponds with the application times for herbicides, which typically occur in early to mid-spring of each year, when there is rapid growth of weeds, and in early autumn, at which point weeds are transporting food from their foliage to their roots in preparation for winter.

5.3.2 Herbicide removal by filter bag configuration

Figure 5.4 shows the herbicide concentrations detected before and after the filter bags at each site, thereby indicating the ability of the filter bags to

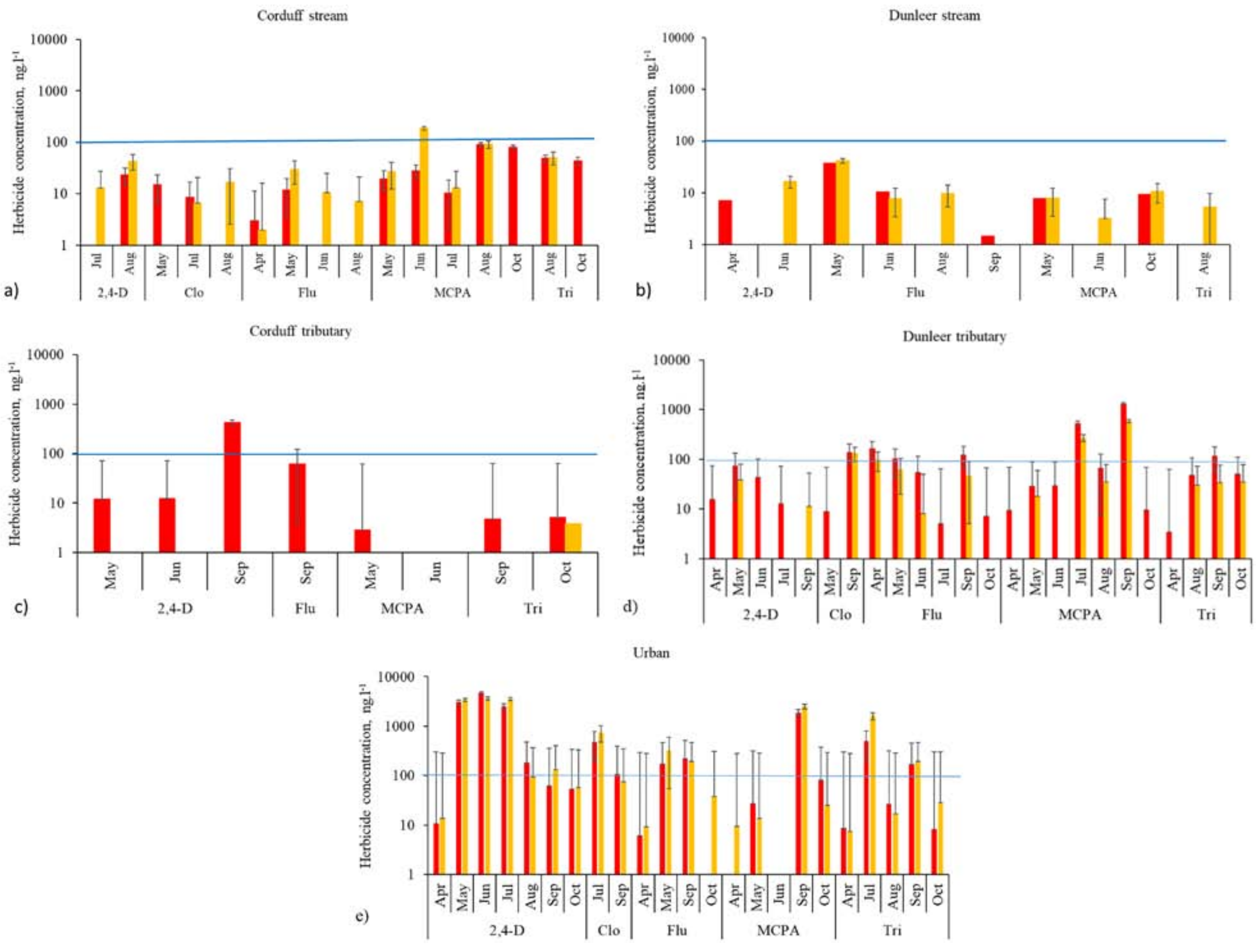


Figure 5.4. Herbicide concentrations detected before and after filter bag interventions across all sampling areas. Red columns indicate herbicide concentrations before the filter bag interventions and yellow columns indicate herbicide concentrations after the filter bag interventions. Average values from the two Chemcatchers have been displayed for each monthly detection. Error bars show standard errors, where $n = 2$. The blue line is the maximum allowable concentration for individual pesticides in drinking water (100 ng l^{-1}). Clo, clopyralid; Flu, fluroxypyr; Tri, triclopyr.

remove the herbicides investigated. Table 5.1 shows the performance data from the interventions. The values shown are the averages of the values recorded by the two devices placed in the water each month at the various sampling points. In the Corduff stream, there were 20 detections of herbicides and one exceedance before the filter bags, compared with 22 detections of herbicides and three exceedances after the filter bags, while, in the Dunleer stream, there were 12 detections of herbicides and no exceedances before the filter bags, compared with 15 detections of herbicides and no exceedances after the filter bags. In the majority of samples from the Corduff and Dunleer streams, the concentrations of herbicides before the filter bags were less than the parametric value of 100 ng l^{-1} (Figure 5.4a,b). Overall, in the two streams, there was a slight, but not statistically significant ($p > 0.05$), decrease in the average concentrations detected after the filter bags, with a reduction of 24% and 17% in the Corduff and Dunleer streams, respectively, across all measured herbicides. Incomplete removal of the herbicides was probably due to the wide body of water (> 1 m in width) in both streams, which meant that a single filter bag could not span the stream. Although the three filter bags were put in staggered positions, there was still room for the water to flow around the filter bags, rather than passing through the adsorbent material. This ability to circumvent the filter bags could account for the incomplete removal of herbicides by this configuration.

In the Corduff tributary, there were nine detections of herbicides and two exceedances before the filter bags compared with three detections of herbicides and no exceedances after the filter bags (Table 5.1). There was a complete removal of 2,4-D from an average concentration of 422.6 ng l^{-1} before the filter bag (Figure 5.4c), indicating that the CAC adsorbent was capable of dealing with incoming herbicide concentrations up to 500 ng l^{-1}. Two possible reasons for this complete removal were (1) the low level of water that was present in the tributary, with the level of water never rising to more than 0.15 m over the base of the stream from April to October, and (2) the fact that the tributary was also only 0.40 m wide at its widest point, so the bag interventions completely filled the path of the stream, thereby forcing the polluted

Table 5.1. Performance data for interventions in Corduff, Dunleer and urban sampling areas for year 1 (2021) and year 2 (2022) of the study

Site location	Filter bag		Filter pipe	
	Before intervention	After intervention	Before intervention	After intervention
Corduff stream				
No. of detections	20	22	22	9
No. of detections > 100 ng l^{-1}	1	3	3	0
Average concentrations (ng l^{-1})	39.3	34.7	34.7	13.7
Corduff tributary				
No. of detections	9	3	3	2
No. of detections > 100 ng l^{-1}	2	0	0	0
Average concentrations (ng l^{-1})	82.5	3.1	3.1	1.5
Dunleer stream				
No. of detections	12	15	15	3
No. of detections > 100 ng l^{-1}	0	0	0	0
Average concentrations (ng l^{-1})	11.6	14.5	14.5	4.6
Dunleer tributary				
No. of detections	48	31	31	10
No. of detections > 100 ng l^{-1}	13	6	6	2
Average concentrations (ng l^{-1})	101.0	83.3	83.3	18.8
Urban				
No. of detections	47	46	46	30
No. of detections > 100 ng l^{-1}	21	18	18	15
Average concentrations (ng l^{-1})	428.3	517.4	517.4	325.1

water through the CAC-filled bags and allowing time for the adsorption of the herbicides to occur.

In the Dunleer tributary, the number of detections before the filter bags was 48, of which 13 were exceedances, while after the bags there were 31 detections and six exceedances (Table 5.1). At the Dunleer tributary, while the number of exceedances decreased by only nine, the filter bags were effective for herbicide removal (an average reduction across all observed herbicides in this study of 67.1%; Figure 5.4d), with either minimal concentrations of or no herbicides detected after the bags on the majority of occasions ($p > 0.05$). However, for MCPA in July and September, the incoming concentrations of 536.8 ng l^{-1} and 1334 ng l^{-1}, respectively, were reduced to only 270.1 ng l^{-1} and 593.7 ng l^{-1}, respectively, which are considerably above the parametric value of 100 ng l^{-1}. This would suggest that the CAC adsorbent does not have the capacity to deal with very high concentrations of herbicides in waterways. The Dunleer tributary was slow moving and the filter bags were able to almost completely span the width of the waterway, with only a few centimetres on either side available for the water to circumvent the filter bags.

The number of herbicide detections in the urban area before the filter bags was 47, of which 21 were exceedances, while after the bags there were 46 detections and 18 exceedances (Table 5.1). Across all herbicides measured in the urban area, there was no significant difference ($p > 0.05$) between the concentrations of herbicides detected before and after the filter bags (Figure 5.4e). The water was slow moving, which would help the removal of herbicides by the treatment system. However, the drain was > 1 m in depth, and the water level was consistently > 0.5 m, even during the summer months. This reduced the amount of water that was passing through the filter bags and making contact with the CAC material. Overall, the filter bags reduced the exceedances from $n = 50$ to $n = 38$ in all three water bodies (McGinley *et al.*, 2024).

5.3.3 Herbicide removal by filter pipe configuration

Figure 5.5 shows the concentrations of herbicides detected before and after the filter pipes at each site, indicating the ability of the filter pipe to remove the herbicides under investigation. The values shown are the averages of the values recorded by the two devices placed in the water each month at the various sampling points. In the Corduff stream, there were 22 detections of herbicides before the filter pipes, of which three were exceedances, which decreased to nine detections and no exceedances after the filter pipes, while, in the Dunleer stream, there were 15 detections and no exceedances before the filter pipes and only three detections and no exceedances after the filter pipes (Table 5.1). Overall, in the two streams, there was a large, statistically significant ($p < 0.05$), decrease in the concentrations of herbicides, with an average reduction of 83% and 88% in the Corduff and Dunleer streams, respectively, across the herbicides measured (Figure 5.5a,b).

In the Corduff tributary, only three detections were measured before the pipe, while two were measured after the pipe (Table 5.1). None of these detections was above the parametric value. In the Dunleer tributary, there were 31 detections of herbicides before the pipe, of which six were exceedances, while there were only 10 detections and two exceedances after the filter pipe (Table 5.1). The filter pipes greatly reduced the herbicide concentrations in the Dunleer tributary ($p < 0.05$), with an average reduction of 64% (Figure 5.5d). The herbicide concentrations before the filter pipe ranged from 8.1 to 593.7 ng l^{-1} and after the filter pipe from below the limit of detection (LOD) to 216.7 ng l^{-1}. In September, the pipe was moved from its original position by the force of the water coming down the tributary as a result of heavy prolonged rainfall earlier that month, so no readings were obtained after the pipe for that month.

At the urban site, the number of herbicide detections decreased from 46 to 30, while the number of exceedances decreased from 18 to 15, after the filter pipes (Table 5.1). There was a decrease in concentrations detected ($p > 0.05$) after the filter pipe, with an average reduction of 47% (no herbicides were detected after the filter pipe on several occasions; Figure 5.5e). The herbicide concentrations varied from 7.5 to 3645 ng l^{-1} before the filter pipe to between below the LOD and 5503 ng l^{-1} after the pipe. When the concentrations of the herbicides were greater than 3000 ng l^{-1}, the filter pipe was unable to reduce the concentration to below the parametric value (Figure 5.5e).

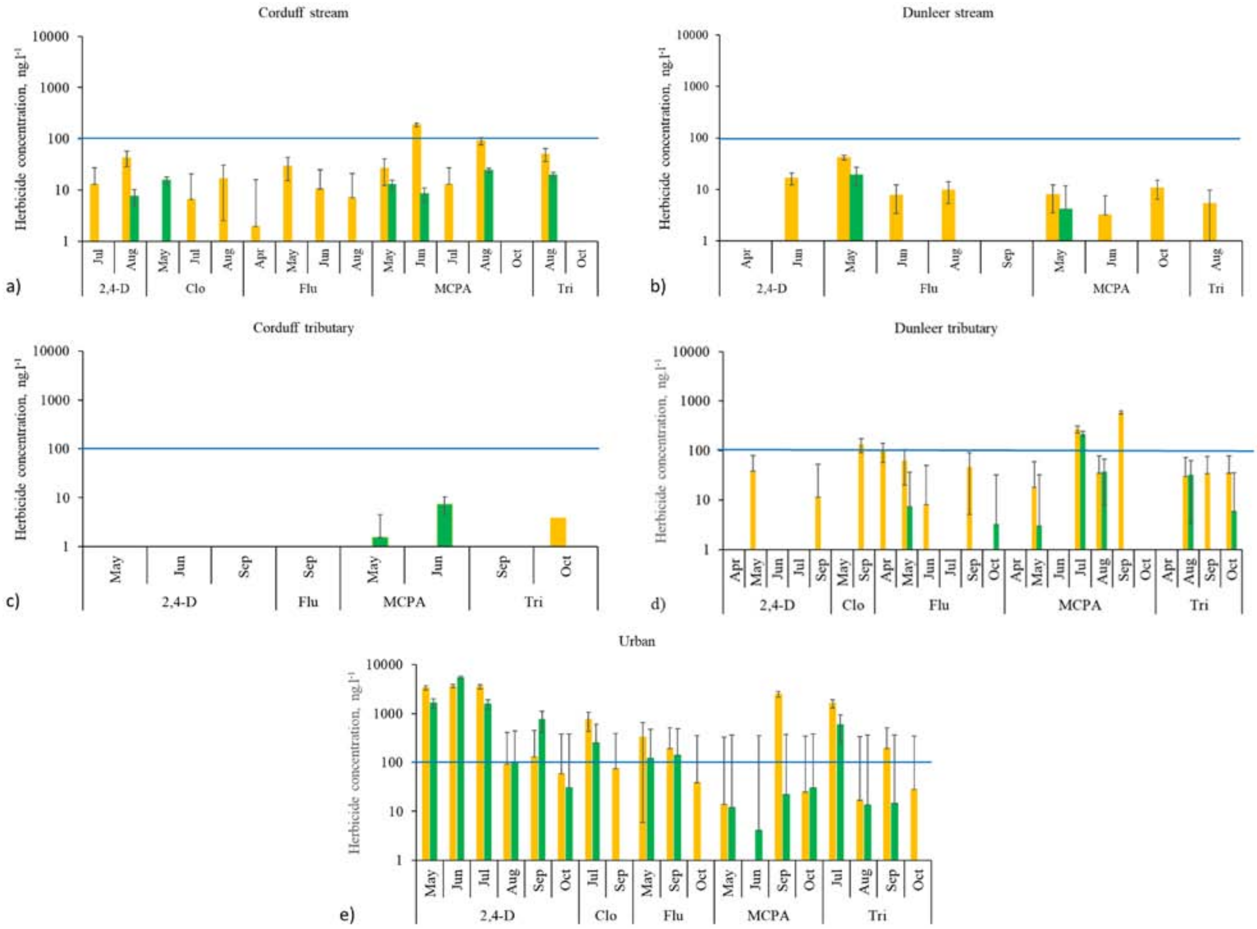


Figure 5.5. Herbicide concentrations detected before and after filter pipe interventions across all sampling areas. Yellow columns indicate herbicide concentrations before the filter pipe interventions and green columns indicate herbicide concentrations after the filter pipe interventions. Average values from the two Chemcatchers have been displayed for each monthly detection. Error bars show standard errors, where $n = 2$. The blue line is the maximum allowable concentration for individual pesticides in drinking water (100 ng l^{-1}). Clo, clopyralid; Flu, fluroxypyr; Tri, triclopyr.

5.4 Conclusions

This study showed that herbicides are present in high concentrations (frequently above the parametric value for drinking water) in two agricultural catchments and one urban area in Ireland, and that the highest concentrations were detected mainly in April to June and September/October, corresponding to the application times for these herbicides. Two different CAC-based *in situ* remediation systems, filter bags and filter pipes, capable of herbicide removal close to the source of contamination, were designed and installed at the agricultural catchment areas and the urban area. Both systems operated effectively when the water flow in the waterways was slow, which allowed time for the adsorption of the herbicides to occur. The reduction in herbicide concentrations was better for the filter pipes than for the filter bags ($p < 0.05$).

6 Investigation into Surface and Subsurface Pathways of Pesticide Loss

6.1 Overview

Herbicides such as MCPA and clopyralid are commonly used in Ireland for the control of weeds in agricultural settings. They are highly water-soluble members of the chlorophenoxy herbicide group, used abundantly in agriculture and horticulture, and operate by disrupting the growth of plants. Following land application, there is a risk of their transmission to surface waters via run-off and/or leaching, and both MCPA and clopyralid were regularly detected in our catchment monitoring programme (Chapter 5). MCPA is the most frequently detected pesticide within Irish drinking water supply zones, accounting for 75% of individual pesticide exceedances (Atcheson *et al.*, 2022), while clopyralid is the fourth most detected pesticide in similar settings (McGinley *et al.*, 2023). This study aimed to assess the pathway of loss of MCPA and clopyralid to the environment, and to determine if a half-dose application would affect run-off and/or leaching.

6.2 Materials and Methods

6.2.1 *Run-off: rainfall simulation study*

Intact soil sods of a high clay mineral soil from mixed permanent grassland were collected from a drystock farm located in Killorglin, County Kerry. The soil had an organic matter (OM) content of 3.4% and a pH of 4.7. The intact sods were trimmed to fit aluminium flumes, measuring 1 m long, 0.25 m wide and 0.05 m deep. Any gaps between sods or the edges of the flumes were sealed with melted paraffin wax to prevent preferential flow pathways other than surface run-off. The flumes were designed to allow collection of run-off into sampling containers during a rainfall event.

Either MCPA (pK_a 3.07) or clopyralid (pK_a 2.01) was applied to triplicate flumes using two potential dosing strategies – a single full-strength dose (equivalent to 13.5 kg MCPA ha^{-1} or 2 kg clopyralid ha^{-1}) or two half-strength doses (equivalent to 6.75 kg MCPA ha^{-1} or 1 kg clopyralid ha^{-1}) spaced 42 days apart, termed “full-dose” and “half-dose”, respectively. The doses selected were 10 times the recommended pesticide application, to ensure detection of the pesticide in the run-off. Soil flumes with no pesticide application were used as controls. During rainfall sampling, the flumes were placed in a rainfall simulator at a slope of 6°, similar to the natural slope of Irish agricultural topography (Gonzalez Jimenez *et al.*, 2023). The simulator was calibrated to achieve an intensity of 10.2 ± 0.1 mm h^{-1} and a droplet impact energy of 260 kJ mm^{-1} h^{-1} at 90% uniformity. This intensity was within the mid-range of the annual rainfall amounts in Ireland (Troy *et al.*, 2013). Each rainfall event lasted 30 min, during which water samples were collected in 10-min intervals at 10 min, 20 min and 30 min. The water volumes were recorded and subsamples taken for pesticide analysis immediately after each event. Rainfall sampling was carried out for all flumes at six time points following the first pesticide application: at 48 hours, 7 days, 21 days, 44 days (corresponding to 48 hours after the second pesticide application), 49 days (corresponding to 7 days after the second pesticide application) and 63 days (corresponding to 21 days after the second pesticide application). Pesticide analysis was undertaken by TelLabs, using high-performance liquid chromatography with UV detectors (HPLC-UV).

6.2.2 *Leaching: column study*

Soil samples were collected from two sites consisting of mixed permanent grassland located in Killorglin, County Kerry. The sites selected consisted of one high clay mineral soil and one high clay organo-mineral soil. Soil was collected from 5 cm to 50 cm, air dried and sieved to 2 mm. Columns (ø 10 cm, height 40 cm) with a perforated base were filled with 5 cm gravel on the bottom, and 30 cm soil, which was packed in 5-cm increments. Columns were maintained at 10°C in a temperature-controlled room for the remainder of the study, with an application of 80 ml of ultrapure water twice per week to simulate typical rainfall. This is in line with previously published methodology used in the laboratory (González Jimenez *et al.*, 2023; Healy *et al.*, 2023). Over the duration of the study, the columns were exposed to a daily photoperiod of 12 hours of light and 12 hours of dark using Spectron T8 LED 1.5 m GB tubes with a light intensity range of 130–180 μmol m^{-2} s^{-1}. Columns acclimated for 10 weeks and were seeded with perennial ryegrass at 14 kg ha^{-1}, which was maintained by cutting to 4 cm every 21 days. MCPA and clopyralid were applied to columns in triplicate 6 and 12 weeks after seeding using two dosing strategies – a single full-strength application (equivalent to 13.5 kg MCPA ha^{-1} or 2 kg clopyralid ha^{-1}) or two half-strength applications (equivalent to 6.75 kg MCPA ha^{-1} or 1 kg clopyralid ha^{-1}) spaced 6 weeks apart, termed "full-dose" and "half-dose", respectively. The application rates selected were 10 times the recommended pesticide application rate, to ensure detection of the pesticide in the leachate and to examine the impact of excessive application rates. Triplicate grassed columns with no pesticide application were used as controls. Leachate samples were collected in weeks 1, 2, 3, 4, 6, 7, 8, 9, 10, 12 and 16 after pesticide application. The volume of each water sample collected was recorded. A 50-ml subsample was taken and filtered through a 0.45-μm filter to remove any particulate matter. Pesticide analysis was undertaken by TelLabs, using HPLC-UV.

6.3 Results and Discussion

6.3.1 Run-off: rainfall simulation study

The flow-weighted mean concentrations of MCPA and clopyralid in the surface run-off were highest immediately after the initial application and decreased in subsequent rainfall events. Both herbicides, for both full- and half-dose applications, were below the LOD (0.1 μg l^{-1} for MCPA and 0.45 μg l^{-1} for clopyralid) at 44 days. For the full-dose applications, the concentration in the run-off was more than double that of the half-dose application (Figure 6.1), and no herbicides were detected following the second of the half-dose applications. These results indicate that the environmental impacts of MCPA and clopyralid loss via run-off may be reduced by splitting herbicide applications.

6.3.2 Leaching: column study

A single dose of clopyralid demonstrated the greatest risk for pesticide loss via leaching for both soil types (Figures 6.2 and 6.3). For the mineral soil, the pesticides leached through within 1 week of their

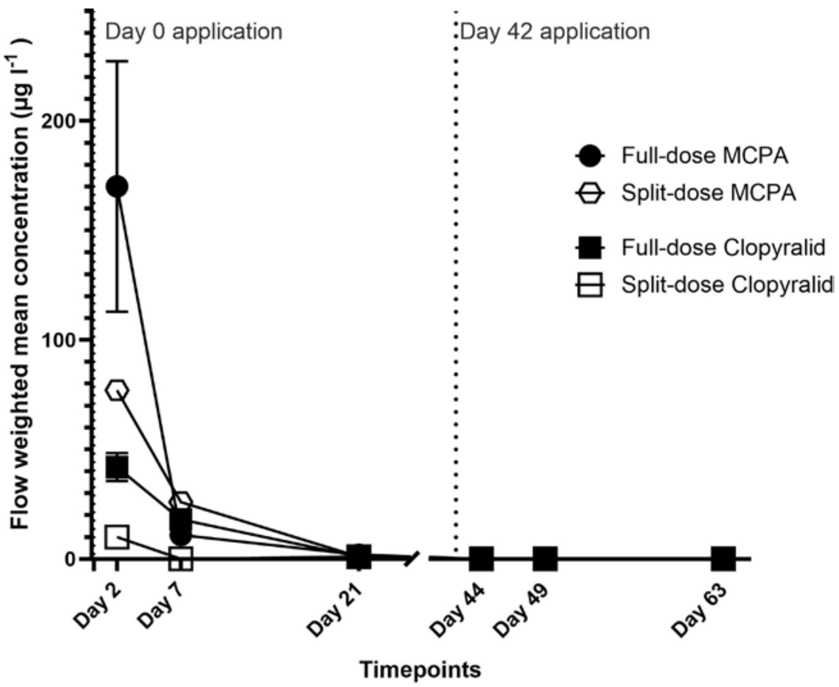


Figure 6.1. Flow-weighted concentrations of surface run-off (μg l^{-1}), detecting MCPA and clopyralid over 63 days, graphed with standard deviation error bars. Pesticide applications were carried out on days 2 and 42.

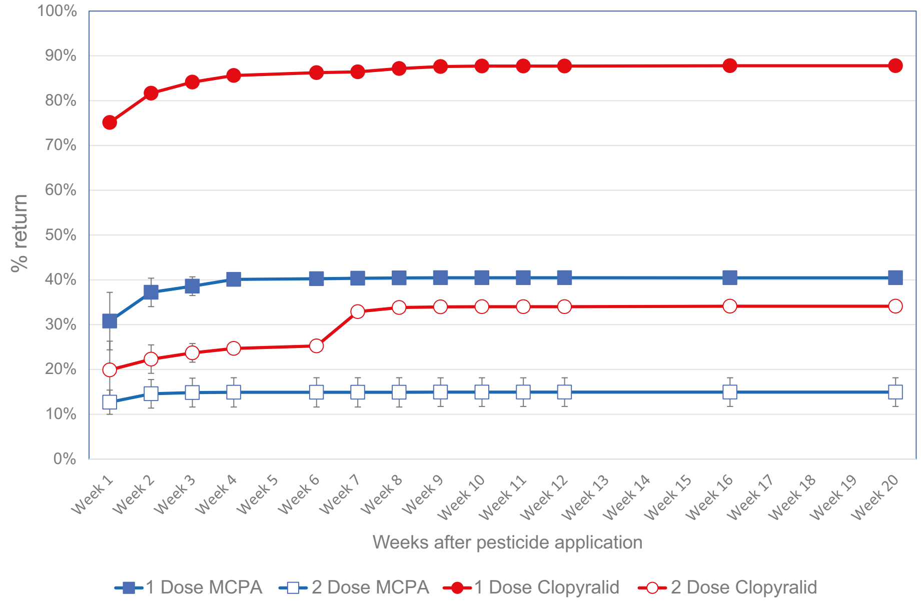


Figure 6.2. Cumulative MCPA and clopyralid percentage return in mineral soil leachate over a period of 20 weeks after application. Error bars denote standard deviations. Pesticides were applied in weeks 0 and 6.

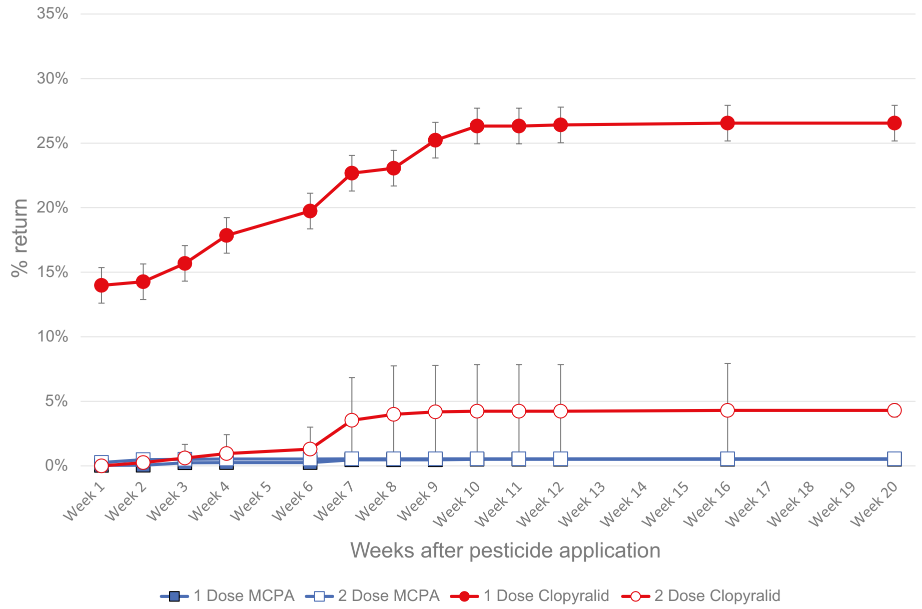


Figure 6.3. Cumulative MCPA and clopyralid percentage return in organo-mineral soil leachate over a period of 20 weeks after application. Error bars denote standard deviations. Pesticides were applied in weeks 0 and 6.

application (Figure 6.2), and the total amount leached was between 15% and 88%, depending on the treatment (Figure 6.2). With respect to the organo-mineral soil, leaching of the full-strength clopyralid dose was more prolonged, over a continual period of 10 weeks (Figure 6.3). Overall, lower concentrations of pesticides leached through the organo-mineral soil, particularly in the case of MCPA, where less than 1% of the applied pesticide was recovered in the leachate. Interestingly, regardless of the specific pesticide or soil type, a single full-strength pesticide application consistently resulted in a concentration of pesticide being recovered in the leachate that was greater than two half-strength pesticide applications. For example, the total amount of clopyralid leached through the organo-mineral soil was more than five times higher when applied as a single dose than as two half-strength doses. The rate of retention of clopyralid or MCPA within columns containing either soil type was low: less than 0.10 mg pesticide kg^{-1} dry matter.

6.4 Conclusions

The findings of this study demonstrate that splitting a pesticide application into two half-doses, spaced 6 weeks apart, results in a lower level of pesticide being lost to the environment, via either surface run-off or leaching. This approach may be of particular benefit in mineral soils, where up to 90% of applied clopyralid was leached and could pose a risk to groundwater, and therefore potentially drinking water, sources. However, it is acknowledged that a highly exaggerated dose rate was used in these experiments, so risk to groundwater may be lower under normal dosing regimes. The results also show that, for mineral soils, MCPA is more likely to be lost to the environment by surface run-off, while clopyralid is more likely to leach through soils. Split herbicide applications have previously been shown to be more effective for weed management than single applications. The findings of this study further support the use of this management strategy by demonstrating that split applications could also reduce unintentional environmental risks and impact.

7 Quantitative Modelling of Pesticide Risk in Irish Drinking Water

7.1 Introduction

As discussed in Chapter 1, pesticides can be transported to water bodies through a number of pathways, and the resulting exposure to pesticides in drinking water may result in negative health outcomes (Kalyabina *et al*., 2021). In response to the potential risk, pesticide regulations concerning the placing of plant protection products on the market (e.g. EU, 2009b) were put in place, requiring comprehensive risk assessments that quantify both the level of exposure and the sensitivity of a population to that level of exposure (Nienstedt *et al*., 2012). Such legislation sets out a multi-stage process for the evaluation and classification of pesticide risks, including data collection, risk screening, risk assessment and risk reduction (Fargnoli *et al*., 2019). This chapter is structured to follow this process by first developing a framework for screening 130 commonly used pesticides in Ireland to identify pesticides of concern (section 7.2; Harmon O'Driscoll *et al*., 2022). From this initial screening process, 15 pesticides of concern were selected for detailed risk assessment, based on their high levels of use, mobility and human toxicity. The detailed assessment consisted of two parts: first, a probabilistic model was developed to quantify the concentrations of pesticides in Irish surface water and groundwater (section 7.3), and then the levels of potential risk to adult and child populations posed by the predicted concentrations were assessed (section 7.4).

7.2 Preliminary Risk Screening

Risk screening is the first step in pesticide risk assessment. It uses qualitative or semi-quantitative risk scoring to identify pesticides of concern, without the need for the considerable resources and time associated with full risk assessments (Baptista *et al*., 2012), and enables the efficient allocation of resources to targeted risk assessments of pesticides identified as high risk (Vryzas *et al*., 2020). Various risk-screening methods and tools exist (Dabrowski *et al*., 2014; Kudsk *et al*., 2018; Choi *et al*., 2020); however, their ability to compare pesticide risks effectively and reliably is limited by factors such as a reliance on pesticide physico-chemical properties to assess mobility, the use of animal health indicators to represent human health risk and the exclusion of metabolites. The aim of this study was to develop an easy-to-use risk-screening tool that builds on existing literature to address these limitations by (1) combining information on pesticide properties and soil characteristics to enable a detailed evaluation of pesticide mobility; (2) assessing the health impacts of pesticides, focusing on evidence of chronic health effects in place of pesticide reference doses; and (3) including information on the risks associated with a pesticide's metabolites. This tool can then be implemented by pesticide users, farm advisors and other stakeholders to screen for high-risk pesticides at a local level or to help catchment managers identify pesticides that may need to be assessed in more detail. The use of the methodology developed was illustrated by applying it to a specific Irish case study.

7.2.1 Methodology

For brevity, the methodology employed in this framework is summarised below; however, a more detailed discussion of the methodology and the development of the scoring system can be found in Harmon O'Driscoll *et al*. (2022). In brief, the framework of the risk-ranking methodology presented in Figure 7.1 comprises three main stages – (1) calculation of the likelihood of exposure score, (2) calculation of the consequence of exposure score and (3) incorporation of metabolite data – with hazard scores being calculated after these steps have been carried out. Data used in scoring each of these steps were obtained from European Food Safety Authority pesticide conclusions or in the case of missing data from the Pesticide Properties DataBase. The likelihood of exposure was evaluated for both groundwater and surface water by scoring the persistence and mobility of each pesticide. These scores were then combined to assess an overall likelihood of exposure score. Users can incorporate the percentage of

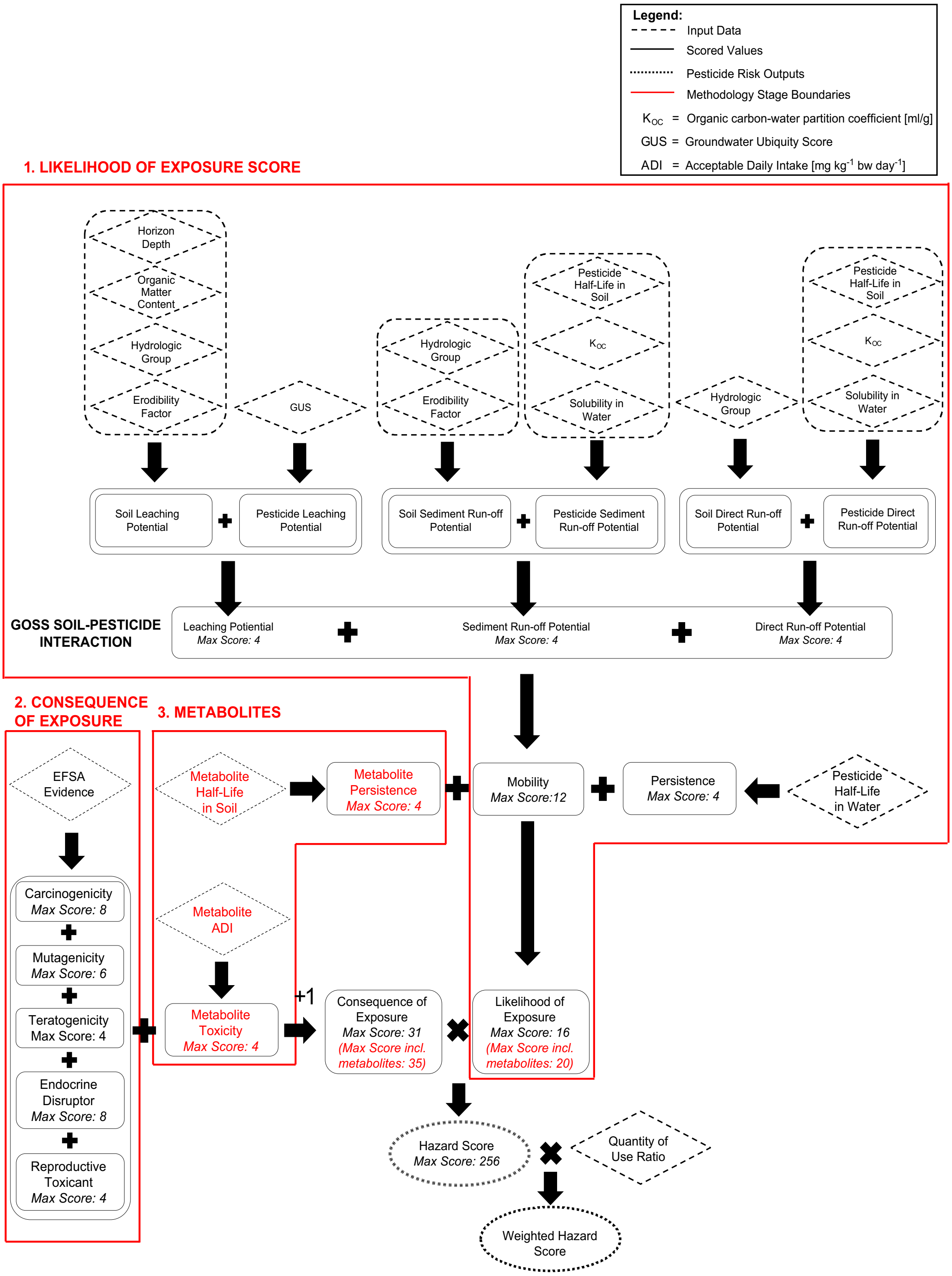


Figure 7.1. Risk-ranking methodology.

drinking water drawn from the two different sources into this likelihood of exposure score using a ratio to reflect the local sources of drinking water. The consequence of exposure was calculated as the sum of the potential chronic health effect scores, weighted by the perceived severity of the health effects. The likelihood and consequence of exposure scores were then multiplied to calculate a hazard score. Finally, the quantity-weighted hazard was determined by expressing the hazard score as a function of the quantity of use for each pesticide in relation to overall pesticide use over the period of investigation. This framework was employed for two of the PestMan study sites, Cregduff and Dunleer, to illustrate the application of the framework and how site conditions can affect pesticide risk. The pesticides considered in this study were selected based on national usage data available for the most recently published years, 2016 and 2017, from the Department of Agriculture, Food and the Marine (DAFM, 2016, 2017). A total of 130 pesticides were used on grassland, fodder and arable crops over this period. A number of pesticides were excluded from assessment based on a minimal quantity of use (1000 kg per annum; Dabrowskie *et al*., 2014) or because they had been withdrawn from the EU market at the time of the analysis.

7.2.2 Results and discussion

The likelihood and consequence of exposure scores of the 25 most used pesticides in Ireland are presented in Figure 7.2, where the size of the bubble is proportional to the value of the score. This analysis was carried out using national pesticide data but with site-specific data being used for the two study sites to highlight how pesticide properties and site conditions may interact and affect overall pesticide hazards. The differing locations of the pesticide bubbles in the two plots highlights how site conditions can affect pesticide mobility, with Dunleer having predominantly poorly draining soils and high run-off potential compared with Cregduff; as a result, several pesticide bubbles are located closer to the top of the plot for Dunleer than for Cregduff. Three pesticides, glyphosate, chlormequat chloride and MCPA, account for almost 35% of pesticide use in Ireland. If quantity of use was the only measure of risk, these pesticides would be the greatest concern for Ireland. However, other pesticides were found to have higher likelihood of exposure scores (bubbles located along the top of the plot), such as prothioconazole, and/or higher consequence of exposure scores (bubbles positioned along the right of the plot), such as mancozeb, despite being used in smaller quantities. Pesticides with the highest risk potential would be associated with high likelihood of exposure and consequence of exposure scores and corresponding bubbles would therefore be located in the top-right corner of Figure 7.2. This highlights how pesticide risk cannot be determined based on quantity alone: the pesticides of greatest concern are those used in high quantities that are also highly mobile and highly toxic.

Figure 7.3 shows the top 15 pesticide hazard scores in Cregduff and Dunleer, and the top 15 quantity-weighted hazard scores in an Irish context. Based on hazard score alone, prochloraz and propyzamide are the pesticides of greatest concern in this study. However, some pesticides have relatively high hazard scores and are used in large quantities, namely mancozeb, 2,4-D and pendimethalin. As a result, these pesticides have the third, fourth and sixth highest quantity-weighted hazard scores, respectively (Figure 7.3). Hazard scores are useful for comparing the relative risk associated with pesticides at a site level prior to application, to select less risky pesticides. The quantity-weighted hazard score incorporates Irish national pesticide use quantity data obtained from pesticide surveys carried out by the Irish Department of Agriculture, Food and the Marine (DAFM, 2016, 2017) and therefore better represents the regional or national risk profile from actual pesticide use. Mancozeb was identified as the pesticide of greatest concern in terms of hazard score, and one of the pesticides of greatest concern on a national scale in terms of quantity-weighted hazard score; the EU has since not approved it for use (EU, 2020).

7.3 Probabilistic Modelling of Pesticide Transport to Water Supplies

The risk-screening analysis above facilitated the identification of 15 pesticides of concern from the 130 pesticides assessed (Harmon O'Driscoll *et al*., 2022). This section, together with section 7.4, describes the detailed health risk assessment of these 15 pesticides. To assess the health risks posed by these pesticides, the level of exposure must be quantified (Ross *et al*., 2015). Pesticide fate and transport models have been developed to assess exposure concentrations in water bodies as a more cost-effective alternative to monitoring programmes (Li and Niu, 2021). These range from simple transport indicators, such as depth to water, net recharge, aquifer media, soil media, topography, impact of the vadose zones media, and hydraulic conductivity of the aquifer (DRASTIC; Aller *et al*., 1985), and simple one-dimensional models, such as the simplified formula for indirect loading caused by run-off (SFIL; Trevisan *et al*., 2009), to complex, computational watershed models, such as the Soil Water Assessment Tool (SWAT; Arnold *et al*., 2012), PRZM (Suárez, 2005)

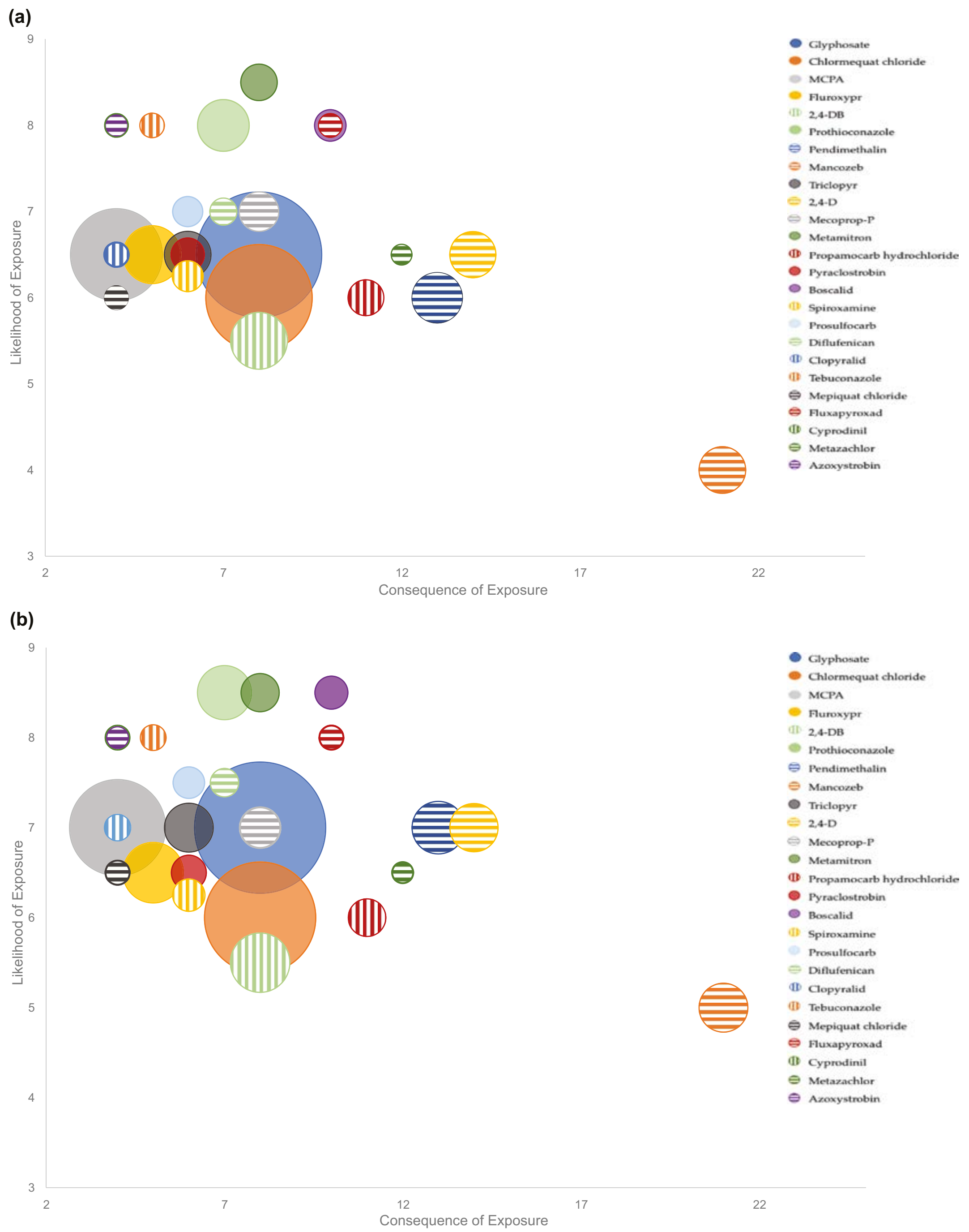


Figure 7.2. Likelihood of exposure vs consequence of exposure vs quantity of use in (a) Cregduff and (b) the Dunleer catchment for the 25 most used pesticides in Ireland. The area of each bubble is proportional to the corresponding pesticide's quantity of use (kg). Note: mancozeb and propamocarb hydrochloride have been removed from the Irish market since these data were collected.

and MACROpore flow (Stenemo and Jarvis, 2010). A major limitation of existing methods is their reliance on deterministic methods that rely on point estimates or average values as input parameters (Gagnon *et al.*, 2014). There is thus a recognised need for probabilistic models to account for uncertainty and variability in pesticide fate and environmental conditions (EFSA and BfR, 2019). A modelling framework was developed by adapting existing models to give a more realistic representation of environmental conditions, and then a probabilistic modelling approach was applied to better account for uncertainty in modelling and data.

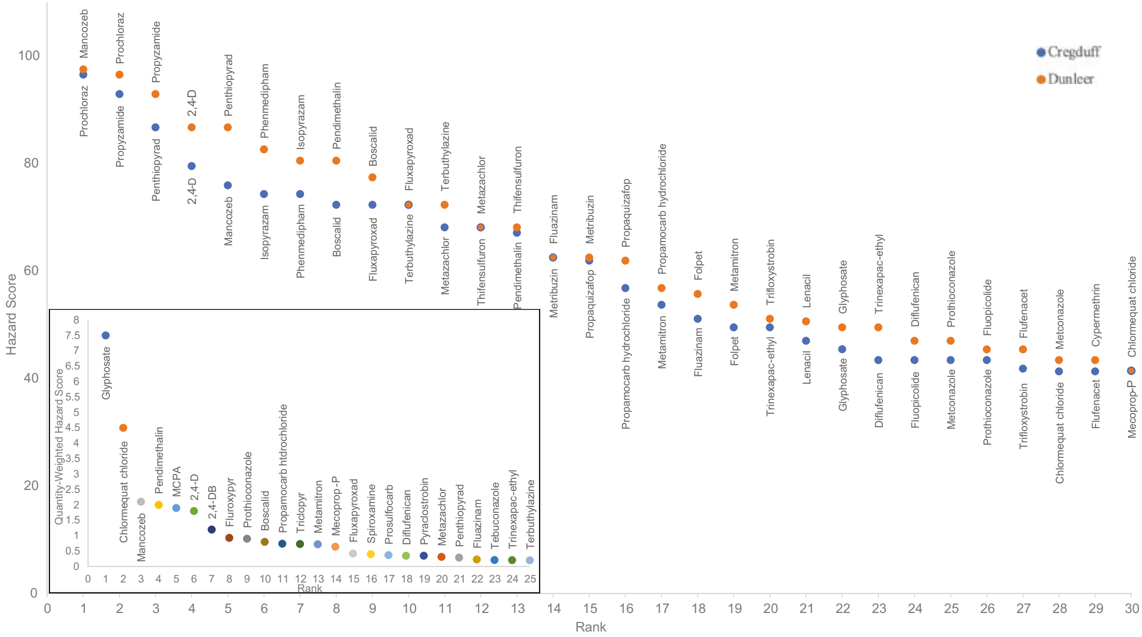
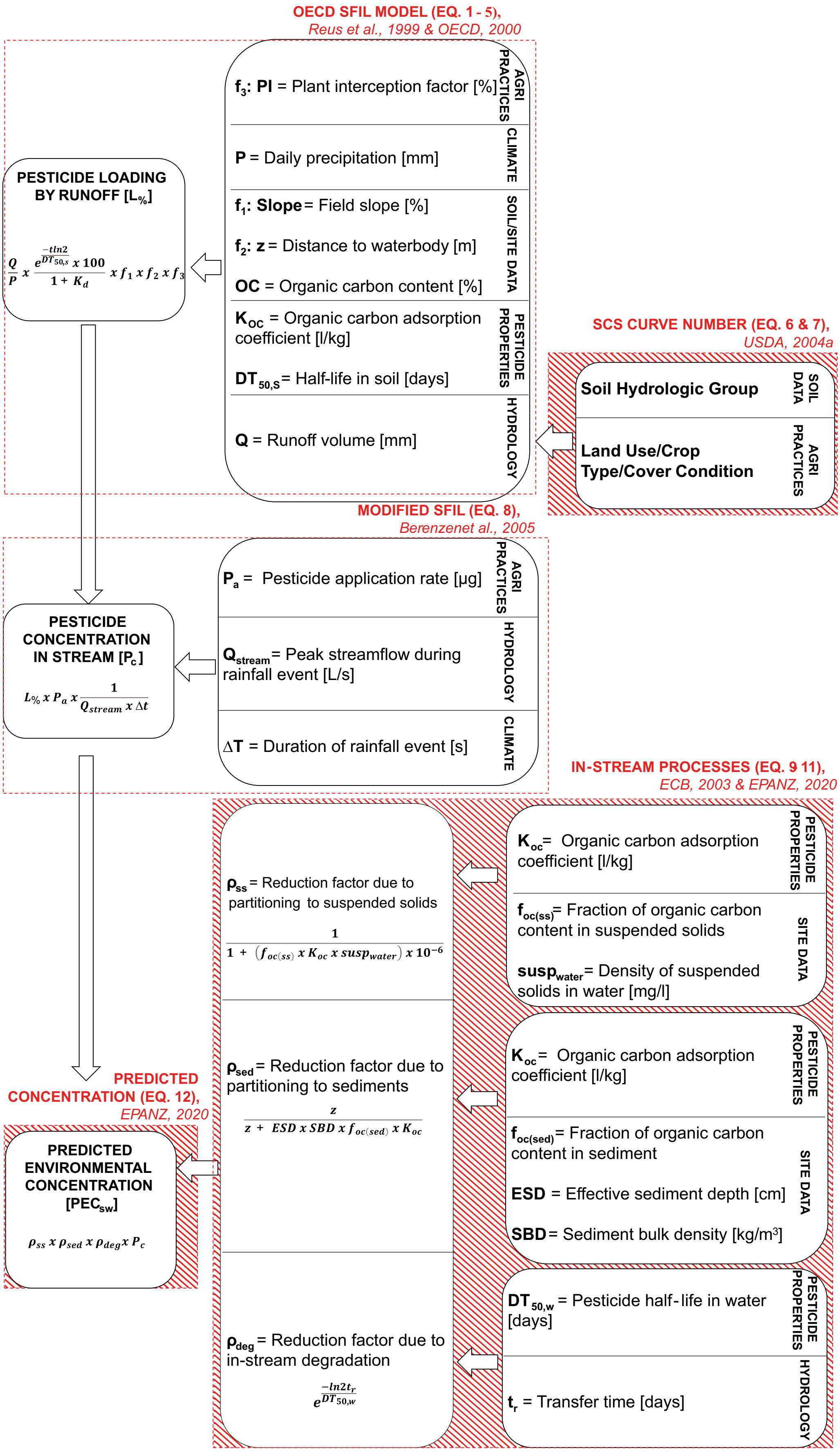


Figure 7.3. Top 15 pesticides of concern in the two study catchments, Cregduff and Dunleer. The inset shows the top 15 pesticides by quantity-weighted hazard score. Note: mancozeb and propamocarb hydrochloride have been removed from the Irish market since these data were collected.

7.3.1 Methodology

To develop a stochastic model to quantify pesticide concentrations, a detailed review of existing modelling approaches was carried out and several deterministic pesticide fate and transport models were examined for suitability for probabilistic modelling. Detailed discussion of this review is available in the supplementary information of Harmon O'Driscoll *et al*. (2024). The models were assessed based on the balance between accuracy, complexity, required parametrisation and the practicality of adapting the model to facilitate probabilistic analysis. The two models selected for this study – SFIL (Berenzen *et al*., 2005) and Leached Quantity Index (LQI) (Padovani *et al*., 2004; Trevisan *et al*., 2009) – allow for the incorporation of a range of factors that influence pesticide transport and facilitate estimation of actual exposure concentrations, unlike simple environmental indicators. Despite this, they require less data input and expert knowledge than more complex modelling software (Troldborg *et al*., 2022). Nonetheless, the models used herein are not without their own limitations. To address some of these limitations, additional pesticide processes were also integrated into the modelling framework to improve the representation of in-stream processes.

The theoretical model used to predict concentrations in surface water was adapted from Berenzen *et al*.'s (2005) modified SFIL (OECD, 2000, Annex 2). This model was further modified here: (1) the US Soil Conservation Service curve number method (USDA, 2004) was used to assess run-off volume as is the case for more complex software such as SWAT and PRZM, and (2) the reduction in in-stream concentrations due to in-stream processes that may take place before raw surface water is abstracted for water treatment were considered as suggested by the European Chemical Bureau (ECB, 2003) and modified by the New Zealand Environmental Protection Agency (EPANZ, 2018). Figure 7.4 details the framework applied for the surface run-off model. To evaluate contamination risks to groundwater supplies, the widely applied pesticide leaching model LQI (Trevisan *et al*., 2009) was selected for this study. Pesticide leaching risk was estimated using a combination of soil and hydrological conditions, pesticide properties and agricultural practices. The model developed was then applied to a hypothetical grassland site in the east of Ireland, representative of the dominant agricultural and soil conditions in Ireland, to assess pesticide concentrations in both surface water and groundwater under normal pesticide application conditions (see Table 7.1 for site details). As conventional water treatment processes do not effectively remove pesticides, and specific pesticide removal processes are not used within the Irish water treatment system (UE, 2021), it was assumed in this



$$L_{\%} = \frac{Q}{P} \times \frac{e^{\frac{-t\ln 2}{DT_{50,s}}} \times 100}{1 + K_d} \times f_1 \times f_2 \times f_3$$

$$P_c = L_{\%} \times P_a \times \frac{1}{Q_{stream} \times \Delta t}$$

$$\rho_{ss} = \frac{1}{1 + \left(f_{oc(ss)} \times K_{oc} \times susp_{water}\right) \times 10^{-6}}$$

$$\rho_{sed} = \frac{z}{z + ESD \times SBD \times f_{oc(sed)} \times K_{oc}}$$

$$\rho_{deg} = e^{\frac{-\ln 2 t_r}{DT_{50,w}}}$$

$$PEC_{sw} = \rho_{ss} \times \rho_{sed} \times \rho_{deg} \times P_c$$

Figure 7.4. Modified surface run-off model framework; modifications to the existing model are shown in the red hatched areas. SCS, Soil Conservation Service.

study that there would be negligible reductions in pesticide concentrations after water was abstracted for drinking water supplies. A more detailed description of model development and parameterisation is available in Harmon O'Driscoll *et al*. (2024).

A probabilistic approach using the Monte Carlo technique was adopted. Monte Carlo simulation involves the random sampling of input parameters and successive model runs to produce statistical distributions of outputs. To ensure the statistical stability of the model's outputs, a Monte Carlo simulation was run for 1,000,000 iterations. Both the model developed in this study and the Monte Carlo simulation were programmed using MATLAB. Distributions were selected for several of the model inputs, e.g. Irish rainfall data from Met Éireann (2022), based on best-fit analysis of data recorded on MATLAB, and a review of distributions used in the literature to date for parameters.

7.3.2 Results and discussion

Pesticide concentration in surface water

The conditions associated with the study site require a rainfall event of 8.3 mm for run-off to occur (USDA, 2004). Based on 35 years of rainfall data in the east of Ireland, such a rainfall event is expected to occur approximately 10% of the time, for an average of 36 days each year. Consequently, the vast majority of modelled days will result in no run-off and, as a result, the in-stream concentration will be zero. Therefore, as there are no predicted concentrations below the 90th percentile, only the 95th and 99th percentile values are presented in Table 7.2 in the interest of clarity and brevity. For the case study site, with moderate flow rate ($\mu = 1592.3\ l\,s^{-1}$), triclopyr was found to have the highest in-stream concentration (8700 ng l^{-1}) followed by MCPA (7560 ng l^{-1}) and mecoprop-P (5130 ng l^{-1}). Varying the flow rate of the site resulted in a range of triclopyr concentrations, from 11,820 ng l^{-1} with a low flow rate (732 $l\,s^{-1}$) to 4370 ng l^{-1} for a high flow rate (3979 $l\,s^{-1}$). Full details of the modelled concentrations for the 15 pesticides examined and discussion of these findings can be found in Harmon O'Driscoll *et al*. (2024). Pesticides predicted to have the highest in-stream concentrations tended to have very low adsorption coefficients, have high application rates and/or degrade slowly in water. The ranking of the pesticides is in broad agreement with EPA monitoring findings in Ireland. Of 14 pesticides monitored in 144 rivers in Ireland over a 5-year period, the EPA found that MCPA was the most widely detected pesticide in Irish rivers, followed by mecoprop-P and 2,4-D (EPA, 2019). Overall, herbicides were found to occur in much higher concentrations than the modelled fungicides because of their differing physico-chemical properties, e.g. modelled fungicides had much higher adsorption coefficients than the herbicides and were therefore less mobile. This is of particular interest in terms of human health assessments, as fungicides tend to be more toxic to humans than herbicides, with prochloraz

Table 7.1. Conditions for the study site

Parameter	Unit	Distribution/model	Values utilised	Source
Organic carbon	%	Normal[a]	$\mu = 2.36$; $\sigma = 2.79$	Fay *et al.*, 2007; EPA, 2021a
Plant interception	%	Uniform	Min. = 0, max. = 70	Labite and Cummins, 2012; FOCUS, 2015
Slope	%	Fixed	3	Clarke *et al.*, 2016
Buffer	m	Fixed	0	Clarke *et al.*, 2016
Flow rate	$l\,s^{-1}$	Log-normal[a]	$\mu = 6.602$; $\sigma = 1.562$	WMO, 1989; EPA, 2021b
Bulk density	$kg\,m^{-3}$	Normal[a]	$\mu = 1.06$, $\sigma = 0.38$	Labite and Cummins, 2012; Clarke *et al.*, 2016; EPA, 2021a
Sand	%	Uniform	Min. = 26, max. = 64	
Clay	%	Uniform	Min. = 5, max. = 38	
PD	$kg\,m^{-3}$	Fixed	2.65	
t	Days	Fixed	3	OECD, 2000, Annex 2
t_r	Days	Fixed	5	FOCUS, 2015
Δt	Seconds	Fixed	3600	Probst *et al.*, 2005; APVMA, 2020

[a]Distribution type has been selected based on recommendations from the literature and distribution parameters developed from best-fit analysis to data.

PD, particle density; t, time; t_r, transfer time.

Table 7.2. Ranking of pesticides based on predicted concentrations in surface water (including zero run-off days)

Pesticide	Application rate (g ha⁻¹)	95th percentile (ng l⁻¹)	99th percentile (ng l⁻¹)	Percentage exceedance of 100 ng l⁻¹ (%)	Rank
Triclopyr	1440	490	870	7.2	1
MCPA	1800	380	756	6.8	2
Mecoprop-P	1200	270	513	6.4	3
2,4-D	750	270	485	6.4	4
Clopyralid	200	210	348	6.1	5
Fluroxypyr	400	100	176	5.0	6
2,4-DB	1800	40	113	3.6	7
Terbuthylazine	570	36	72	3.4	8
Penthiopyrad	500	[a]3.6	9.5	0.95	9
Propyzamide	1500	[a]2.2	6.0	0.63	10
Prochloraz	450	[a]0.12	[a]0.4	0.05	11
Glyphosate	2160	[a]5.5×10^{-3}	[a]0.26	0.07	12
Pendimethalin	1600	[a]3.1×10^{-3}	[a]0.08	0.005	13
Prothioconazole	200	[a]1.8×10^{-3}	[a]0.06	0.003	14
Phenmedipham	320	[a]1.3×10^{-10}	[a]2.1×10^{-6}	0	15

[a]Predicted concentration less than the LOD.
2,4-DB, 4-(2,4-dichlorophenoxy)butyric acid.

and prothioconazole being the second and fifth most toxic of the modelled pesticides, respectively, based on their acceptable daily intake (ADI) values (see section 7.4 for more discussion of health risks).

Comparison with monitoring data

To provide insight into the performance of the model, the predicted surface water concentrations presented herein were compared with the monitoring data collected as part of the PestMan project discussed in Chapter 5. Figure 7.5 compares the modelled results and the monitoring data for two of the pesticides. Data for the other pesticides can be found in Harmon O'Driscoll *et al.* (2024). At the concentrations that may exceed the legal limit of 100 ng l⁻¹ for drinking water and may pose health risks, there was good agreement between the modelled results and the monitoring data as shown in Figure 7.5. For the purpose of pesticide risk assessments, it is favourable to have conservative results allowing for a protective risk assessment (EFSA, 2013).

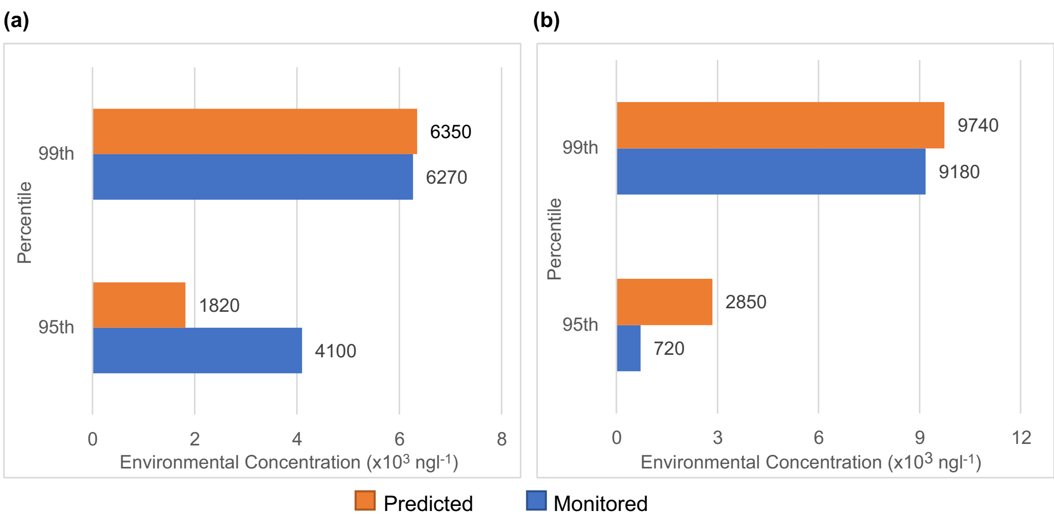


Figure 7.5. Monitored vs predicted concentrations of 2,4-D (a) and MCPA (b) in surface water.

Pesticide concentrations in groundwater

The predicted leached quantities for the 15 modelled pesticides are given in decreasing order in Table 7.3. Triclopyr was the only pesticide predicted to exceed the EU's legal limit for drinking water in this surface water, and only at the 99th percentile concentration. The four pesticides that were predicted to occur in the highest concentrations had very low adsorption coefficients, making them more mobile and available for leaching. On the other hand, the pesticides with the highest adsorption coefficients, glyphosate and pendimethalin, were predicted to leach to groundwater in concentrations well below the LOD. Overall, the model shows that groundwater is far less vulnerable to pesticide pollution than surface water. The selected pesticides are all predicted to occur in significantly lower concentrations in groundwater, and often in concentrations well below the LOD. This agrees with monitoring programmes of Irish water bodies and European monitoring programmes. A European-wide assessment of 16,886 groundwater monitoring sites reported that only six pesticides had exceedance rates of more than 1%, compared with 35 pesticides in surface water (Mohaupt *et al.*, 2020). In Ireland, pesticides have not been identified as a concern for groundwater contamination based on the monitoring of 541 groundwater sites from 2007 to 2021 (EPA, 2021c).

7.4 Human Health Risk Assessment

The environmental concentrations of 15 pesticides used in Ireland were predicted in the previous section. Overall, the concentrations were very low, and therefore the level of exposure of consumers of Irish water is expected to be minimal. However, a number of pesticides were predicted to exceed the EU's legal pesticide concentration limit of 100 ng l^{-1} in drinking water at 95th and 99th percentile concentrations. In addition, low but repeated exposure to pesticides from contaminated food and water has been linked to several human health disorders such as cancers, organ toxicity, and respiratory, reproductive and development disorders (Kalyabina *et al.*, 2021). Both the EU and the World Health Organization (WHO) have recommended a risk quotient method to assess the likelihood of chronic health impacts for the human population due to exposure to pesticides via drinking water (EFSA Scientific Committee *et al.*, 2019). A probabilistic approach was applied to this method to assess and compare the potential level of risk posed to human health by the predicted environmental concentrations of the 15 pesticides obtained in

Table 7.3. Predicted concentrations of pesticides in groundwater due to leaching

Pesticide	Percentile predicted concentration (ng l^{-1})				Percentage exceedance of 100 ng l^{-1} (%)
	50th	75th	95th	99th	
Triclopyr	[a]7.4×10^{-10}	[a]9.9×10^{-4}	20	120	1.3
MCPA	[a]4.2×10^{-22}	[a]3.5×10^{-8}	4.0	76	0.73
2,4-D	[a]4.1×10^{-11}	[a]5.6×10^{-4}	1.5	70	0.45
Clopyralid	0.7	20	4.2	62	0.04
Terbuthylazine	[a]1.7×10^{-25}	[a]4.1×10^{-10}	[a]0.046	20	0.02
Fluroxypyr	[a]8.0×10^{-23}	[a]4.4×10^{-9}	[a]0.046	1.5	0.002
2,4-DB	[a]7.3×10^{-92}	[a]1.9×10^{-30}	[a]5.9×10^{-5}	6.0	0.15
Penthiopyrad	[a]4.6×10^{-42}	[a]1.8×10^{-16}	[a]0.001	6.0	0.005
Mecoprop-P	[a]2.0×10^{-68}	[a]1.2×10^{-26}	[a]2.2×10^{-5}	3.0	0.023
Propyzamide	[a]1.9×10^{-173}	[a]7.9×10^{-66}	[a]7.0×10^{-14}	[a]8.0×10^{-4}	0.008
Prochloraz	≈0	[a]2.4×10^{-71}	[a]1.2×10^{-14}	[a]2.2×10^{-4}	≈0
Phenmedipham	≈0	[a]8.7×10^{-96}	[a]1.0×10^{-21}	[a]6.4×10^{-7}	≈0
Glyphosate	≈0	≈0	[a]3.3×10^{-39}	[a]2.1×10^{-7}	≈0
Pendimethalin	≈0	≈0	[a]1.3×10^{-84}	[a]6.2×10^{-26}	≈0
Prothioconazole	≈0	≈0	≈0	[a]5.3×10^{-128}	≈0

[a]Predicted concentration is lower than the LODs.
2,4-DB, 4-(2,4-dichlorophenoxy)butyric acid.

section 7.3. Risks posed to both the adult and child populations were evaluated, to determine if any pesticides commonly used in Ireland have the potential to have long-term negative effects on the health of Irish consumers.

7.4.1 Methodology

First, the estimated daily intake (EDI) value for a pesticide was obtained for both the adult and child populations using guidelines of the Food and Agricultural Organization of the United Nations and WHO (FAO and WHO, 1997) based on the predicted concentrations from section 7.3, daily water consumption and body weight. A Monte Carlo simulation was utilised to probabilistically assess the EDI values for the Irish adult and child populations. Statistical parameters and distributions for population data were obtained from the Irish Universities Nutritional Alliance and the United States Environmental Protection Agency to enable the application of this probabilistic approach (USEPA, 2004; IUNA, 2011, 2021). The risk quotient for chronic exposure was calculated as a simple ratio of EDI to ADI (i.e. risk quotient = EDI/ADI), whereby the ADI value (mg kg^{-1} day^{-1}) is the level of exposure at which no adverse effects are expected. If the risk quotient is greater than 1, the risk associated with the level of pesticide exposure is deemed unacceptable and adverse health effects are considered likely to occur. If the risk quotient is less than 1, there is deemed to be no likelihood of health risk and therefore the level of exposure is deemed to be acceptable.

7.4.2 Results and discussion

The 99th percentile EDI values obtained from the modelled surface water and groundwater concentrations for drinking water intake only are presented in Table 7.4. Triclopyr, as the pesticide predicted in section 7.3 to occur at the highest concentrations, also has the highest EDI value for adults and children. Overall, the rate of exposure to pesticides in drinking water is higher among children than among adults because of children's higher water consumption rate in terms of body weight (Rezaei Kalantary *et al.*, 2022). However, the daily levels of exposure for both adults and children were predicted to be well below the ADI values for all pesticides, even at the most extreme concentrations.

As was the case for the modelled EDI values, the risk quotient for children's health is higher than for adults' health; for example, exposure to mecoprop-P is associated with a 99th percentile risk quotient of

Table 7.4. The 99th percentile EDI values (mg kg^{-1} day^{-1}) for adults and children from surface water and groundwater, and pesticide ADI values (mg kg^{-1} day^{-1})

	Surface water			Groundwater			
Pesticide	Rank	EDI$_{adult}$	EDI$_{child}$	Rank	EDI$_{adult}$	EDI$_{child}$	ADI
Triclopyr	1	2.33×10^{-4}	3.03×10^{-4}	1	3.32×10^{-6}	4.2×10^{-6}	0.03
MCPA	2	2.02×10^{-4}	2.54×10^{-4}	3	2.03×10^{-6}	2.53×10^{-6}	0.05
Mecoprop-P	3	1.50×10^{-4}	1.92×10^{-4}	9	6.61×10^{-6}	8.33×10^{-8}	0.01
2,4-D	4	1.34×10^{-4}	1.70×10^{-4}	4	1.94×10^{-6}	2.48×10^{-6}	0.02
Clopyralid	5	9.57×10^{-5}	1.20×10^{-4}	2	2.18×10^{-6}	2.90×10^{-6}	0.15
Fluroxypyr	6	4.91×10^{-5}	6.27×10^{-5}	6	3.60×10^{-7}	4.48×10^{-7}	0.8
2,4-DB	7	3.10×10^{-5}	3.94×10^{-5}	7	1.82×10^{-7}	2.30×10^{-7}	0.02
Terbuthylazine	8	1.93×10^{-5}	2.42×10^{-5}	5	4.37×10^{-7}	5.48×10^{-7}	0.004
Penthiopyrad	9	2.50×10^{-6}	3.14×10^{-6}	8	1.37×10^{-7}	1.75×10^{-7}	0.1
Propyzamide	10	1.59×10^{-6}	2.04×10^{-6}	10	2.09×10^{-10}	2.71×10^{-10}	0.05
Prochloraz	11	9.98×10^{-8}	1.27×10^{-7}	11	1.10×10^{-10}	1.40×10^{-10}	0.01
Glyphosate	12	6.78×10^{-8}	8.52×10^{-8}	12	3.77×10^{-13}	5.25×10^{-13}	0.5
Pendimethalin	13	2.06×10^{-8}	2.60×10^{-8}	14	1.19×10^{-32}	1.61×10^{-32}	0.125
Prothioconazole	14	1.91×10^{-8}	2.43×10^{-8}	15	9.37×10^{-137}	1.30×10^{-126}	0.05
Phenmedipham	15	5.11×10^{-13}	6.51×10^{-13}	13	1.67×10^{-13}	2.13×10^{-13}	0.03

2,4-DB, 4-(2,4-dichlorophenoxy)butyric acid.

0.015 for adults but 0.019 for children. As shown in Figure 7.6, the pesticides found to have the highest potential to harm human health from exposure via surface water are mecoprop-P, triclopyr and 2,4-D (risk quotients of 0.019, 0.011 and 0.009, respectively). The risks from exposure via groundwater are significantly lower as a result of the very low predicted environmental concentrations. For groundwater supplies, triclopyr, terbuthylazine and 2,4-D were predicted to have the highest risk quotients, with 99th percentile risk quotients of 1.4×10^{-4}, 1.37×10^{-4} and 1.25×10^{-4}, respectively. Terbuthylazine's risk quotient is the second highest in terms of pesticide risk via groundwater and fourth highest in terms of surface water, despite having only the fifth and eighth highest exposure rates of the 15 pesticides, respectively. Terbuthylazine has a very low ADI value, of $0.004\,mg\,kg^{-1}\,day^{-1}$, compared with pesticides such as mecoprop-P (ADI = $0.01\,mg\,kg^{-1}\,day^{-1}$) and triclopyr (ADI = $0.03\,mg\,kg^{-1}day^{-1}$). However, terbuthylazine is not widely used in Ireland, with its annual quantity of use being only 3% that of MCPA; therefore, the likelihood of exposure among the general population is very low. Of the most widely used pesticides in Ireland, both fluroxypyr and glyphosate are ranked very low (8th and 14th lowest risk quotients). MCPA, however, has a much higher risk quotient because of its high level of mobility into water supplies, and as a result it ranks among the top five pesticides in terms of risk quotients. However, given the low exposure levels for all pesticides shown in Table 7.4, with no EDI values exceeding their respective ADI values, the 99th percentile risk quotients for pesticides in surface water and groundwater supplies are well below an unacceptable level of risk. Therefore, the results suggest that, despite pesticide concentrations potentially occurring in drinking water supplies at levels higher than the EU legal limit of $100\,ng\,l^{-1}$, there is currently a very low level of risk to human health via drinking water under normal pesticide application patterns. In fact, if a child with average weight (32.5 kg) and water consumption ($0.5\,l\,day^{-1}$) (IUNA, 2021) was exposed to legal drinking water concentrations ($100\,ng\,l^{-1}$) of terbuthylazine, the most toxic pesticide in the study, and fluroxypyr, the least toxic, the resulting risk quotients would be 3.85×10^{-4} and 1.92×10^{-6}, respectively. Conversely, to be exposed to an unacceptable level of risk, a child would have to be exposed to a concentration of terbuthylazine of $260\,ng\,l^{-1}$, which is over 350 times the 99th percentile of modelled surface water concentration (Table 7.2). These findings broadly agree with Dekant *et al.*'s (2010) suggestion that the EU limits were set with little consideration of a pesticide's evaluated toxicological significance and therefore can be overly restrictive for pesticides that have been found to have low human toxicity.

On the basis of the study site conditions and the 15 pesticides assessed, it can be suggested that the

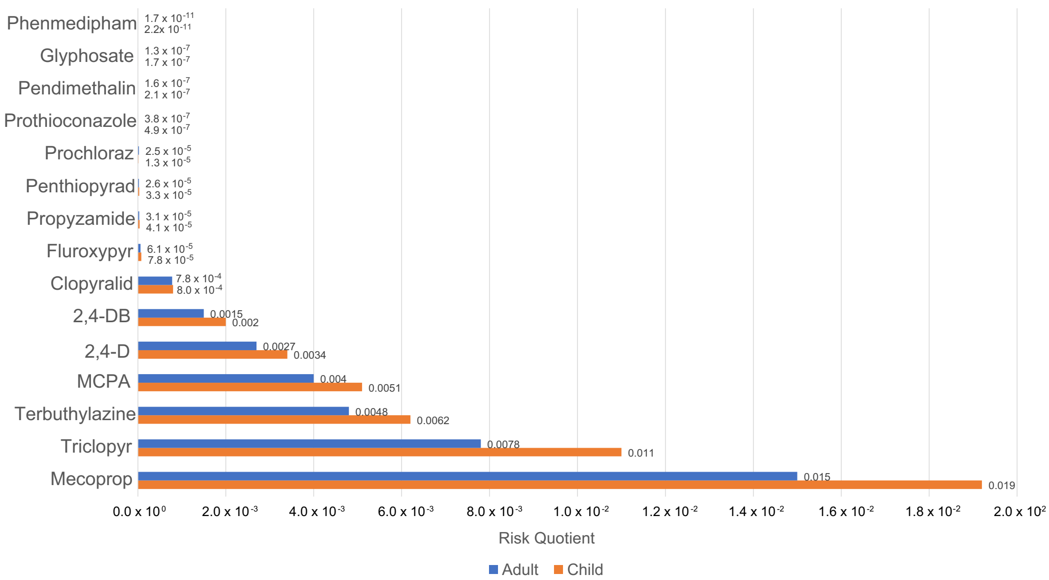


Figure 7.6. Ninety-ninth percentile risk quotient for Irish adults and children based on predicted concentrations in surface water (from section 7.3).

level of pesticide contamination of Irish drinking water sources poses little risk. However, different agricultural management practices and site conditions will result in varying levels of exposure and health risks; therefore, it cannot be assumed that the contamination of Irish water supplies poses no risk to human health. The risk to health in this study was assessed using individual pesticides' ADI values. ADI values are defined on the basis of health studies in animals, supplied to organisations such as the WHO and the EU (FSAI, 2009); however, they are supplied by pesticide manufacturers or companies commissioned by them (Mie and Rudén, 2023). Damalas and Eleftherohorinos (2011) have highlighted that the methods used in health studies and criteria selected to determine acceptable exposure levels can affect how pesticide toxicity is classified. Within the EU, Regulation (EC) No. 1107/2009 requires that pesticide manufacturers provide transparent data reports and meet stringent testing protocols when assessing pesticide health effects (EU, 2009b). However, the International Agency for Research on Cancer has provided reports of the harmfulness of some pesticides that contradict European Food Safety Authority findings (IARC, 2015), and Mie and Rudén (2023) have suggested that some pesticides have been incorrectly classified as relatively low risk because of the recent misreporting of some pesticides' neurotoxicity. Conversely, some pesticides have been found to have overly conservative exposure limits and therefore restrictions on their use may be overprotective (Moxon *et al*., 2020). It is therefore important to interpret the results of this study in the context of the recently revealed limitations that exist around international pesticide toxicity classification, the case-specific nature of such detailed case studies and unavoidable modelling limitations.

7.5 Conclusion

An incremental pesticide risk assessment approach was presented involving risk screening, pesticide transport modelling and health risk assessments. For each stage, a framework was developed and applied to the Irish context to illustrate its application in risk assessment. First, the risk-screening framework allows users to score the relative risks posed by pesticides and to rank pesticides from greatest to least concern based on drinking water intake. The approach presented allows for the comparison of pesticides based on a range of criteria: quantity of use, environmental fate, toxicity, overall hazard and quantity-weighted hazard incorporating national pesticide use data. This work has expanded on existing methods by including the effects that site conditions have on pesticide mobility, through the use of a more comprehensive mobility indicator, and has led to the development of one of the first pesticide-screening tools that attempts to address the impact that metabolites have on overall pesticide risk. In the context of Irish drinking water, on a national scale and at two different sites, mancozeb, 2,4-D, pendimethalin and glyphosate are among the pesticides of greatest concern based on their scores for likelihood of exposure and consequence of exposure, quantity of use or a combination of these factors. Full details of results and findings from the risk-screening process are available in Harmon O'Driscoll *et al*. (2022). Pesticides that were identified as having the potential to cause greatest harm to human health based on hazard and quantity-weighted hazard scores were selected for a more detailed assessment, as described in the following paragraph; however, as mancozeb was removed from the EU market after the initial risk-screening analysis, it was not considered in detailed quantitative analyses, despite being found to be of relatively high risk initially.

Fifteen pesticides identified as potential "high-risk" pesticides in this risk-screening study were selected for a detailed risk assessment. Triclopyr, MCPA, mecoprop-P and 2,4-D were found to be the most mobile pesticides and were predicted to occur in the highest concentrations. The model results showed that pesticides were more likely to occur in surface water, and in higher concentrations, than in groundwater, with some pesticides exceeding the legal limit for drinking water in surface water at higher percentile concentrations. This is of particular interest in Ireland, where 80% of public drinking water supplies are drawn from surface water bodies (DHPLG, 2018). The modelled results were shown to compare well with data from Irish and European monitoring programmes as well as studies described in the literature. The framework developed could be modified for use by catchment managers and water quality monitoring programmes. The modelled concentrations of 15 pesticides obtained from the pesticide transport model were used to assess the level of exposure to pesticides and resulting potential for causing harm to human health from pesticides in Irish drinking water.

Adult and child EDI values were determined, and the EDI values for all pesticides were well below their respective ADI values based on the most extreme level of exposure (99th percentile). For surface water, the pesticides found to have the highest level of health risk were mecoprop-P followed by triclopyr then terbuthylazine; for groundwater, they were triclopyr followed by terbuthylazine then MCPA. It is interesting to note that some pesticides that were identified as priority pesticides from the initial screening process, such as glyphosate and pendimethalin, were found to pose little health risk in the detailed assessment. This highlights that initial risk screening is useful, but that detailed risk analysis should be carried out for further investigation to ensure the efficient use of resources. Despite being used in relatively low quantities nationally compared with glyphosate and MCPA, mecoprop-P was identified as a priority pesticide in this study in terms of predicted surface water concentrations and resulting potential heath risk, and its use nationally should be monitored to ensure that exposure levels do not increase, to avoid potential health risks in future. Overall, the EDI values in this study were well below their respective ADI values, based on drinking water intake only, and it is unlikely that acceptable exposure levels would be exceeded under current legal application patterns and current climatic conditions. However, work is currently under way to analyse how climate change projections may affect pesticide transport and determine whether future climate conditions may increase health risks due to changes in pesticide exposure.

8 Conclusions and Recommendations

8.1 Overview

The inefficient use of pesticides in agriculture on a global scale for over 50 years, to produce foodstuffs to cater for the expanding global population, is having a profound and unacceptable environmental effect on waterways, soil and ecosystems. Pesticides are, as a result of this inefficient use, widespread in both soils where crops have been planted and grown and in the sediments of waterways to which pesticides have been transported and are subsequently adsorbed.

8.2 Conclusions

The main conclusions from this study are as follows:

- Pesticides that are not approved continue to be detected in European surface water and groundwater bodies at levels exceeding the drinking water parametric value of 100 ng l^{-1}. Current remediation methods employed at drinking water facilities, consisting of GAC filters, do not completely remove pesticides, particularly weakly adsorbable and highly polar pesticides. Of the new and emerging remediation methods for legacy pesticides, vegetated buffers are the most cost-effective method for protecting streams and waterways, but remediation methods are still needed to address existing contamination from legacy pesticides.
- The screening tool developed in this study, based on soil texture-specific adsorption isotherm data and pesticide properties (i.e. water solubility, soil half-life and soil permeability), allows farmers to determine if a pesticide for a required job is environmentally friendly or if its use would pose a potential threat to the environment.
- A semi-quantitative risk-scoring method was developed that combines information on pesticide physico-chemical properties, site conditions, metabolite risk and human health outcomes in one framework. This framework allows users to identify high-risk pesticides and examine how pesticides may contribute to health risks for a population on a regional or national scale using quantity-weighted hazard scores.
- A probabilistic modelling approach was developed to quantitatively assess pesticide concentrations in drinking water supplies. This approach was applied to 15 pesticides in an Irish context and the results broadly agreed with data from local and national monitoring programmes for surface water and groundwater bodies, carried out by both the authors and the EPA. This modelling approach may be combined with human health risk models and assessments, or environmental risk models, to provide a better understanding of the impact of pesticides on drinking water resources and to quantify the risks posed to consumers and non-target organisms. Mecoprop-P, triclopyr and 2,4-D are predicted to pose the greatest health risks; however, under current exposure rates through drinking water, the risk to health is still well below an unacceptable level.
- The evaluation of 12 materials (including seven industrial and agricultural waste materials, four biochars and GAC) as potential adsorbents for the removal of five commonly used herbicides in Ireland showed that GAC removed all herbicides with > 95% efficiency, while the industrial and agricultural materials demonstrated little or no capacity for herbicide adsorption. Even though biochars have been reported in the literature to be good adsorbents for herbicides, they showed poor adsorption capacities in this study. CAC, on the other hand, adsorbed herbicides with > 97% efficiency (John McGinley, University of Galway, unpublished data) and so is a good sustainable alternative to GAC.
- A field study using two types of intervention systems containing CAC as the adsorbent medium, namely filter bags and a filter pipe, demonstrated that the filter pipe reduced herbicide concentrations more efficiently than the filter bags. Where the water flow was slow and when water was not able to flow around either the filter bags or filter pipe, substantial reductions in the herbicide concentrations in the streams and drains were observed.
- Split pesticide applications significantly reduced the loss of pesticides to the environment, via

both leaching and surface run-off, and should be considered as a management strategy for minimising the environmental impact of pesticide use in agriculture.

8.3 Recommendations

The recommendations from this study are as follows:

- Further work on the design of the intervention systems, including modifying the size of the filter bags and the shape of the pipe, should be explored. Given that the width and depth of streams and drains at the sides of fields vary considerably, having a number of differently sized filter bags/pipes should be considered. Rather than targeting pesticides alone, the use of these intervention systems to address chemicals of emerging concern, such as pharmaceuticals, antibiotics, personal care products and veterinary products, could also be investigated.
- As CAC is a relatively expensive adsorbent, the possibility of removing the adsorbed herbicides from the spent CAC to recover the CAC should be investigated. This desorption process should be carried out at room temperature, as, otherwise, unwanted chemical reactions involving the herbicides and desorption solvent could occur.
- It will be important to identify key stakeholders and work with them to identify and circumvent any barriers to the implementation of this system in the field on a national scale. These stakeholders would include the Department of Agriculture, Food and the Marine, Teagasc, Inland Fisheries Ireland, non-governmental organisations and fisheries owners, as well as the various farming communities and drinking water suppliers.
- Areas where mecoprop-P (found in this study to have the greatest potential to pose risks to health) is widely used should be identified and advice should be provided on the appropriate use of mecoprop-P. Should national usage of mecoprop-P increase from its current relatively low level, specific monitoring programmes, similar to the MCPA monitoring programme implemented in the Lough Derg catchment, may also be required.

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Abbreviations

2,4-D	2,4-Dichlorophenoxyacetic acid
ADI	Acceptable daily intake
CAC	Coconut-based activated carbon
EDI	Estimated daily intake
GAC	Granulated activated carbon
HPLC-UV	High-performance liquid chromatography with UV detectors
LOD	Limit of detection
LQI	Leached Quality Index
MCPA	4-Chloro-2-methylphenoxyacetic acid
PestMan	Pesticide Management for Better Water Quality
PRZM	Pesticide root zone model
PTFE	Polytetrafluoroethylene
S-BC	Spruce biochar
SFIL	Simplified formula for indirect loading caused by run-off
SWAT	Soil Water Assessment Tool
WHO	World Health Organization

An Ghníomhaireacht Um Chaomhnú Comhshaoil

Tá an GCC freagrach as an gcomhshaol a chosaint agus a fheabhsú, mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol 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 ardchaighdeáin, spriocdhírithe 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 peitril ar scála mór;
> Sceitheadh fuíolluisce uirbigh;
> 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 uirbigh 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 chomhshaol.

Bainistíocht Dramhaíola agus Ceimiceáin sa Chomhshaol

> 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 ceimiceán 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 leibhéil 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 Ghníomhú ar son na hAeráide;
> Tacú le gníomhaíochtaí forbartha Náisiúnta, AE agus NA um Eolaíocht agus Beartas Aeráide.

Monatóireacht & Measúnú ar an gComhshaol

> 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 chomhshaol 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 leibhéil 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 taismí 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 ionadaíocha agus ranna rialtais chun cosaint chomhshaoil 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 Inbhunaitheacht 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 Ghníomhaireacht agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

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