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QUANTITATIVE RISK ASSESSMENT OF PESTICIDES IN DRINKING WATER UNDER CURRENT AND FUTURE CLIMATES

Thesis presented by

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for the degree of

Doctor of Philosophy

University College Cork

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ABSTRACT

Risk assessment approaches have become critical for pesticide risk management and mitigation. Despite this, scientists and pesticide regulators have acknowledged the need to improve representation of variability in input data, and uncertainty in pesticide fate processes in existing approaches. Additionally, current methods are limited in their ability to represent the inherent uncertainty and variability associated with climate change, and therefore cannot inform future planning under changing climates. This thesis presents the development of a novel, practical risk assessment framework to assess the risks posed by pesticide contamination in drinking water under current and future climates, incorporating novel risk scoring systems, probabilistic risk modelling frameworks, and climate change projections.

The main body of the thesis discusses the different stages involved in the development of the risk assessment framework. Firstly, a novel risk screening tool was developed to rank pesticide risks to human health, considering pesticide use, chronic health effects, environmental fate, and site-specific soil conditions. This approach incorporated both pesticide properties and site conditions in the scoring of pesticide mobility to enable more a realistic representation of the effects of location on pesticide transport; metabolite data was also used to inform overall risk scores based on EU recommendations. This method aids in identifying high-risk pesticides from a wide range of pesticides to better inform monitoring programs and further detailed risk assessments.

Secondly, an existing deterministic simulation model was modified to better represent both site scenarios and transport processes involved in pesticide runoff to drinking water supplies. Additionally, a Monte-Carlo approach was utilised to enable probabilistic assessment and account for variability in pesticide properties, population characteristics, site conditions, and climatic factors. This framework enables farm advisors and catchment managers to predict concentrations of pesticides in drinking water supplies, quantify potential risks to human health arising from pesticide exposure, and implement risk mitigation measures using a practical and accessible probabilistic model. An Irish case study was used to illustrate the implementation of the framework to predict pesticide concentrations in surface water and assess health risks to adults and children at a grassland site typical of Irish agriculture. The results

found pesticide concentrations exceeding EU drinking water limits for several pesticides, including MCPA, mecoprop, and 2,4-D, but indicated that health risks were low under current conditions despite these exceedances.

Finally, this thesis investigates the impact of climate change on pesticide transport and health risks, integrating high-resolution climate model projections into the proposed probabilistic risk model. Standardised climate projections for Ireland were used to demonstrate how the probabilistic risk model developed in this thesis can be adapted for future climates. A risk assessment of pesticides for three timeframes (current, 2050, 2100), under two climate scenarios (RCP4.5 and RCP8.5) showed that pesticide risks will increase with future climate conditions. The study found significant regional variations, with higher risks in the south-west compared to the north-east of Ireland, and projected overall risk increases ranging from 18% to 85%, depending on the scenario and timeframe. Despite the projected increases in pesticide risk, the impact to human health remained below EU regulatory health thresholds even under worst-case climate conditions. This approach can be adapted to account for indirect impacts of climate change e.g. land-use, pest prevalence and agricultural policy, to better represent overall changes to pesticide risks under a changing climatic and legislative landscape.

Overall, this research highlights the importance of incorporating site-specific conditions, variability in environmental and climatic factors, and future climate change projections into pesticide risk assessments. The methodologies developed provide robust tools for managing pesticide risks and can be adapted for various locations and conditions, thus informing future pesticide management, climate adaptation approaches, and public health protection strategies.

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First and foremost, I would like to express my sincere gratitude to my supervisors Dr. Páraic Ryan, who encouraged me to undertake this doctoral journey to begin with, Prof. Mark Healy and Prof. Jerry Murphy, for their guidance and expert knowledge throughout this thesis. I am incredibly grateful for all the support and encouragement, as well as the opportunities that have been given to me to help develop my skills as a researcher.

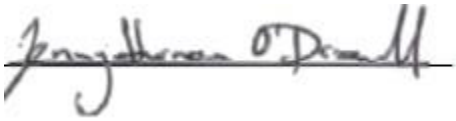
I would also like to thank the rest of my research team in PestMan, Dr. Alma Siggins and Dr. John McGinley for the opportunity to collaborate and bounce ideas off of, as well as Dr. Per-Erik Mellander, Dr. Liam Morrison and Shane Scannell for their helpful suggestions. To all my colleagues in the office in UCC thank you for making long days in the office more enjoyable, it was so lovely to be able to finally chat in person again after almost two years of remote working.

Last but not least, I would like to thank my family and friends for all their love, support, and never-ending encouragement. Thanks to all my friends who have always been there to listen to me ramble on about my work when things were good and rant when they weren't, and for all the fun we have had together. I owe all of you a round when this is all done! I am so incredibly grateful to all my family, especially my parents Joanne and Rory, my sister Róisín and brother Sam, there is no way I would have reached this stage without you. Thank you for shaping me to be the person I am today.

DECLARATION

This is to certify that the work I am submitting is my own and has not been submitted for another degree, either at University College Cork or elsewhere. All external references and sources are clearly acknowledged and identified within the contents. I have read and understood the regulations of University College Cork concerning plagiarism and intellectual property.

Signed:



Jenny Harmon O'Driscoll

Date: 24/07/2024

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ABBREVIATIONS

2,4-D	(2,4-dichlorophenoxyacetic acid)
2,4-DB	4-(2,4-Dichlorophenoxy)butanoic acid
ADI	Acceptable Daily Intake
AGNPS	Agricultural Non-Point Source Pollution Model
AMPA	Aminomethylphosphonic Acid
APVMA	Australian Pesticide and Veterinary Medicine Authority
CES	Consequence of Exposure Score
DAFM	Irish Department for Agriculture, Food and the Marine
DT_{50}	Pesticide Half-Life
EC	European Commission
ECB	European Chemical Bureau
EDI	Estimated Daily Intake
EEA	European Environmental Agency
EFSA	European Food Safety Authority
EIQ	Environmental Impact Quotient
EPA	Environmental Protection Agency
EPRIP	Environmental Potential Risk Indicator for Pesticides
ERI	Environmental Rating Index
EU	European Union
EYP	Environmental Yardstick for Pesticides
FAO	Food and Agricultural Organisation
FOCUS	Forum for the Coordination of Pesticide Fate Models and their Use
GIS	Geographic Information System
GSI	Geological Survey Ireland
GSL	Growing Season Length
GUS	Groundwater Ubiquity Score
GW	Groundwater
IPCC	Intergovernmental Panel on Climate Change
IUNA	Irish Universities Nutrition Alliance
K_{OC}	Organic Carbon Partition Coefficient
LD_{50}	Median Lethal Dose
LES	Likelihood of Exposure Score

LOD	Limit of Detection
MCPA	2-methyl-4-chlorophenoxyacetic acid
NEPC	National Environmental Protection Council for Australia
NOEC	No Observable Effects Concentration
OC	Organic Carbon Content
OECD	Organisation for Economic Co-operation and Development
OM	Organic Matter Content
PEC	Predicted Environmental Concentration
PI	Plant Interception Factor
PIRI	Pesticide Impact Rating Index
PPDB	Pesticide Property Database
PRZM	Pesticide Root Zone Model
RCP	Representative Concentration Pathways
REXTOX	Ratio of Exposure to Toxicity
RICEQW	Rice Water Quality
RQ	Risk Quotient
SCI-GROW	Screening Concentrations In Ground Water
SCS	Soil Conservation Service
SFIL	Simplified Formula for Indirect Loading due to Runoff
SI	Supplementary Information
SOM	Soil Organic Matter
SW	Surface Water
SWASH	Surface Water Scenario Help
SWAT	Surface Water Attenuation Tool
SWPP	Surface Water Protection Programme
TFI	Treatment Frequency Index
TOXSWA	Toxic Substances in Surface Waters
UN	United Nations
UNEP	United Nations Environmental Programme
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
WISPE	World Integrated Pesticide Exposure
WMO	World Meteorological Organisation

CHAPTER 1

INTRODUCTION

1.1 Background and Motivation

Pesticides are chemicals used in agriculture to improve crop yields and ensure food security by deterring or eliminating a range of pests including insects, weeds and fungi (Tang and Maggi, 2021). The intensification of agriculture has led to a rise in pesticide use, which increased by 30% from 2002 to 2018 concurrent with a 44% increase in global grain production (UNEP, 2022). Although pesticides are widely used to benefit agriculture, it has been found that less than 1% of applied pesticides actually reach target organisms, with the remaining being lost to the surrounding environments (Bernardes et al., 2015). Pesticides in aquatic and terrestrial environments have been shown to negatively impact biodiversity, water quality and human health (Chow et al., 2020; Kalyabina et al., 2021; Tudi et al., 2022).

The concerns around pesticides use and their safety have led to the development of integrated pest management systems and organic farming practices, with the aim of reducing the reliance on synthetic pesticides in the agricultural sector (Baker et al., 2020; Benbrook et al., 2021). Within the European Union (EU), the Farm to Fork strategy has been issued to deliver healthy and environmentally friendly food systems, and aims to reduce pesticide use by 50% by 2030 (European Union, 2020). Similar European agricultural policies promoting sustainable farming practices have resulted in more than a 50% increase in organic agricultural land between 2011 and 2020 (Willer et al., 2023). Despite this increase in organic agriculture, there has not been a corresponding decrease in pesticide use, with application rates staying relatively constant over the same ten-year period (McGinley et al., 2023a). Internationally, there has been a relatively limited uptake of organic farming to-date, with only 2% of global agricultural land farmed organically (Gamage et al., 2023), due to costs of adoption, associated low-yields, and lack of access to new technologies (Wreford et al., 2017; Łuczka and Kalinowski, 2020). Additionally, further uptake of organic farming may be impeded due to the need for intensification of agriculture to meet growing food demands. It is estimated that global crop yields will need to increase by approximately 25% – 70% to meet food supply demands of a growing population by 2050 (UNEP, 2022). This is likely to be a significant challenge in many regions experiencing the largest population increases (e.g. Sub-Saharan Africa, South Asia) due to the detrimental effects of climate change on land productivity in these regions (Molotoks et al., 2020). As a result, it is likely that the use of pesticides will remain a critical tool

in global food production for the foreseeable future (Kaur et al., 2024). The future of pesticide risk reduction, therefore, cannot depend solely on reduced use through the implementation of sustainable agriculture. Instead, it hinges on the adoption of such practices coupled with stricter regulations of harmful pesticides, and improved risk assessment models that can better predict and manage environmental and human health impacts.

In light of this, many countries have introduced legislation to restrict pesticide use and ban extremely harmful chemicals which has enabled a reduction in the risk of exposure and negative outcomes to the, general public (Dias et al., 2023). Nevertheless, pesticides are regularly detected in foods, soils and water supplies in concentrations much higher than legal limits (Wanwimolruk et al., 2016; Mojiri et al., 2020). Reduction in future pesticide use and associated risks will likely become more challenging due to growing populations which may lead to increased intensification of agriculture (Van Dijk et al., 2021) Additionally, the impacts of climate change on crop yields, weather conditions and pest prevalence may lead to higher rates of pesticide application (Noyes et al., 2009; Biswas et al., 2018; Grünig et al., 2020).

Pesticide risk assessments enable the quantification of human health impacts arising from unwanted exposure to pesticides in drinking water, and are a useful tool to inform decision-making for pesticide mitigation strategies (USEPA, 2014). Pesticide exposure rates in risk assessments can be obtained from monitoring studies of waterbodies (Teklu et al., 2015; Derbalah et al., 2019; Cantoni et al., 2021; Rezaei Kalantary et al., 2022), but often simulation models are used to predict pesticide exposure from water supplies as a quick and inexpensive alternative to measuring actual concentrations (Reaney et al., 2019; Troldborg et al., 2022). A range of simulation models have been used in research and pesticide regulation including the Surface Water Attenuation Tool (SWAT (Arnold et al., 2012a)), Agricultural Non-Point Source Pollution Model (AGNPS (Bingner and Theurer, 2001)) and a suite of exposure models (e.g. PRZM, MACRO, TOXSWA, etc.) used for pesticide regulation within the EU under the recommendations of the Forum for Co-ordination of Pesticide Fate Models and their Use (FOCUS, 2024). However, the majority of pesticide risk assessment frameworks rely on a traditional, deterministic modelling approach which fails to account for the uncertainty in physical and chemical processes involved in

pesticide exposure as well as the variability in input data (Moe et al., 2022). Therefore, such approaches are restricted in their ability to develop fully transparent and realistic assessments of risk under current conditions, and can underestimate or overestimate health impacts as a result (Uusitalo et al., 2015; Topping et al., 2020). Additionally, as climate change is inherently uncertain, and climate projections are associated with significant variability, pesticide assessments are limited in their ability to consider these effects on future pesticide risk, thereby restricting the future-proofing of risk assessment approaches (Sperotto et al., 2019; Kaikkonen et al., 2021). A need for probabilistic approaches in pesticide risk assessment, capable of incorporating the variability in pesticide fate in current and future conditions, has been recognised by regulatory bodies (USEPA, 2014; EFSA, 2019).

However, many simulation models used in pesticide regulation are very complex and physically-based, with significant computational processing and model parameterisation requirements (Wang et al., 2019b). Therefore, the application of probabilistic approaches to such models have been limited to date to the development of probabilistic distributions for only one or two key parameters (Rutkowska et al., 2015; Tasdighi et al., 2018), or by only modelling application scenarios probabilistically (Winchell et al., 2018; Janney and Jenkins, 2019; Rathjens et al., 2022). Furthermore, there are over 450 pesticides licensed for use within the EU (EC, 2024), with hundreds more used globally (Handford et al., 2015). Excessive resources, time and data would be required in order to carry out a detailed, probabilistic assessment of every pesticide used within a region or nation, particularly when many pesticides pose negligible risk (Tincani et al., 2023). Therefore, this study seeks to develop an iterative and tiered risk assessment framework that provides a practical progression from deterministic to probabilistic analysis. This is facilitated through the initial use of a semi-quantitative risk screening of a wide range of pesticides to inform a probabilistic risk assessment of pesticides under current and future climatic conditions, focused on key pesticides of concern. The probabilistic approach used in this study will be based on an accessible simulation model, with more manageable computational and data input requirements than models currently used in pesticide assessment as a first step towards fully probabilistic, physical-based risk modelling.

1.2 Research Objectives

The overall aim of this study is to develop a practical and applicable pesticide risk assessment framework to analyse human health risks under current and future climates using a tiered approach, beginning with a semi-quantitative risk screening to identify high-risk pesticides, followed by detailed, probabilistic risk modelling of pesticide transport and risk for current and future conditions. This overall aim is addressed in the body of work through the following specific objectives:

Specific Objectives:

1. Investigate state-of-art, high-level, risk screening approaches and quantitative pesticide models, and gaps in the existing approaches to identify suitable methods for the development of the proposed practical assessment framework.
2. Modify existing risk-screening approaches to facilitate the high-level assessment of a wide range of pesticides in order to identify key pesticides of concern for further detailed probabilistic analysis.
3. Develop a tool for probabilistic risk assessment of surface water contamination by pesticides and resulting health impacts in adults and children from first principles.
4. Establish a framework to enable the quantification of climate change impacts on future pesticide risks through the combination of probabilistic risk assessment tool and bias-corrected, downscaled climate projections.

1.3 Thesis Outline

This thesis consists of six chapters with associated references and appendices at the end of the thesis. **This chapter is intended to** introduce the topic, providing the reader with background and context for the research. It seeks to establish the rationale behind the body of work by discussing the research objectives and aims, as well as detailing how the thesis is structured. **Chapter 2** provides a detailed review of pesticide risk assessment, the stages involved in framework development and factors that may influence the assessment. This work considers the state-of-the-art scientific literature relevant to pesticide risk assessments, and highlights some limitations in the current literature that will be addressed in later chapters. **Chapters 3 – 5** contain the main body of research carried out during the PhD programme. Each chapter is an original journal paper manuscript: **Chapters 3 and 4** have been published in peer-reviewed

journals and **Chapter 5** is currently under review with a peer-review journal. Each chapter has its own introduction, methodology, results, discussion and conclusion, and therefore they can be read in isolation. However, each chapter expands on the work of the previous in the development of a multi-stage risk assessment. It is noted that **Chapters 3 – 5** appear as published, with some minor adjustments to reduce repetition and improve the flow of the text as a complete work. Finally, **Chapter 6** summarises the main findings of the research and provides overall conclusions and recommendations arising from the work in the previous chapters. Figure 1.1 illustrates the structure of the thesis, highlighting where research objectives are addressed and how each chapter is related.

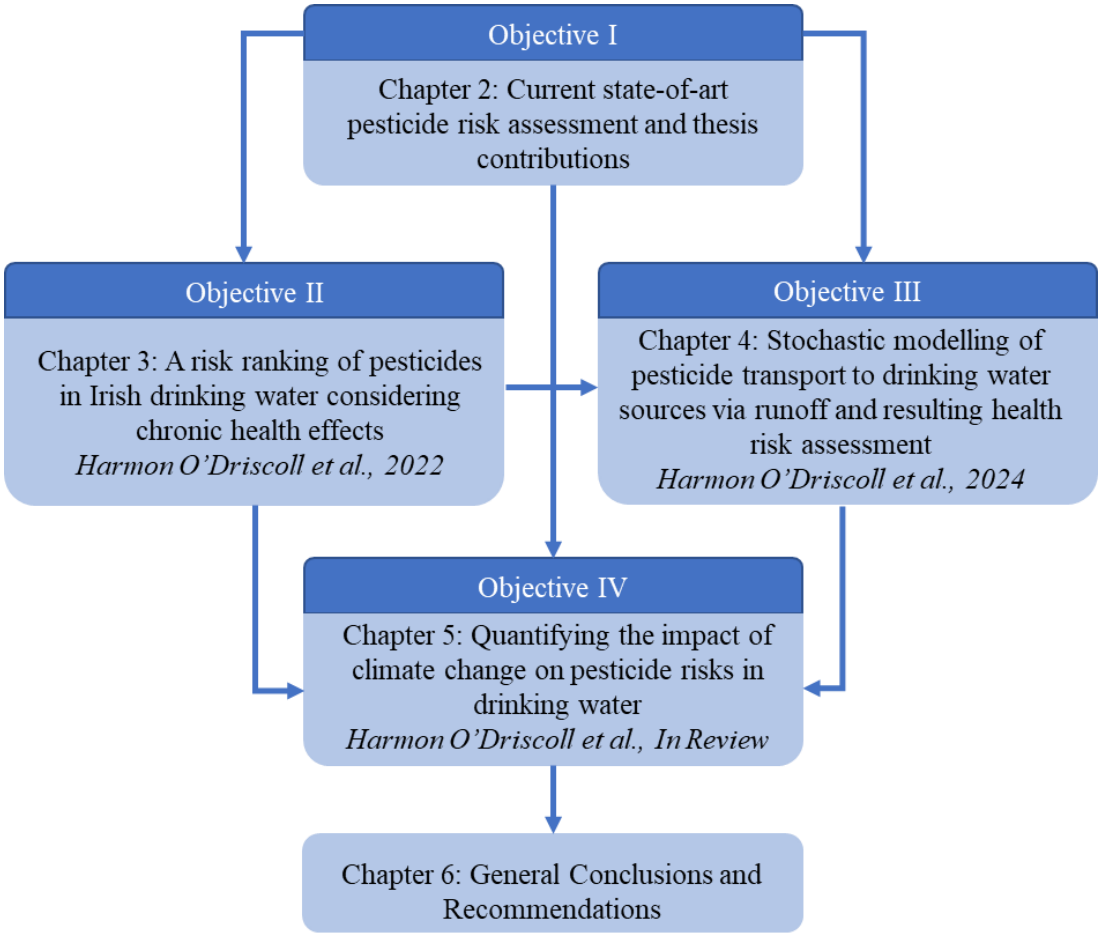


Figure 1.1: Organisation of thesis chapters

1.4 Contributions to Existing Knowledge

Journal Papers

At the time of writing two chapters in this thesis, Chapters 3 and 4, have been published as papers in high-ranking peer-review journals, with Chapter 5 currently under review with a high-ranking peer-review journal:

J. Harmon O'Driscoll, A. Siggins, M. G. Healy, J. McGinley, P.-E. Mellander, L. Morrison, P.C. Ryan, 2022. A Risk Ranking of Pesticides for Chronic Health Effects in Irish Drinking Water. Science of the Total Environment, 829, 154532. https://doi.org/10.1016/j.scitotenv.2022.154532 (published).

J. Harmon O'Driscoll, J. McGinley, M. G. Healy, A. Siggins, P.-E. Mellander, L. Morrison, E. Gunnigle, P.C. Ryan. 2024. Stochastic modelling of pesticide transport to drinking water sources via runoff and resulting human health risk assessment. Science of the Total Environment, 918, 170589. https://doi.org/10.1016/j.scitotenv.2024.170589 (published).

J. Harmon O'Driscoll, M. G. Healy, E. O'Brien, A. Siggins, J. McGinley, P.-E. Mellander, L. Morrison, S. Scannell, P.C. Ryan. Quantifying the influence of climate change on pesticide risks in drinking water. Science of Total Environment (In review).

Additionally, the work carried out in Chapter 3 was used to inform development of another risk-screening tool in collaboration with project partners University of Galway which was included in a publication in a peer-reviewed journal, however the text is not included in this thesis as it does not form part of the core work of the PhD research:

J. McGinley, **J. Harmon O'Driscoll**, M.G. Healy, P.C. Ryan, P.-E. Mellander, L. Morrison, O. Callery, A. Siggins, 2022. An assessment of potential pesticide transmission, considering the combined impact of soil texture and pesticide properties: A meta-analysis. Soil Use and Management, 38, 1162-1171. https://doi.org/10.1111/sum.12794 (published).

Conference Papers

Two conference papers have been published based on this work:

J. Harmon O'Driscoll, M.G. Healy, A. Siggins, J. McGinley, P.-E. Mellander, L. Morrison, P.C. Ryan, Quantitative modelling of human health risks arising from pesticide use in Irish agriculture, 14th International Conference on Applications of Statistics and Probability in Civil Engineering (ICASP14), Dublin, Ireland, 2023.

J. Harmon O'Driscoll, M. G. Healy, E. O'Brien, A. Siggins, P.C. Ryan, 2024. Probabilistic assessment of pesticide health risks via drinking water under future climatic conditions. Civil Engineering Research in Ireland 2024 (CERI2024), Galway, Ireland, 2024.

CHAPTER 2

CONTRIBUTIONS OF THESIS TO STATE-OF-ART PESTICIDE RISK MODELLING

2.1 Overview

The body of work presented in this thesis aims to develop an iterative probabilistic risk assessment framework following the tiered risk assessment approach recommended for use in pesticide risk protocols (USEPA, 1992; NEPC, 2007; European Commission, 2009b). Figure 2.1 outlines the stages involved in a tiered pesticide risk assessment, as well as how each chapter in the thesis addressed different stages of the framework. The following subsections discuss the existing literature and state-of-art models examining pesticide risks under current and future climates, which were considered in the selection of appropriate approaches when developing the proposed framework herein. Additionally, limitations of current approaches and gaps in the existing knowledge are analysed in order to identify key areas where modifications can be made to improve representation of modelled scenarios, reliability of model outputs, and practicality of framework implementation.

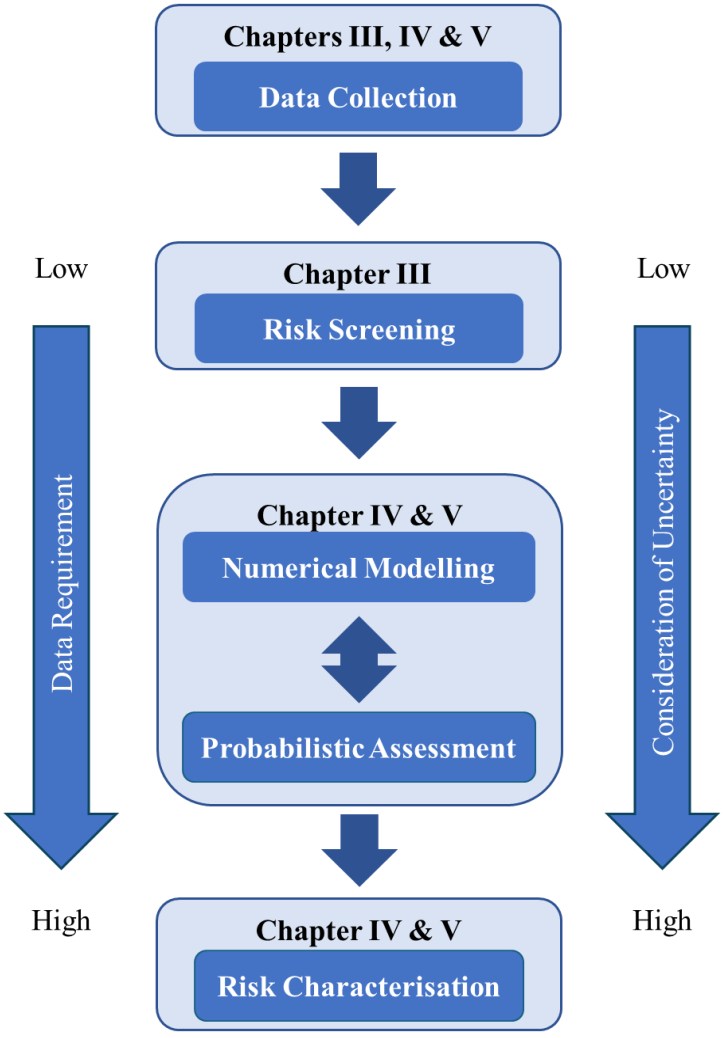


Figure 2.1: Tiered approach to pesticide risk assessment

2.2 TIERED RISK ASSESSMENT

Many national and international bodies have issued pesticides regulations, such as the EU Regulation (EC) No. 1107/2009 (European Commission, 2009b), which set out guidelines for an iterative risk assessment with increasing complexity at each stage of assessment (Topping et al., 2020). These guidelines develop an efficient and flexible framework that can be adapted for different ecosystems and availability of data (Mackay et al., 2023). While the framework can be altered for specific purposes, in general, the risk assessment consists of three major stages: (1) screening (2) analysis, and (3) risk characterisation (USEPA, 2008; Tincani et al., 2023).

Screening-level assessment is used to exclude pesticides with negligible risk from further analysis using conservative, qualitative/semi-quantitative approaches based on accessible data (EFSA, 2013; Topping et al., 2020; Tincani et al., 2023). Further analysis is then carried out for key pesticides identified as potential high-risk pesticides. The analysis stage refines the assessment using numerical models and detailed datasets to provide a more realistic assessment of risk, based on pesticide fate and transport, as well as the behaviours of the study population. Exposure profiles of key pesticides are developed using their individual physiochemical properties and the environmental conditions that may influence the exposure rate (Fargašová, 2017; Michel et al., 2022). This analysis can be deterministic, which produces point-estimates of exposure from a combination of single-value inputs based on protective data (worst-case-scenario) or average values to represent typical exposure. They can also be probabilistic, which uses distributions of input values to develop a range of possible exposure estimates (Moe et al., 2021). The selection of analysis type depends on data-availability, and the users' needs and expertise (USEPA, 2024). Finally, risk characterisation combines the exposure profile with assessment of the consequence of exposure, based on regulatory thresholds, to produce a quantitative estimate of risk (EFSA et al., 2017). Often this risk characterisation involves the use of a risk quotient approach, by comparing the estimate exposure rates with acceptable exposure levels defined by regulatory bodies (EFSA, 2019). This information can then be used as a basis for informed decision-making to develop risk management and intervention measures (Finizio and Villa, 2002; Tincani et al., 2023).

The work presented in this thesis implements the stages of the tiered risk assessment frameworks, as shown above in Figure 2.1, with reference to the various chapters. The main body of work of this thesis is focused on the analysis of existing risk-screening and numerical assessment approaches. There is a wide range of approaches taken in the current literature which are discussed in Section 2.3 and 2.4, together with the contributions this work makes to address gaps in existing studies. In terms of the risk characterisation stage, this study will apply the risk quotient approach as recommended for use within the EU by the European Food Safety Authority (EFSA, 2019), as it was found to be the most widely used approach for this stage in the risk assessment framework, with relatively little variation in applied approaches (Hursthouse and Kowalczyk, 2009; Li et al., 2022). The following sections describe the state-of-the-art work available for risk screening, exposure analysis and quantifications of climate change impacts on pesticide risks, along with the steps taken to develop the novel risk assessment approach utilised in this study.

2.3 Pesticide Risk Screening

Simple transport indicator-based methods and pesticide risk screening tools have been used to prioritise key pesticides for efficient allocation of finite resources for monitoring and/or management programmes (Fairbrother et al., 2019; Vryzas et al., 2020). The EFSA has recommended the use of risk screening methods to accelerate the implementation of detailed analysis for priority pesticides (EFSA, 2024). As a result, these preliminary risk screening/prioritisation methods are widely used in research and pesticide management, with indicator-based methods accounting for 59 % of pesticide risk studies from 1975 to 2010 (Payraudeau and Gregoire, 2012). Their low data requirements, as well as the ease of application and interpretation of the tools, allows them to quickly provide initial risk information for detailed assessments and management at low-cost, and form an essential component to tiered risk analysis approaches such as those applied within the EU (EFSA, 2023).

Despite the wide use of indicator-based risk screening in literature, there is no standardised approach in developing such risk indicators (Vryzas et al., 2020). Numerous methods incorporate different criteria such as mobility, persistence, ecotoxicological effects, human toxicity and site conditions, and various combinations of these criteria. Table 2.1 presents a non-exhaustive list of existing risk-indicators

and screening methods in literature, and the criteria used to develop risk scores or priority lists in each case, which are highlighted by asterisks in the relevant columns for each indicator. In brief, these approaches can be classified into two main categories: (1) prioritisation of pesticides based on their likelihood to reach water supplies using mobility, persistence, application rates, or a combination of these criteria such as the Ground Water Ubiquity Score (GUS) (Gustafson, 1989), SCI-GROW (Barrett, 1998), or prioritisation methods developed by Narita et al. (2021), and (2) production of risk scores for pesticides that are based on both likelihood of exposure and consequence of exposure to non-target organisms in the environment, human health or a combination of the two such as the Environmental Impact Quotient (EIQ) (Kovach et al., 1992), PestScreen (Juraske et al., 2007) or approaches developed by Sugeng (2013), Kudsk et al. (2018) and Choi et al. (2020).

While such methods have been widely applied in the literature to inform pesticide risk management and develop priority lists, a number of limitations reduce their ability to identify priority pesticides for assessment. A major limitation is the reliance on pesticide properties only in assessing exposure scores in the majority of approaches, as illustrated by the sparsity of asterisks in the columns under the site conditions headings in Table 2.1. Some of the most commonly used mobility indicators such as GUS (Gustafson, 1989), and environmental risk indicators such as EIQ (Kovach et al., 1992), assess pesticide exposure using pesticide degradation and adsorption only, while other risk indicators also incorporate factors such as solubility and volatilisation (Juraske et al., 2007; Sugeng et al., 2013). However, of the 34 risk indicators detailed in Table 2.1, only a few mobility indicators, used to identify site vulnerability to pesticides (Table 2.1: Rows 3-8), and two environmental/health risk screening (Table 2.1: Rows 9 and 28) approaches incorporate soil properties into their risk scores: I-Phy (Van Der Werf and Zimmer, 1998), EYP (Reus and Leendertse, 2000).

Table 2.1: Scoring criteria for pesticide risk screening approaches in literature (An asterisk indicates that the indicator considers this criterion in their risk scoring approach).

	Method	**Pesticide Mobility**							**Site Conditions**			**Agricultural Management**		**Ecotoxicity**			**Chronic Human Health**								**Acute Human Health**				
		Persistence	*Adsorption*	*Solubility*	*Volatilisation*	*Drift*	*Bioaccumulation*	*Monitoring Data*	*Soil Conditions*	*Hydrologic Features*	*Rainfall*	*Application Rate*	*Application Timing*	*Environmental LD_{50}*	*Environmental EC_{50}*	*Environmental NOEC*	*ADI*	*Carcinogenicity*	*Mutagenicity*	*Neurotoxicity*	*Teratogenicity*	*Developmental/ Reproduction*	*Endocrine*	*Risk Phrase*	*LD_{50}*	*Dermal toxicity*	*Inhalation toxicity*	*Oral toxicity*	*Eye toxicity*
		Pesticide Mobility/Site Vulnerability Indicators																												
1	TFI (Kudsk, 1989)											*	*																	
2	GUS (Gustafson, 1989)	*	*																											
3	SCI-GROW (Barrett, 1998)	*	*							*	*	*																		
4	DRASTIC (Aller et al., 1985)								*	*																				
5	Goss (1992)	*	*	*					*			*	*																	
6	Yang et al., (2017)	*		*	*		*		*	*		*	*																	
7	Narita et al. (2021)	*	*								*	*																		

Table 2.1 Continued

	Method	Pesticide Mobility							Site Conditions			Agricultural Management		Ecotoxicity			Chronic Human Health									Acute Human Health				
		Persistence	*Adsorption*	*Solubility*	*Volatilisation*	*Drift*	*Bioaccumulation*	*Monitoring Data*	*Soil Conditions*	*Hydrologic Features*	*Rainfall*	*Application Rate*	*Application Timing*	*Environmental LD_{50}*	*Environmental EC_{50}*	*Environmental NOEC*	*ADI*	*Carcinogenicity*	*Mutagenicity*	*Neurotoxicity*	*Teratogenicity*	*Developmental/ Reproduction*	*Endocrine*	*Risk Phrase*		*LD_{50}*	*Dermal toxicity*	*Inhalation toxicity*	*Oral toxicity*	*Eye toxicity*
	Pesticide Mobility/Site Vulnerability Indicators																												
8	Menezes and Heller (2008)	*	*	*					*	*	*																		
	Environmental Risk Indicators																												
9	EYP (Reus and Leendertse, 2000)	*	*						*	*		*	*		*	*													
10	Anderson et al. (2021)							*								*													
11	Tsaboula et al. (2016)							*																					
12	Nikolopoulouet al. (2022)							*																					
13	Whiteside et al., (2008)	*	*			*						*		*	*														

Table 2.1 Continued

	Method	Pesticide Mobility							Site Conditions			Agricultural Management		Ecotoxicity			Chronic Human Health									Acute Human Health				
		Persistence	*Adsorption*	*Solubility*	*Volatilisation*	*Drift*	*Bioaccumulation*	*Monitoring Data*	*Soil Conditions*	*Hydrologic Features*	*Rainfall*	*Application Rate*	*Application Timing*	*Environmental LD_{50}*	*Environmental EC_{50}*	*Environmental NOEC*	*ADI*	*Carcinogenicity*	*Mutagenicity*	*Neurotoxicity*	*Teratogenicity*	*Developmental/ Reproduction*	*Endocrine*	*Risk Phrase*		*LD_{50}*	*Dermal toxicity*	*Inhalation toxicity*	*Oral toxicity*	*Eye toxicity*
		Human Health Risk Indicators																												
14	Gunier (2001)	*	*	*	*							*						*												
15	Chou et al., (2019)							*				*					*													
16	Choi et al. (2020)						*					*						*	*			*		*		*	*	*	*	*
17	Cha et al., (2014)											*						*					*			*				
18	Troisi et al., (2004)	*	*	*	*		*																	*						
19	Dabrowski et al. (2014)	*	*									*						*	*	*	*		*							
20	Li et al., (2018)							*				*					*													
21	Yu et al., (2019)							*				*					*	*				*				*				

Table 2.1 Continued

	Method	Pesticide Mobility							Site Conditions			Agricultural Management		Ecotoxicity			Chronic Human Health									Acute Human Health				
		Persistence	*Adsorption*	*Solubility*	*Volatilisation*	*Drift*	*Bioaccumulation*	*Monitoring Data*	*Soil Conditions*	*Hydrologic Features*	*Rainfall*	*Application Rate*	*Application Timing*	*Environmental LD_{50}*	*Environmental EC_{50}*	*Environmental NOEC*	*ADI*	*Carcinogenicity*	*Mutagenicity*	*Neurotoxicity*	*Teratogenicity*	*Developmental/ Reproduction*	*Endocrine*	*Risk Phrase*		*LD_{50}*	*Dermal toxicity*	*Inhalation toxicity*	*Oral toxicity*	*Eye toxicity*
	Human Health Risk Indicators																													
22	Valcke et al. (2005)	*																*	*		*									
23	Steingrímsdóttir et al. (2018)																*													
24	Sugeng et al. (2013)	*	*	*	*							*						*				*		*						
25	van Asselt et al., (2018)							*									*	*												
	Combined Risk Indicators (Environmental and Human Health Risks)																													
26	EIQ (Kovach et al., 1992)	*	*											*	*			*	*		*	*				*	*			
27	ERI (Alister and Kogan, 2006)	*	*		*		*					*		*	*		*									*				
28	I-Phy (Van Der Werf and Zimmer, 1998)	*	*		*	*			*	*		*				*	*													

Table 2.1 Continued

	Method	Pesticide Mobility							Site Conditions			Agricultural Management		Ecotoxicity			Chronic Human Health									Acute Human Health				
		Persistence	*Adsorption*	*Solubility*	*Volatilisation*	*Drift*	*Bioaccumulation*	*Monitoring Data*	*Soil Conditions*	*Hydrologic Features*	*Rainfall*	*Application Rate*	*Application Timing*	*Environmental LD_{50}*	*Environmental EC_{50}*	*Environmental NOEC*	*ADI*	*Carcinogenicity*	*Mutagenicity*	*Neurotoxicity*	*Teratogenicity*	*Developmental/ Reproduction*	*Endocrine*	*Risk Phrase*		LD_{50}	*Dermal toxicity*	*Inhalation toxicity*	*Oral toxicity*	*Eye toxicity*
	Combined Risk Indicators (Environmental and Human Health Risks)																												
29	Pesticide Load (Kudsk et al., 2018)	*	*				*					*		*	*	*								*					
30	Yazgan and Tanik (2005)	*						*				*		*	*										*				
31	Casado-Martinez et al. (2018)	*					*						*		*		*												
32	PestScreen (Juraske et al., 2007)	*	*	*	*	*	*					*	*		*		*								*				
33	Swanson et al., (1997)	*					*							*	*	*		*							*	*			
34	Daginnus et al., (2011)	*					*	*				*				*		*	*			*		*					

In fact, I-Phy is the only risk indicator in Table 2.1 that can be used to prioritise high risk pesticides in terms of human health that incorporates soil conditions (as can be seen by the lack of asterisks under soil conditions in Table 2.1: Rows 14 – 34). This is despite the fact that soil properties such as texture, organic matter content, moisture content, pH, etc, have been shown to influence pesticide adsorption and transport (Bedmar et al., 2017; Gaona et al., 2019; Galon et al., 2021). Organic matter content of a soil has been found to be positively correlated with the adsorption of pesticides, thereby reducing transport to waterbodies (Dutta et al., 2015; Kumari and John, 2020). Additionally, the likelihood of a pesticide to be lost via runoff or leaching can be strongly influenced by the soil texture, with sandy soils being vulnerable to leaching and clayey soils more vulnerable to runoff (McGinley et al., 2022). Therefore, assessing pesticide mobility using pesticide properties only can give a misleading representation of likelihood of exposure, and as a result soil properties should be included in preliminary risk-screening tools to better identify high-risk pesticides.

An additional limitation of existing approaches is the use of LD_{50} (median lethal dose ($mg.kg^{-1}$)) or ADI (acceptable daily intake ($mg.kg\text{-}^{1}.day^{-1}$)) values in screening for high risk pesticides. This approach is widely used in the combined risk indicators, which consider both human and environmental health (Table 2.1: Rows 29 – 33). The use of these reference doses indicates an acceptable exposure level for acute/chronic health effects, but do not relate to specific health risks (Bos et al., 2009). While the use of such thresholds to screen for high risk pesticides has been widely used in preliminary risk screening (Juraske et al., 2007; Casado-Martinez et al., 2018), studies such as Sugeng et al. (2013) and Dabrowski et al. (2014) have highlighted the importance of considering evidence of specific chronic health effects in screening pesticides in drinking water supplies. For example, penthiopyrad is a category 2 carcinogen (i.e. a suspected carcinogen in humans) and a suspected endocrine disruptor (EFSA, 2021). However, it has a high LD_{50} (> 2000 $mg.kg^{-1}$) and a high ADI (0.1 $mg.kg^{-1}.day^{-1}$), which would suggest that it is a low-toxicity pesticide. Therefore, if a screening approach was used based on LD_{50} or ADI only, penthiopyrad would likely be given a low toxicity score despite evidence of serious health impacts. The incorporation of evidence of chronic health impacts, is becoming more common in human health risk indicators (Table 2.1: Rows 14 - 25), and can be used to identify

key pesticides in terms of chronic health effects that may not be labelled as high-risk under current risk screening approaches.

Pesticide regulations EC No. 1107/2009 (European Commission, 2009b) and No 2018/676 (European Commission, 2018) require the consideration of metabolites in pesticide registration in EU markets. Many metabolites are more toxic than their parent compound, such as those resulting from the degradation of prothioconazole and triclopyr (Matsushita et al., 2018), or are more mobile and persistent, such as glyphosate's metabolite AMPA (Meftaul et al., 2020). Therefore, pesticides may be considered low-risk based on their own mobility and toxicity using existing risk screening approaches, but the overall risk is underestimated due to the exclusion of their metabolites in screening (Li, 2021). Despite the growing concerns regarding metabolite risks (Hintze et al., 2020), very few studies have considered the effects of metabolites on overall potential pesticide risk. Steingrímsdóttir et al. (2018) developed a simple risk screening approach to identify high-risk metabolites, but, overall, little work has been done to incorporate metabolite risk into a pesticide risk screening approach.

The work in this thesis seeks to contribute to the existing knowledge gaps by building on approaches discussed in this section through improving the representation of chronic health risks and pesticide mobility in the scoring system, and incorporating metabolite risks into overall risk scores. These contributions are discussed in detail in Chapter 3, which develops and implements a new risk screening approach to identify pesticides of concern for further study in Chapters 4 and 5.

2.4 Pesticide Fate Modelling for Numerical Assessment

Although risk indicators as described in Section 2.3 are useful for screening purposes, as they can identify pesticides of concern or areas vulnerable to pesticide pollution, they do not simulate the processes involved in pesticide transport or pesticide concentrations in water, and cannot be used to predict the exposure profiles of pesticides (Dubus and Surdyk, 2006; Troldborg et al., 2022). Therefore, comprehensive models that can mathematically represent pesticide fate and transport processes to predict pesticide concentrations should be used in the development of quantitative risk assessments. The following section details several pesticide transport models used to predict pesticide concentrations in surface water which were

considered for use in the development of the quantitative risk assessment in Chapter 4, their suitability for probabilistic analysis, and the adaptations that will be made to the selected model for detailed numerical assessment in this thesis. Their suitability for probabilistic modelling is assessed under a number of criteria including: (1) balance between model complexity and proven realistic representation of pesticide transport process, (2) the practicality of applying probabilistic approaches to theoretical models considering level of expertise required to apply the model, the development of probabilistic distributions for a large number of data inputs, and the number of equations and theoretical complexity of the equations and (3) the availability of probabilistic data for the majority of the model parameters. The advantages and disadvantages of the models in relation to their use in pesticide fate modelling, and the development of a probabilistic model that can simulate pesticide runoff are summarised in Table 2.2.

Table 2.2: Strengths and limitations of surface water models

Model	Strengths	Limitations	Source
PRZM	Well-established and widely accepted for use in pesticide regulation in many jurisdictions such as the EU and USA. Simulates various processes involved in pesticide transport through soil, water, and air using physically-based approach. Can account for various conditions that affect pesticide transport, including land-use, agricultural management, and soil properties. Can simulate both overland runoff and subsurface flow. Can be integrated with other fate models.	Can be resource intensive to run for conditions outside of predefined FOCUS scenarios, development of probability distributions increases data demands. Extensive input data required, can be difficult to obtain accurate data for all parameters to develop probability distributions. Computationally complex and often needs to be combined with additional models e.g. TOXSWA to fully represent pesticide transport	Holvoet et al. (2007) FOCUS (2010) Luo et al. (2011) Labite et al. (2013) Te Roller et al (2015) Ippolito and Fait (2019) Marín-Benito et al. (2020)
MACRO	Detailed simulation of processes involved in subsurface flow, including infiltration and effects of macropores. Physically-based model better represents hydrological and chemical processes involved in subsurface flow than conceptual models. Widely used to simulate pesticide fate for pesticide regulation within the EU. Can account for various conditions that affect pesticide transport, including land-use, agricultural management, and soil properties.	Can be resource intensive to run for conditions outside of predefined FOCUS scenarios, development of probability distributions increases data demands. Only simulates transport through soil profile for single plot, does not account for pesticide fate processes once in a waterway. Physically-based approaches increases model computational demands and complexity, incorporation of probabilistic approaches can compound this complexity.	Stenemo and Jarvis (2010) Labite et al. (2013) Te Roller et al. (2015) Bach et al. (2017) Ippolito and Fait (2019) Troldborg et al. (2022)

Table 2.2 Continued

Model	Strengths	Limitations	Sources
TOXSWA	Simulates hydrodynamic and chemical processes affecting pesticide fate in aquatic environment. Can be easily integrated with other fate models or monitoring data. Widely used to simulate pesticide fate in waterbodies within the EU. Estimates concentrations at abstraction points instead of edge-of-field.	Requires detailed input data and significant computational power; development of probabilistic approaches can increase resource and data demand. Can be difficult to set-up and calibrate without software training. Only simulates pesticide fate within aquatic environment, not transport processes such as runoff or subsurface flow so must be used with additional models or monitoring data.	Labite et al. (2013) Te Roller et al. (2015) Bach et al. (2017) Holmes et al. (2018) Adriaanse et al. (2022)
SFIL	User-friendly model with relatively simple computational basis. Incorporates key factors in pesticide transport e.g. soil conditions, topography, agricultural management practices. Low input requirement allows for reduced resource demand for development of probability distributions. Can be easily adapted to a wide range of study sites. Has been shown to compare well to measured concentrations.	Simplified approach limits ability to represent complex processes involved in pesticide transport. Edge-of-field runoff model so does not consider in-stream hydrologic processes that can affect pesticide concentrations in waterbodies. Current representation of rainfall-runoff relationship in model limits applicability to many agricultural scenarios.	Reus et al. (1999) Berenzen et al. (2005) Probst et al. (2005) Oliver et al. (2016) Asfaw et al. (2018) Utami et al. (2020) Astaykina et al. (2020)

Table 2.2 Continued

Model	Strengths	Limitations	Sources
AGNPS	Simulates pesticide concentrations on a catchment scale, rather than just field scale so can better account for pesticide input into a waterbody. Simulates various processes involved in pesticide transport, enabling more realistic representation of system. Has been successfully integrated with GIS, which has improved representation of landscape characteristics and interpretation of results. Fewer data input requirements that fully physically-based models.	Substantial data input requirements, which would increase with application of probabilistic approaches. Uses empirical relationships to model some processes, which may oversimplify pesticide fate. AGNPS was not originally developed for modelling pesticide transport and therefore is somewhat limited in its incorporation of pesticide properties.	Young et al. (1989) Bosch et al. (2004) Xie et al. (2015) Adu and Kumarasamy (2018) Bigner et al. (2018) Zhang et al. (2020)
SWAT	Simulates pesticide concentrations on a catchment scale, rather than just field scale so can better account for pesticide input into a waterbody. Widely used and accepted in both pesticide research and regulation, one of the most widely used hydrologic model in literature. One of the best performing models for simulating pesticide concentrations compared to monitored data. Simulates various processes involved in pesticide transport, enabling more realistic representation of system.	Comprehensive modelling of pesticide concentrations requires substantial data input compared to other simulation models; resource demands are amplified when developing probability distributions. Computationally complex, requiring a level of knowledge and expertise, users may need training to accurately set-up and calibrate software. Integrating probabilistic approaches into computationally complex model can compound model complexity.	Quilbé et al. (2006) Gassman et al. (2007) Arnold et al. (2012a) Mottes et al. (2014) Xie et al. (2015) Adu and Kumarasamy (2018) Card et al. (2019) Wang et al. (2019) Dos Santos et al. (2020)

In order to numerically assess pesticide fate and hydrologic processes that influence the transport of pesticides to water bodies, various pesticide fate models have been developed (Payraudeau and Gregoire, 2012). Within the European Union, FOCUS was established to develop a framework for the assessment of pesticide concentrations in groundwater and surface water, and to define realistic worst-case scenarios that represent conditions in the European Union (FOCUS, 1995, 1997). FOCUS proposed the use of a surface water modelling framework (SWASH) to predict environment concentrations for pesticide regulation in European countries. This framework consists of three pesticide fate models: $PRZM_{SW}$, MACRO and TOWSWA (Te Roller et al., 2015). $PRZM_{SW}$ and MACRO are used to estimate pesticide transport via overland flow and drainage flow, respectively. The outputs from these models then inform TOXSWA, which generates the predicted concentrations of pesticides, considering the fate of pesticides in surface water (Holmes et al., 2018). Other processes that affect the transport of pesticides to waterbodies, such as volatilisation, absorption by crops, sorption and degradation, are also considered in the above models. Software has been made available to the general public based on the defined scenarios, resulting in the wide use of FOCUS models in regulation and research (Teklu et al., 2015; Pereira et al., 2017; Marín-Benito et al., 2020).

Such models are very helpful when the model user intends to implement the model using a parameterised scenario developed by FOCUS. Within the surface water modelling framework, 12 generalised scenarios are available for use to represent runoff sites in European countries. However, the use of generalised scenarios limits the spatial relevance of the models' outputs and cannot reflect the actual pesticide concentrations at a study site (Labite et al., 2013; Ippolito and Fait, 2019). These models are computationally demanding and require significant amounts of soil, climate, hydrologic data, etc. to run, which makes adapting the models for use outside of FOCUS scenarios difficult and time consuming (Vanderborght et al., 2011; Whelan et al., 2020). For example, to apply even just the $PRZM_{SW}$ component of the SWASH model, up to 40 parameters may need to be defined by the user should the models be used outside of FOCUS-defined scenarios (FOCUS, 2010). Significant costs would be associated with developing datasets to allow FOCUS models to be widely applied outside of the generalised scenarios (Rainford et al., 2020). The large range of input parameters makes applying probabilistic distributions to data very time consuming

(Whelan et al., 2020; Troldborg et al., 2022), and limits the practicality and efficiency of applying a probabilistic approach in using the FOCUS models. Additionally, running each element of the SWASH modelling shell would also be very time consuming because of the level of processing required. Bach et al. (2017) suggested that running MACRO for 1000 site combinations could take up to 120 hours, and TOXSWA even longer. Therefore, even if the models were incorporated to allow for a fully probabilistic model, with all parameters represented by developed probabilistic distributions, the running time for using these models with a large amount of probabilistic parameterisation is not realistic for most users.

The FOCUS framework is also limited to field-scale or edge-of-field analysis which may not consider input data from more than one field and tends to overestimate pesticide concentrations in large catchments (Holvoet et al., 2007). To address the need for catchment/watershed-scale analysis, software for a number of hydrologic models has been developed to assess pesticide fate and transport from field to surface water on a catchment-scale. Two such software programmes are SWAT (Arnold et al., 2012a) and AGNPS (Young et al., 1989; Bingner and Theurer, 2001). SWAT is a deterministic, process-based watershed model and has been widely used in hydrologic and pollutant transport assessments under various conditions (Gassman et al., 2007; Arnold et al., 2012a; Wang et al., 2019b; dos Santos et al., 2020). It is one of the most widely used hydrologic models globally (Card, 2019), and has been shown to be one of the best performing models in simulating pesticide processes at catchment-scale in reviews of a number of pesticide models (Quilbé et al., 2006; Payraudeau and Gregoire, 2012; Mottes et al., 2014). AGNPS is an event-based simulation model that has been used to estimate runoff and pollutant transport from agricultural watersheds (Young et al., 1989). It has been found to be a useful method for identifying areas in a watershed at higher risk of chemical transport (Zhang et al., 2020). Both SWAT and AGNPS apply a similar technique of using hydraulic units or spatial cells to divide a watershed into smaller homogenous areas to represent spatial variability within a watershed (Bigner et al., 2018).

However, the use of such comprehensive software results in significant data and resource requirements, with over 60 user-defined input parameters required to calibrate SWAT, and 34 individual input categories involved in setting-up AGNPS (Bosch et al., 2004; Arnold et al., 2012a). This can make model parameterisation for

specific study sites difficult (Arnold et al., 2012b; Shen et al., 2012; Adu and Kumarasamy, 2018; Troldborg et al., 2022), and the lack of available data affects the accuracy of the model output (Troldborg et al., 2022). While some studies have developed useful approaches to apply probabilistic modelling to process-based models, such as Winchell et al. (2018), who modelled pesticide application scenarios probabilistically, and Tasdighi et al. (2018), who applied probabilistic approaches to model the rainfall-runoff relationship, they tend to be relatively limited to just a handful of the many required input parameters. Some studies have found watershed models such as SWAT to be overly complex to set-up and parameterise for pesticide modelling (Baris et al., 2012; dos Santos et al., 2020). Furthermore, the use of either model requires an in-depth understanding of the modelled hydrological processes and significant programming competence (Adu and Kumarasamy, 2018; Wang et al., 2019b), making such models unsuitable for a broad user-base (Schulz and Matthies, 2007; Whelan et al., 2020).

Models are typically only as accurate as the input data used (Ross et al., 2015), therefore the lack of real data and the use of extrapolated or assumed values can result in significant inaccuracies in data-intensive models, such as those previously discussed. Consequently, the adoption of more simplistic models with fewer data inputs can avoid the use of inaccurate or extrapolated data, and the resulting outputs may be comparable to much more complex models (Pullan et al., 2016). Simplified models may also encourage the application of transport models into pesticide management systems among a wider user-base, as users are not deterred by the complexity or training requirements (Xie et al., 2015). In the process of selecting suitable models, the importance of balancing the accuracy of model output with model complexity and data requirement should be considered (Whelan et al., 2020).

The OECD's 'Simplified Formula for Indirect Loading from runoff' (SFIL) is a less computational and resource demanding approach to assess pesticide fate and transport than some of the other models used in pesticide assessments. The SFIL is based on the deterministic RETOX submodel proposed by Reus (Reus et al., 1999) and can be used to estimate the percentage of an applied dose that will be lost in runoff after a rainfall event. It allows for the incorporation of pesticide physio-chemical properties, soil, hydrologic and climate conditions, and agricultural practices, unlike simple risk

indicators, but with a reduced data and computational demand compared to the more complex modelling software. The SFIL has formed the basis of many environmental indicators such as the Pesticide Impact Rating Index (PIRI) (Kookana et al., 2005) and the Environmental Potential Risk Indicator for Pesticides (EPRIP) (Padovani et al., 2004). The SFIL, and the indicators based on this submodel, have been widely applied in literature to estimate pesticide runoff (Oliver et al., 2016) and have been modified for GIS-based modelling approaches (Verro et al., 2002; Schriever and Liess, 2007) as well as some probabilistic approaches (Clarke et al., 2016). However, the original SFIL can only estimate the percentage of the applied pesticide lost to field runoff and does not account for the concentrations of pesticide in the water phase of a stream. Berenzen et al. (2005) added another mathematical expression to the SFIL, incorporating stream flowrate to account for in-stream concentrations. This runoff model has the benefit of considering the relationships between pesticide physiochemical properties, site conditions, agricultural management, and climate, with reduced computational and data demands compared to more complex models. The modified SFIL only has a total of 22 input parameters, compared to SWAT's 60-plus (Utami et al., 2020). This modified SFIL has been used in several runoff studies and has compared relatively well to monitoring data from several German catchments (Berenzen et al., 2005; Probst et al., 2005) and a river in Indonesia (Utami et al., 2020). It also forms the basis of pesticide risk assessments methods used by the Australian Pesticide and Veterinary Medicine Authority for pesticide regulation in Australia (APVMA, 2020), has been recommended for use by the New Zealand EPA (EPA NZ, 2020), and has been combined with other pesticide transport models to create a physically distributed surface runoff model which was successfully used to predict peak metaldehyde concentrations in a British catchment (Asfaw et al., 2018).

However, there are several limitations associated with the SFIL that affect its applicability and reliability. Firstly, both the original SFIL and the modified SFIL estimate runoff volume using a method described by Lutz (1984) and Maniak (1992), which cannot represent localised soil and site conditions (Astaykina et al., 2020). The SFIL is also hindered by the fact that it is an edge-of-field model like PRZM simulated runoff, and therefore does not account for any changes to pesticide concentrations once pesticides enter a waterway. Another issue with the existing SFIL model is that the accuracy of modelled outputs from simple, mathematical models will always be

affected by its limited ability to consider complex chemical and hydrologic processes involved with pesticide fate and behaviour (Siber et al., 2009). Additionally, as the model is used deterministically, it fails to account for the uncertainties in model inputs and the inherent variabilities associated with the modelled processes (Troldborg et al., 2022).

The SFIL model was selected for this thesis on the balance of strengths and limitations as discussed in Table 2.2, considering (1) accuracy of output compared to model complexity, (2) resource demands for development of probabilistic distributions for model input, and (3) model suitability for probabilistic approaches considering number of input parameters and mathematical complexity. However, as discussed, the SFIL in its current state is limited in its ability to represent a range of realistic site conditions and the fate of pesticides once they enter a waterbody. Therefore, model outputs may over or underestimate pesticide concentrations in drinking water. In order to address these limitations a number of novel modifications were made to improve model output: (1) the current approach to assess runoff volume, which is limited to only two soil types and three land-use scenarios, was replaced with the USDA's Soil Conservations Service (SCS) curve number approach (USDA, 2004b) which produces runoff volume estimates for a much wider range of specific site scenarios, and is widely used in more complex pesticide transport models, (2) modelling of pesticide fate was expanded beyond edge-of-field through the inclusion of in-stream processes such as in-stream degradation, sedimentation and adsorption that may take place while pesticides are in a waterbody prior to abstraction for drinking water, and (3) development of probability distributions for a range of model input parameters to improve the consideration of data uncertainty and variability in the existing model. Chapter 4 provides more detail of these novel modifications made to the SFIL model to improve model output, as well as the steps taken to adapt the model to a probabilistic approach.

2.5 Climate Change Influences on Pesticide Risks

The Intergovernmental Panel on Climate Change (IPCC) has concluded that greenhouse gas emissions have caused substantial global warming, resulting in changes to the long-term climate characteristics in different regions (IPCC, 2023). The changes in weather patterns and hydrological effects are projected to have detrimental

effects on water security (Chantal et al., 2023), and resulting changes to pollutant loading, including pesticides, are likely to reduce water quality (Kaka et al., 2021). It has been suggested that climate change will also affect the fate and mobilisation of pollutants such as pesticides, altering the rate of exposure to such chemicals and therefore resulting risks (Balbus et al., 2013; Nadal et al., 2015). The fate and mobility of pesticides is highly dependent on-site conditions and the physio-chemical properties of the pesticide, which, in turn, are affected by climatic conditions (Bernardes et al., 2015). Therefore, climate change has the potential to have direct impact on pesticide risks due to this influence on fate and transport, but also may indirectly impact pesticide risks due to changes in pest prevalence and agricultural practices in response to a changing environment (Biswas et al., 2018; Grünig et al., 2020; Hader et al., 2022).

Changes in temperature and rainfall patterns are predicted to have the greatest influence on pesticide risk as direct impacts of climate change (Noyes et al., 2009). Intense rainfall can increase the transfer of pesticides from application sites to waterbodies via runoff and leaching (Biswas et al., 2018). Therefore, any changes to frequency and intensity of precipitation is expected to have a direct impact on pesticide mobility. As higher latitudes are projected to experience heavier precipitation as a result of climate change, this is likely to increase pesticide loading to drinking water supplies particularly in Northern Europe (Noyes et al., 2009). Additionally, rising daily temperatures in higher latitudes are associated with a more productive agriculture sector and prolonged growing seasons, but also increased pest prevalence (Grünig et al., 2020; Nolan and Flanagan, 2020). This may indirectly impact pesticide risk due to changes in agricultural management in response, as increased pest prevalence may require higher application rates of pesticides, resulting in greater pesticide loading to waterbodies (Tudi et al., 2021). Additionally, the prolonged growing season may result in pesticide applications coinciding with periods of heavy winter rainfall, which would also intensify pesticide transfer to waterbodies (Rosenzweig et al., 2001; Delcour et al., 2015).

Despite the valuable work done in identifying key climate change parameters on pesticide transport and risk, there is still a recognised need to develop a quantitative understanding of these impacts for the provision of informed decision-making and management strategies (Hader et al., 2022; Bolan et al., 2024). Climate change

projections are associated with significant uncertainty due to the spatial and temporal variability within climate systems (Kong et al., 2013). Therefore, probabilistic modelling approaches should be utilised in order to capture this inherent uncertainty in order to fully integrate climate change projections into pesticide risk assessments (Steffens et al., 2015; Sperotto et al., 2019). However, this area of research is still very limited, with the majority of probabilistic risk modelling focused on predicting pesticide risk under current climatic conditions, without consideration of climate projections in modelling that may change future risk profiles (Oldenkamp et al., 2024).

The limited work in this area has focused on a few key areas of pesticide assessment to date. Kattwinkel et al. (2011), Steffens et al. (2015), and Gagnon et al. (2016) worked on incorporating climate projections into pesticide transport models to assess the environmental fate of pesticides within Europe and Canada, through the use of Monte-Carlo simulations. Gagnon et al. (2016), found that the changes in pesticide concentrations in Canadian surface waters for mid-century were statistically insignificant. However, both Kattwinkel et al. (2011) and Steffens et al. (2015) found that climate change is likely to increase pesticide concentrations in surface waters and groundwaters within the EU and Sweden, respectively. More recently, Moe et al. (2024) have developed a framework to incorporate climate projections into environmental risk assessments using Bayesian Networks. This framework has been utilised in a number of case studies in order to assess the environmental impact of pesticides under future climates in Norwegian waterbodies using WISPE model (Mentzel et al., 2022a; Oldenkamp et al., 2024) and in Mediterranean rice-fields using RICEQW (Martínez-Megías et al., 2023). While environmental risks arising from the majority of modelled pesticides under future climates were found to decrease in a Mediterranean climate due to increased temperatures and decreased precipitation (Martínez-Megías et al., 2023), climate change was shown to moderately increase environmental risks in Norwegian case-studies (Mentzel et al., 2022a; Oldenkamp et al., 2024).

These studies have contributed significantly to the area of quantifying climate change impacts on pesticide risks by developing approaches to incorporate climate projections into environmental risk models. However, the approaches taken in these studies to assess changes in climate have been restrained due to the selected base climate models used in their assessments. For example, both Mentzel et al. (2022) and Oldenkamp et

al. (2024) used only two climate model ensembles in developing their climate variables for future climates, which were not bias-corrected. The use of a limited number of ensembles can restrict the ability to represent uncertainty and variability in climate change due to the intrinsic variability of climate projections (Moe et al., 2022), and the use of projections that have not been bias-corrected provide a less robust and reliable representation of future climates and are more likely to contain systematic biases arising from the base climate models (Navarro-Racines et al., 2020; Copernicus, 2021). Additionally, the use of lower-resolution climate projections (>12 km) such as those used in the discussed studies (Mentzel et al., 2022a; Martínez-Megías et al., 2023), can limit the representation of localised variability in climate change effects (Tapiador et al., 2020; Kotamarthi et al., 2021).

It has been found that climate change is likely to alter pesticide concentrations in waterbodies and resulting environmental risks, depending on the combination of climate effects in different regions (Kattwinkel et al., 2011; Moe et al., 2024). Therefore, it is critical to quantify the potential impacts of climate change may also have on human health risks in order to better inform the need for future climate adaptation strategies and public health plans. However, little to no work has been done in this area (Gatto et al., 2016; Langreiter et al., 2023). The work presented in Chapter 5 of this thesis aims to adapt the probabilistic human health risk assessment framework developed in Chapter 4 to facilitate the quantification of future pesticide health risk under changing climates for one of the first times in published literature. The work detailed in Chapter 5 also seeks to improve on the existing work in environmental risk assessments through the development of climate variables based on multiple climate ensembles obtained from bias-corrected and downscaled regional climate projections.

2.6 Summary of Existing Limitations and Thesis Contributions

An analysis of existing risk screening tools and health risk modelling approaches were carried out to investigate the limitations of state-of-art risk assessments under current and future climatic conditions. This analysis revealed several key areas that could be built on to improve consideration of site conditions, application of probabilistic approaches and adaptation for climate projections:

- Current risk screening tools tend to be limited in their consideration of human health impacts, effects of metabolites on overall risk, and influence of site conditions on pesticide mobility. These identified gaps may result in over simplistic representation of risk, and the incorporation of these factors into semi-quantitative risk screening tools would provide a more realistic representation of overall risk.
- The computational complexities and high resource demands required for developing probability distributions for wide range of input parameters associated with complex, process-based pesticide fate models poses significant challenges for the use of probabilistic modelling. It was found that the use of a more accessible simulation model as a base model, with fewer data requirements, would provide a more practical approach for probabilistic analysis.
- Existing approaches to quantify the impacts of climate change on future pesticide risks are constrained by the use of a limited number of low-resolution climate models that lack bias correction. This can lead to significant biases and poor representation of model uncertainty and localized variability. Improvement in this area can be achieved through the utilisation of high-resolution, bias-corrected climate projections obtained from multiple ensembles, enhancing the accuracy and reliability of future risk predictions.

This thesis aims to develop a practical approach for probabilistic pesticide risk assessment under current and future climates, following a framework of tiered risk assessment. The following chapters detail the work carried out to develop these new tools and build on existing approaches addressing the limitations identified above as follows:

- Chapter 3 presents the development of a new human health risk screening approach that contributes to the existing state-of-art discussed in Section 2.3 by (1) incorporating a pesticide mobility indicator that considers the relationship between pesticide properties and site conditions into a health risk screening framework, thereby better representing pesticide mobility, (2) using EFSA evidence of key chronic health effects to assess pesticide health impacts, in place of reference doses, and (3) considering how a pesticide's metabolite may alter the pesticide risk profile by including metabolite risk in the overall risk screening approach.

- Chapter 4 develops a new probabilistic health risk assessment approach based on the SFIL model and discusses how the model has been adapted by (1) better representing real site scenarios by incorporating additional factors to model rainfall-runoff relationship, (2) improving model outcomes by including in-stream processes in transport modelling, and (3) by expanding the model to facilitate probabilistic approaches through development of probability distributions for input parameters.
- Chapter 5 adapts the work presented in Chapter 4 for future climate scenarios to present a novel approach for the quantification of climate change impacts on future pesticide risks on human health. This will be achieved by (1) developing a framework to generate growing season-specific climate variables to incorporate into probabilistic health risk assessment and (2) building on the learnings of limited work in quantifying climate change impacts on pesticide human health risks through the use of bias-corrected and downscaled (1 km resolution) climate projections from multiple ensembles (more than 27 ensembles). The use of these projections in developing probability distributions for climate variables will enable better representation of the regional variability of climate projections, and help address the innate uncertainties and systematic biases that exist in climate models.

CHAPTER 3

A RISK RANKING OF PESTICIDES FOR CHRONIC HEALTH EFFECTS IN IRISH DRINKING WATER

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ABSTRACT

This paper presents a novel scoring system which facilitates a relative ranking of pesticide risk to human health arising from contaminated drinking water. This method was developed to identify risky pesticides to better inform monitoring programmes and risk assessments. Potential risk was assessed considering pesticide use, chronic human health effects, and environmental fate. Site-specific soil conditions, such as soil erodibility, hydrologic group, soil depth, clay, sand, silt, and organic carbon content of soil, were incorporated to demonstrate how pesticide fate can be influenced by the areas in which they are used. The indices of quantity of use, consequence and likelihood of exposure, hazard score and quantity-weighted hazard score were used to describe the level of concern that should be attributed to a pesticide. Metabolite toxicity and persistence were also considered in a separate scoring to highlight the contribution metabolites make to overall pesticide risk. This study presents two sets of results for 63 pesticides in an Irish case study, (1) risk scores calculated for the parent compounds only and (2) a combined pesticide-metabolite risk score. In both cases the results are assessed for two locations with differing soil and hydrological properties. The method developed in this paper can be adapted by pesticide users to assess and compare pesticide risk at site level using pesticide hazard scores. Farm advisors, water quality monitors, and catchment managers can apply this method to screen pesticides for human health risk at a regional or national level.

3.1 INTRODUCTION

Pesticides are fundamental in securing food supplies by reducing crop losses through the deterrent, elimination, or regulation of pests, fungi, insects, and weeds (FAO and WHO, 2014; Cerda et al., 2017). However, pesticide use has been found to pose a major threat to the environment (Carvalho, 2017), and low but repeated exposure has been linked to several human health disorders (Abreu-Villaça and Levin, 2017; Parker et al., 2017; Wee et al., 2019; Yin et al., 2020; El-Nahhal and El-Nahhal, 2021a). Governmental legislation regulates approval of pesticides on the European market and promotes their sustainable use to reduce overall pesticide risks (European Commission, 2009a, b). Such legislation requires the evaluation and classification of pesticide risk through incremental stages including data collection, priority-setting, risk-assessment, and risk reduction, before official registration for use (Handford et al., 2015; Fargnoli et al., 2019). Priority-setting is a first step in pesticide risk assessment using qualitative or semi-quantitative risk scoring to identify pesticides of concern without the considerable resources and time associated with full risk assessments (Baptista et al., 2012; Reist et al., 2012). This should be carried out at the start of any assessment to screen high risk pesticides and enable efficient allocation of resources for targeted risk-assessments and the implementation of monitoring programmes of high-risk pesticides (Chou et al., 2019; Vryzas et al., 2020).

Earlier efforts to develop risk ranking methods, such as the Treatment Frequency Index (Kudsk, 1989), were based on the quantity of pesticide applied relative to the acceptable dosage. Over the last thirty years, risk ranking has progressed using criteria such as mobility and persistence in the environment, ecotoxicological effects on non-target organisms (Alister and Kogan, 2006), toxic effects on the human population (Gunier et al., 2001; Cha et al., 2014; Choi et al., 2020), or a combination of these criteria (Sugeng et al., 2013; Dabrowski et al., 2014; Kudsk et al., 2018). While such methods may be considered useful, various limitations, such as a reliance on pesticide physio-chemical properties to assess mobility, the use of animal health indicators to represent human health risk and the exclusion of metabolites, reduce their effectiveness and reliability for ranking and comparing pesticide risk. This limits their ability to properly inform future risk assessments or pesticide monitoring programmes.

Understanding pesticide mobility is key in evaluating the likelihood of exposure to pesticides from drinking water. Detailed risk assessments methods and pesticide transport modelling tools used in pesticide registration recognise that site and climatic conditions, soil and hydrologic properties, and agricultural management have considerable effects on pesticide mobility (Sabatier et al., 2014; Bedmar et al., 2017); therefore, these parameters are included in such analysis (Young and Fry, 2014). Despite the recognised need to consider this relationship, existing pesticide prioritisation and pesticide risk ranking tools tend to base mobility assessment solely on a pesticide's physio-chemical properties. Most studies use pesticide-specific properties such as half-life and soil adsorption coefficients (Valcke et al., 2005; Yazgan and Tanik, 2005; Sugeng et al., 2013); or physio-chemical based mobility indicators such as GUS as used by Dabrowski et al. (2014), and the SCI-GROW index as used by Kudsk et al. (2018). This study aims to improve on existing pesticide risk ranking tools by considering both pesticide properties and soil conditions using a more comprehensive mobility indicator, thus demonstrating that more realistic representations of pesticide mobility can be considered in easy-to-use risk screening tools.

The use of various toxicity indicators in literature to represent the human health risks posed by pesticide use presents another significant challenge in scoring pesticide risk. Two commonly used indicators are the reference doses, LD_{50} and ADI, for example in the risk screening approaches developed by Alister and Kogan (2006) and Juraske et al. (2007), respectively. These reference doses are based on animal testing and are extrapolated to describe the levels of acceptable exposure to humans. However, neither indicator describe the type of health effect or its severity. An exceedance of the ADI cannot determine if the resulting effect is a minor or major health concern (Bos et al., 2009), and LD_{50} represents the dose that would be fatal to 50% of a population as opposed to providing information about the health effects resulting from pesticide exposure. This study will use an adapted method of ranking pesticide toxicity based on several risk scoring studies (Gunier et al., 2001; Valcke et al., 2005; Sugeng et al., 2013; Dabrowski et al., 2014). Like these studies, the toxicity potential will be scored based on evidence of chronic health effects in place of reference doses that can only suggest a potential harm to human health.

Pesticide risk is dependent on its toxicity and environmental fate, but its metabolites can also contribute to this risk. Once released into the environment, pesticides are liable to breakdown into transformation products known as metabolites (Sinclair et al., 2006), which may move into drinking water sources and expose consumers to both metabolites and their parent compounds. There are growing concerns surrounding metabolites (Hintze et al., 2020) as they tend to be more mobile and persistent, have been detected at higher concentrations (Sinclair et al., 2006; Kameya et al., 2012; Escher et al., 2020) and may be more toxic than parent compounds such as the metabolites of glyphosate, prothioconazole and triclopyr (Fenner et al., 2013; Matsushita et al., 2018). Regulation EC 1107/2009 requires that relevant metabolites be included in assessments of pesticides for registration in the EU (European Commission, 2009b) and as a result models used for pesticide registration and legislation in the EU consider metabolites (Boesten et al., 2014). However, no pesticide risk ranking tools could be identified by the authors that combine metabolite and pesticide risk. This study attempts to combine the direct risk associated with contamination of drinking water due to the use of a pesticide with the indirect risk due to the formation of metabolites in drinking water supplies. This will highlight how some pesticides that are considered "low-risk" may need to be prioritised due to their higher-risk metabolites (Labite and Cummins, 2012).

The aim of this study was to develop an easy-to-use risk screening tool, which builds on existing literature by (1) combining pesticide properties and soil characteristics to give 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 the risks associated with a pesticide's metabolites. This tool can then be implemented by pesticide users, farm advisors, and other stakeholders to screen high-risk pesticides at a local level or help catchment managers identify pesticides that may need more detailed assessments. The developed methodology was illustrated by applying it to a specific Irish case study.

3.2 Materials and Methodology

3.2.1 General Approach

The risk associated with pesticide use can be defined as a function of the likelihood of exposure and the consequence of this exposure (FAO, 2018). The framework of the

risk ranking comprises of three main stages that (1) calculate the likelihood of exposure score, (2) calculate the consequence of exposure, and (3) incorporate metabolite data, with hazard scores calculated at the end of these steps (Figure 3.1). Each stage involves gathering and scoring parameters. The parameters required for user implementation of the risk ranking scheme and sources for these data in the study's case study are provided Appendix A1. 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 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. 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 the overall pesticide use over the period of investigation. This study also attempted to assess the risk from metabolites and consider how this affects their parent compound risk (Stage 3: Figure 3.1). This method was applied to an Irish case study with two locations to assess pesticide risk at site-scale and national-scale using Irish quantity data.

3.2.2 Likelihood of Exposure

The first stage of the assessment shows how mobility in soil and persistence in water scores are combined to score the likelihood of exposure to water consumers (Stage 1: Figure 3.1).

3.2.2.1 Mobility in Soil

Mobility in soil is a key component of pesticide risk as it represents the potential for a pesticide to leave its application site and enter water sources, increasing exposure risk to consumers (Oliver et al., 2016). As both groundwater and surface water can be used for drinking water supplies, the mobility to both sources should be evaluated separately to fully understand the risk associated with pesticide mobility.

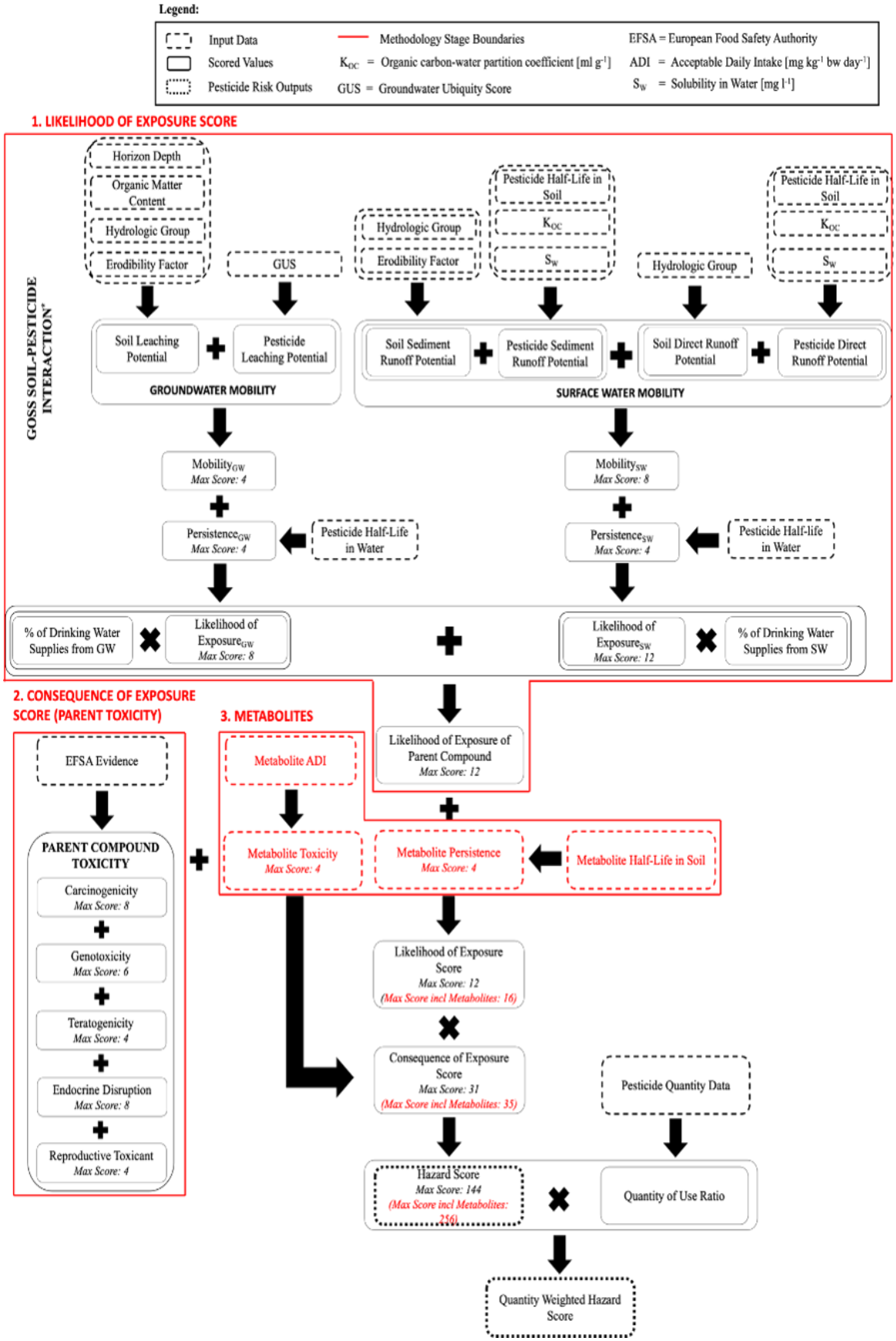


Figure 3.1: Methodology framework showing the interaction between Likelihood of Exposure (Stage 1), Consequence of Exposure (Stage 2) and Metabolites (Stage 3). Maximum values given for parameters and risk scores in each stage are discussed in Sections 3.2.2 – 3.2.4

Several methods have been used in literature to predict the transport of pesticides (Gurdak, 2014; Perez Lucas et al., 2018; Akay Demir et al., 2019). The Goss method (Goss, 1992) was selected to assess the mobility of pesticides as it considers leaching to groundwater and runoff to surface water in a single indicator. It is relatively simple to use, and the data required to carry out assessment are easily accessible using online pesticide and soil databases or site-based soil tests. The scoring consists of (1) a soil rating for leaching and runoff based on soil characteristics (Table A2), and (2) a pesticide rating for leaching and runoff based on the pesticide parameters (Table A3), combined for a leaching and runoff score for each soil-pesticide interaction. The mobility potential of the soil and pesticide was qualitatively rated using soil properties, such as organic matter content and hydrologic group, etc. and pesticide properties such as half-life (Table 3.1). Soil-pesticide mobility matrices (Table 3.2) scored the leaching and runoff potential for each soil-pesticide interaction based on the ratings from Table 3.1 (Zhang et al., 1997). Separate mobility scores for groundwater ($Mobility_{GW}$) and surface water ($Mobility_{SW}$) were obtained from the combined soil-pesticide mobility matrices in Table 3.2 as shown in Stage 1 of Figure 3.1 and Eqs. 3.1 and 3.2:

$$Mobility_{GW}\ Score = Leaching\ Score \tag{3.1}$$

$$Mobility_{SW}\ Score = Sediment\ Runoff\ Score + Direct\ Runoff\ Score \tag{3.2}$$

The Goss method used here to score pesticide mobility assesses mobility via leaching, direct runoff, and sediment-based runoff. It is important to note that sediment-sorbed pesticides may not be a priority exposure pathway for many consumers of treated surface water, and therefore readers are advised to consider the relevance of sediment runoff when assessing pesticide mobility.

Table 3.1: Goss' criteria for evaluating soil-pesticide mobility potential

	Transport Method	High	Low	Very Low	Moderate	References
Soil	Leaching	HG A & OM x D ≤ 30 **OR** HG B & OM x D ≤ 9 & K ≤ 0.48 **OR** HG B & OM x D ≤ 15 & K ≤ 0.26	HG B & OM x D ≥ 35 & K ≥ 0.4 **OR** HG B & OM x D ≥ 45 & K ≥ 0.2 **OR** HG C & OM x D ≤ 10 & K ≥ 0.28 **OR** HG C & OM x D ≥ 10	HG D	Anything else	Adapted from Goss 1992
	Runoff (sediment)	HG C & K ≥ 0.21 **OR** HG D & K ≥ 0.1	HG A **OR** HG B & K ≤ 0.1 **OR** HG C & K ≤ 0.07 **OR** HG D & K ≥ 0.05	-	Anything else	
	Runoff (direct)	HG C **OR** HG D	HG A	-	HG B	
Pesticide	Leaching	GUS > 2.8	0 < GUS < 1.8	GUS < 0	1.8 ≤ GUS ≤2.8	
	Runoff (sediment)	DT_{50} ≥ 40 & K_{OC} ≥ 1000 **OR** DT_{50} ≥ 40 & K_{OC} ≥ 500 & S_W ≤ 0.5	DT_{50} ≤ 1 **OR** DT_{50} ≤ 2 & K_{OC} ≤ 500 **OR** DT_{50} ≤ 4 & K_{OC} ≤ 900 & S_w ≥ 0.5 **OR** DT_{50} ≤ 40 & K_{OC} ≤ 500 & S_W ≥ 0.5	-	Anything else	
	Runoff (direct)	S_W ≥ 1 & DT_{50} > 35 & K_{OC} < 100000 **OR** S_W > 10 & DT_{50} < 100 & K_{OC} ≤ 700	K_{OC} ≥ 100000 **OR** K_{OC} ≥ 1000 & DT_{50} ≤ 1 **OR** S_W < 0.5 & DT_{50} < 35	-	Anything else	

HG = Soil Hydrologic Group (USDA, 2009), K = Soil K (Erodibility) Factor (Panagos et al., 2014), OM x D = Soil Organic Matter Content x Horizon 1 Depth, GUS = Groundwater Ubiquity Score = log(DT_{50}) x (4-log(K_{OC})) (Gustafson, 1989), DT_{50} = Pesticide Half-Life, K_{OC} = Pesticide Organic Carbon Adsorption Coefficient, S_w = Pesticide Solubility in Water

Table 3.2: Soil-Pesticide interaction matrix for mobility potential

	Pesticide Leaching Potential				
Soil Leaching Potential	Very Low	Low	Moderate	High	Reference
Very Low	1	1	2	2	Zhang et al. 1997
Low	1	2	2	3	
Moderate	2	2	3	4	
High	2	3	4	4	
	Pesticide Sediment Runoff Potential				
Sediment Runoff Potential	Low	Moderate	High		Reference
Low	1	2	3		Zhang et al. 1997
Moderate	2	3	4		
High	3	4	4		
	Pesticide Direct Runoff Potential				
Soil Direct Runoff Potential	Low	Moderate	High		Reference
Low	1	2	3		Zhang et al. 1997
Moderate	2	3	4		
High	3	4	4		

3.2.2.2 Persistence in Water

Consumers are more likely to be exposed to a persistent substance, allowing for a greater opportunity to cause toxic effects, thus making it a crucial factor in pesticide risk (Valcke et al., 2005). Pesticide persistence in soil and water affect potential for water contamination. Half-life in soil was considered in assessing mobility in soil, so only aqueous persistence was considered herein. Pesticide persistence is influenced by the type of water body they contaminate due to the physical, chemical, and microbial conditions of the different environments. Therefore, pesticide persistence is assessed separately for groundwater and surface water.

Aqueous hydrolysis, the chemical degradation of a pesticide in water, was selected to assess persistence in surface water as it was considered to be the main degradation pathway based on literature (Sinclair et al., 2006; Yang et al., 2017). If a pesticide does not undergo hydrolytic degradation, the water-sediment half-life was used for persistence in surface water (Sinclair et al., 2006). Persistence in groundwater was determined using hydrolysis half-life only as this is considered to be the most relevant degradation process in groundwater (Sinclair et al., 2006; Yang et al., 2017). A nominal half-life of 30 days was used for groundwater persistence if the pesticide does

not undergo hydrolytic degradation, as suggested by the EFSA (EFSA, 2014). Data can be obtained from the EFSA (EFSA, 2021) or Pesticide Property Database (PPDB) (Lewis et al., 2016) in the case of missing EFSA data and were scored as shown in Table 3.3. In line with the approach commonly used in literature, a higher score was given in the case of missing data than was given for very low persistence, due to the uncertainty associated with missing data (Valcke et al., 2005; Dabrowski et al., 2014).

Table 3.3: Pesticide persistence scoring system

Half-life	Score	Reference
180 days ≤ DT_{50}	4	Yang et al 2017
60 days ≤ DT_{50} < 180 days	3	
15 days ≤ DT_{50} < 60 days	2	
No Data	1.5	
DT_{50} < 15 days	1	

As is common practice in literature, the likelihood of exposure for groundwater (LES_{GW}) and surface water (LES_{SW}) was assessed by adding persistence in groundwater and surface water scores to their respective mobility scores (Figure 3.1 and Eqs. 3.3 and 3.4) (Whiteside et al., 2008; Choi et al., 2020).

$$LES_{GW} = Mobility_{GW} + Persistence_{GW} \quad (3.3)$$

$$LES_{SW} = Mobility_{SW} + Persistence_{SW} \quad (3.4)$$

The final likelihood of exposure was obtained by combining groundwater and surface water scores, for a maximum score of 12. The ratio of drinking water from groundwater and surface water was considered to reflect the localised variability in drinking water sources (Eq. 3.5). Therefore, users may calculate risk for drinking water contamination sourced from groundwater or surface water only or for both.

$$LES = (LES_{GW} \times \%\ Drinking\ Water_{GW}) + (LES_{SW} \times \%\ Drinking\ Water_{SW}) \quad (3.5)$$

3.2.3 Consequence of Exposure

The consequence of exposure (Stage 2: Figure 3.1) was assessed using methods from existing studies (Valcke et al., 2005; Sugeng et al., 2013; Dabrowski et al., 2014). This approach was selected in place of reference doses as it can provide more specific epidemiological information (Valcke et al., 2005) about chronic health effects that are required to be considered in chemical risk assessments by Regulation (EC) No.

1907/2006 (European Commission, 2006). This is particularly valuable for the identification of potential carcinogenic pesticides as ADIs are only used to assess non-carcinogenic chronic health risks (USHHS, 2022). The use of pesticide-relevant toxicological concerns enables users to identify pesticides that may result in a particular health concern, and therefore avoid the application of these specific pesticides. Additionally, such data can be used for prioritisation to better inform detailed risk assessments (e.g. cumulative risk assessments for specific health concerns) as recommended by the EFSA (EFSA, 2024), as opposed to reference doses which only provide information for overall associated risk levels (Bos, 2009). This study builds on these methods by (1) assessing health effects prioritised in Regulation (EC) No. 1107/2009 (European Commission, 2009b), and (2) using EFSA data (EFSA, 2021) to score potential health effects.

In line with existing studies, the health effects were categorised as follows: "Probable", there is significant evidence that the pesticide causes the toxic effect in humans; "Possible" there is limited evidence from animal testing that the pesticide causes the toxic effect in humans; "No data", no studies have been carried out to confirm if the pesticide does or does not cause the toxic effect or the studies that exist are inconclusive; "No", there is definitive evidence that the pesticide does not cause the toxic effect in humans (Valcke et al., 2005; Sugeng et al., 2013; Dabrowski et al., 2014). These categories were then scored for each health effect (Table 3.4) based on the available evidence of pesticide toxicity (Appendix A2). Evidence was taken from the EFSA or, in the case of data gaps, from PPDB (Lewis et al., 2016). To account for uncertainty, "No data" was given a higher score than conclusive evidence of no effect ("None") as is done in literature (Gunier et al., 2001; Valcke et al., 2005). The scores were weighted with respect to the perceived severity of the health effect in accordance with the methods used by Valcke et al. (2005) and Dabrowski et al. (2014), therefore carcinogenicity and endocrine disruption were weighted higher than the other health effects.

It is important to note that pesticides have the potential to cause health effects not included in the study such as cardiotoxicity (El-Nahhal and El-Nahhal, 2021b), respiratory disorders, hepatoxicity, immunotoxicity, etc. (Kalyabina et al., 2021). Pesticide can also be acutely toxic and the level of a pesticide's acute and chronic toxicity can be very different (Damalas and Koutroubas, 2016). Therefore, the acute

toxicity classes of the pesticides examined in the case study are included (Appendix A2) (WHO, 2019). However, due to the constraints of available toxicological data and the need to maintain a user-friendly risk screening tool, the existing study is limited to health effects that have been prioritised in existing pesticide health risk screening studies (Valcke et al., 2005; Alavanja and Bonner, 2012; Dabrowski et al., 2014) and legislation (European Commission, 2009b).

Table 3.4: Scoring for chronic health effects

Health Effect	Category	Score	Reference
Carcinogenicity	Probable	8	Valcke et al., 2005
	Possible	6	
	No data	3	
	None	0	
Endocrine Disruption	Probable	8	Dabrowski et al., 2014
	Possible	6	
	No data	3	
	None	0	
Genotoxicity	Probable	6	Valcke et al., 2005
	Possible	4	
	No data	2	
	None	0	
Teratogenicity	Probable	4	Valcke et al., 2005
	Possible	2	
	No data	1	
	None	0	
Reproductive Toxicant	Probable	4	
	Possible	2	
	No data	1	
	None	0	

The final consequence of exposure score (CES) was calculated by summing the toxicity scores for the five chronic health effects to a maximum possible score of 30 (Stage 2: Figure 3.1 and Eq. 3.6). As some uncertainty is to be expected in the scores due to the exclusion of some potential health effects in this study, an additional score of one was included to avoid giving a pesticide with potentially harmful effects a risk score of zero, as is common practice in literature (Valcke et al., 2005; Dabrowski et al., 2014). Therefore, the final maximum score is 31:

$$CES = Carcinogenicity + Mutagenicity + Teratogenicity + Endocrine\ Disruption + Reproduction\ Toxicant + 1 \quad (3.6)$$

3.2.4 METABOLITES

Metabolites have properties independent of their parent compounds and should be incorporated into the evaluation of pesticide risk (Labite and Cummins, 2012; Matsushita et al., 2018). Current pesticide risk ranking methods neglect to consider the contribution metabolites make and so this study attempts to address this gap. However, metabolites tend to be less researched than their parent compounds and existing literature is limited (Sinclair et al., 2006; Escher and Fenner, 2011; Zhou et al., 2019). A less detailed evaluation method using only metabolite toxicity and persistence data from EFSA reports or the PPDB (Lewis et al., 2016) was used in the current paper to assess key metabolites. Metabolite data were independently scored and incorporated into pesticide scores to assess combined pesticide-metabolite hazard scores (Stage 3: Figure 3.1).

Metabolite toxicity was assessed using the ADI due to a lack of toxicology studies, or if unavailable, the ADI of the parent compound. This approach has been used in existing metabolite only studies, as it is conservatively assumed that the toxicity of the metabolite that have not been studied would be less or equally toxic as the pesticide (Sinclair et al., 2006; Labite and Cummins, 2012). Toxicity was scored based on ADI classifications from literature (Table 3.5) (Juraske et al., 2007; Chou et al., 2019).

The half-life in soil was used to represent persistence as it is the most researched degradation indicator for metabolites. If this was not available, a very conservative value of 300 days has been suggested by the European Commission (2002). Four classification levels were used to score the persistence of metabolites (Table 3.5), based on the categories suggested in literature (Valcke et al., 2005).

Metabolite scores were considered in a separate analysis to assess the effects metabolite data has on the overall risk ranking as shown in Figure 3.1. The score awarded to the metabolite toxicity was included in the consequence of exposure score, for a maximum consequence of exposure score of 35 (Figure 3.1 and Eq. 3.7). The score given for the metabolite persistence was included in the likelihood of exposure score for a maximum score of 16 (Figure 3.1 and Eq. 3.8).

$$Consequence\ of\ Exposure_{MET} = Consequence\ of\ Exposure\ Score + Metabolite\ Toxicity \quad (3.7)$$

$$Likelihood\ of\ Exposure_{MET} = Likelihood\ of\ Exposure\ Score + Metabolite\ Persistence \quad (3.8)$$

Table 3.5: Scoring system for key metabolite toxicity and persistence

Criteria	Measure	Category	Score	Reference
Toxicity	ADI ($mg.kg^{-1}$ $bw.day^{-1}$)	≤ 0.005	4	Juraske et al, 2007
		$0.005 \leq ADI < 0.01$	3	
		$0.01 \leq ADI < 0.05$	2	
		≥ 0.05	1	
		No data	1.5	
Persistence	$DT_{50,s}$ (days)	$60 \leq DT_{50}$	4	Valcke et al, 2005
		$30 \leq DT_{50} < 60$	3	
		$15 \leq DT_{50} < 30$	2	
		$DT_{50} < 15$	1	
		No data	1.5	

3.2.5 Hazard Score and Quantity-Weighted Hazard Score

Hazard scores (HS) combine the likelihood of exposure with the effects of this exposure and can represent the relative risk of a pesticide compared to others used in the same area or for the same purpose. In line with methods used in literature, the hazard score is the product of consequence and likelihood of exposure scores (Sugeng et al., 2013; Dabrowski et al., 2014; Choi et al., 2020). However, these studies do not normalise the scores, resulting in the weighting of one parameter. In this study, the consequence of exposure was normalised so both scores contribute equally to the hazard score (Eq. 3.9):

$$HS = \frac{12}{31} Consequence\ of\ Exposure\ Score\ x\ Likelihood\ of\ Exposure\ Score \quad (3.9)$$

The hazard score of a pesticide may be very high due to its high toxicity and/or exposure potential. Assessing a pesticide's hazard score may help pesticide users select less risky pesticides, specific to their site or purpose, prior to application. On a national or policy level, it is important to also consider the quantity of each pesticide used in a region or country to accurately capture contribution of that pesticide to the national risk profile. For instance, a very harmful pesticide (high hazard score) may be used in a given country in very small quantities, meaning its contribution to overall national pesticide health risk may be minimal. To address this need existing studies

have combined consequence of exposure, likelihood of exposure, and a ratio for quantity of use in relation to quantity of overall pesticide use in a country or site to provide a quantity-weighted hazard score as follows (Valcke et al., 2005; Dabrowski et al., 2014) (Eq. 3.10):

$$\textit{Weighted Hazard Score} = \quad HS\ x \frac{Quantity\ of\ Use}{Total\ Annual\ Pesticide\ Use} \tag{3.10}$$

The same method was used to calculate the risk for all pesticides with the metabolite scores included (Eq. 3.11 and 3.12):

$$HS_{MET} = \quad \frac{16}{35} Consequence\ of\ Expsoure\ Score_{MET}\ x\ Likelihood\ of\ Exposure \tag{3.11}$$

$$WHS_{MET} = \quad Hazard\ Score_{MET}\ x \frac{Quantity\ of\ Use}{Total\ Annual\ Pesticide\ Use} \tag{3.12}$$

The pesticides may then be ranked based on their hazard score and their quantity-weighted hazard score. The pesticide with the highest score, and therefore the greatest perceived risk, was ranked 1.

3.3 Case Study

3.3.1 Pesticide Selection

An Irish case study was used to illustrate how the developed risk ranking method can be used to identify pesticides of concern on site-level and/or national-level. Table A1 shows the national and international databases used to obtain the parameter data for this case study. Irish pesticide usage data were obtained from the Pesticide Usage Reports published by the Irish Department of Agriculture, Food and the Marine (DAFM) for the most recently published years (DAFM, 2020, 2021). A total of 130 pesticides were used on grassland, fodder, and arable crops over this period. Based on common practice in literature, a minimal quantity of 1000 kg over the study period was selected as the exclusion point, as quantities below this point were subjectively considered too low to be of national importance (Valcke et al., 2005; Dabrowski et al., 2014). Seventy-three pesticides quantities exceeded 1000 kg between 2016 and 2017; however, ten have since been banned and are not included in the assessment. The method described in Section 3.2 was then applied to the remaining 63 pesticides to rank them by relative risk. Twelve of the sixty-three pesticides analysed do not have

any key relevant metabolites according to the EFSA pesticide reports; therefore, only the scores of the remaining 51 pesticides are affected by the inclusion of metabolites.

3.3.2 Site Selection

Pesticide hazard scores were calculated in two sites, selected from the Irish Teagasc Agricultural Catchment Programme (Teagasc, 2017a): Cregduff in the west of Ireland (53°36'54.4"N 9°10'44.1"W), a predominately grassland site (92%) with well-draining, shallow brown earth soils on a karst landscape (Mellander et al., 2013); and Dunleer in the east (53°50'08.7"N 6°25'04.1"W), a mixed-use site of 44% grassland, 34% arable land and 22% woodland/other with poorly drained, mixed soils (McDonald et al., 2019). Site data were obtained from the EPA's Irish Soil Information System (EPA, 2021b). As information regarding drinking water sources in these sites were unavailable, and to allow this case study to be used as a general guide for methodology implementation, it was nominally assumed that 50% of drinking water was drawn from groundwater and 50% drawn from surface water supplies.

3.4 Results and Discussion

3.4.1 Quantity, Likelihood of Exposure and Consequence of Exposure

The likelihood and consequence of exposure of the 25 most used pesticides in Ireland in the two locations are presented in Figures 3.2 and 3.3, where the size of the bubble is proportional to quantity. Three pesticides, glyphosate, chlormequat chloride and 2-methyl-4-chlorophenoxyacetic acid (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, as previously discussed, pesticide risk is influenced by the multiple factors such as mobility, persistence, and toxicity, as well as quantity. Therefore, several pesticides in Figures 3.2 and 3.3 can be identified as pesticides of concern due to their high likelihood and/or consequence of exposure scores such as boscalid and mancozeb, despite being used in lower quantities.

In both catchments metamitron is located at the top of Figures 3.2 and 3.3, with the highest likelihood of exposure (8.5 of a maximum of 12) due to its moderate-high runoff potential to surface waters and its very high persistence in both groundwater

and surface water. Both prothioconazole and boscalid also have a likelihood of exposure score of 8.5 in Dunleer and a similarly high score of 8 in Cregduff. This suggests the drinking water sources in Cregduff and Dunleer are most likely to be impacted by these mobile and persistent pesticides. Based on Figures 3.2 and 3.3, it can be seen that likelihood of exposure is marginally higher in Dunleer than in Cregduff. Dunleer consists mainly of poorly draining soils and experiences significant loss of pesticides due to surface runoff and a moderate risk for leaching and sediment runoff compared to low-moderate runoff potential in Cregduff (Table A2). These conditions result in higher pesticide mobility in Dunleer, hence a higher likelihood of exposure score. Therefore, the use of highly mobile pesticides can be considered a higher risk in a site like Dunleer, and a pesticide user may consider using a less mobile pesticide in locations that behave like Dunleer.

The consequence of exposure does not vary between the catchments as it is not dependent on location. Mancozeb is found on the far-right side of Figures 3.2 and 3.3, suggesting a very high consequence of exposure score relative to the pesticides examined in this study. In assessing the consequence of exposure score, five toxicological endpoints from the EFSA were considered and identifying mancozeb as a probable or known carcinogen, teratogen, and endocrine disruptor, hence its high score (Table A7). Many pesticides have been identified as potential toxicants under one or more of the health outcomes examined in this study based on the EFSA reports. A significant number of pesticides used in Ireland are potentially toxic to reproductive organs and foetal development, as there is evidence that 54% of pesticides used in Ireland have some kind of teratogenic effects and 24% have some impact on reproductivity.

This study demonstrates how pesticide risk cannot be determined using quantity alone. As illustrated by Figures 3.2 and 3.3, the pesticides of greatest concern result from a combination of quantity, mobility, and toxicity. The hazard scores, calculated in Section 3.4.2, attempt to numerically represent how this combination varies between pesticides and to identify the pesticides of greatest concern in Irish site.

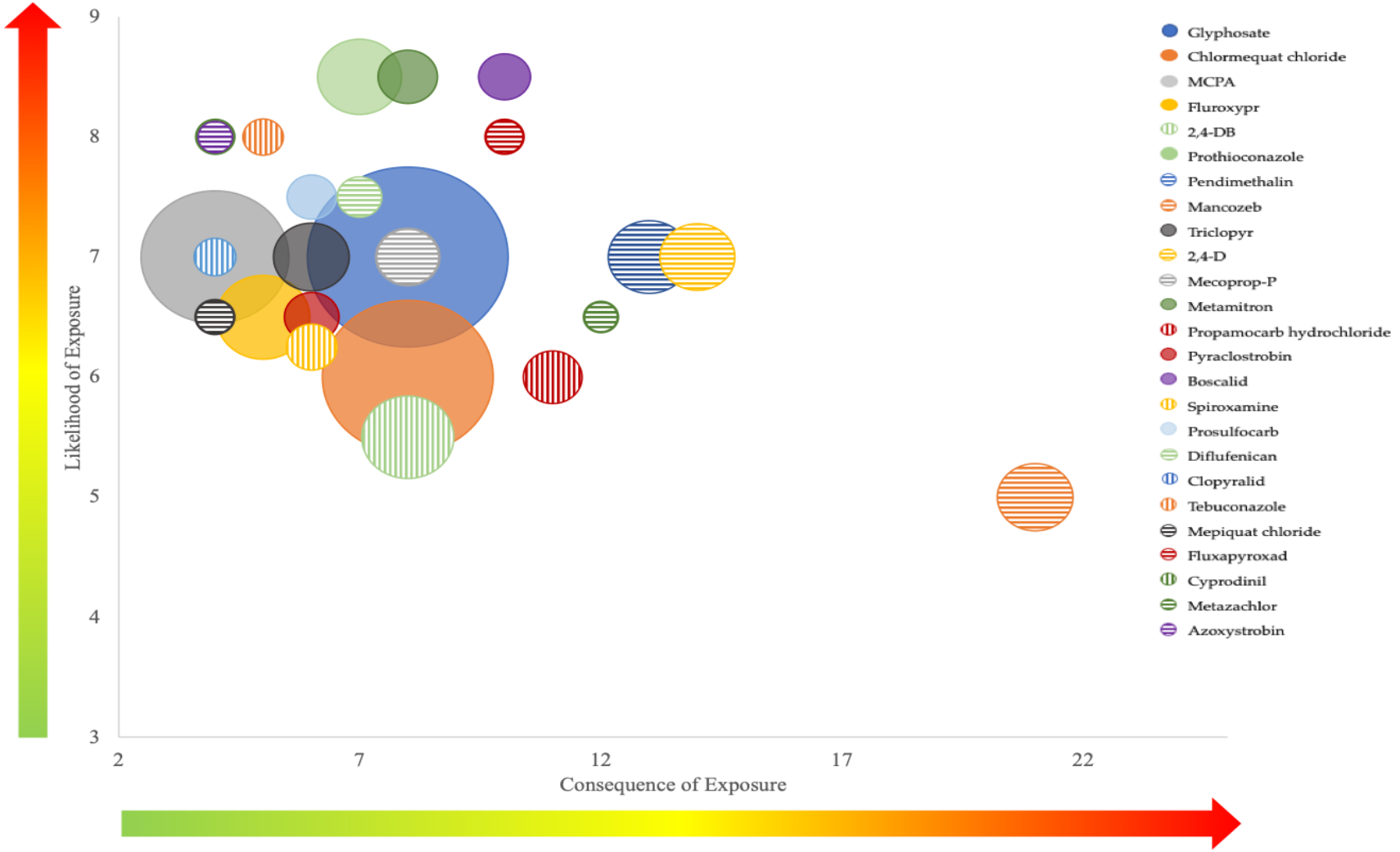


Figure 3.2: Likelihood of exposure vs consequence of exposure vs quantity of use in Cregduff catchment for 25 most used pesticides in Ireland. Area of bubble is proportional to the pesticide's quantity of use (kg).

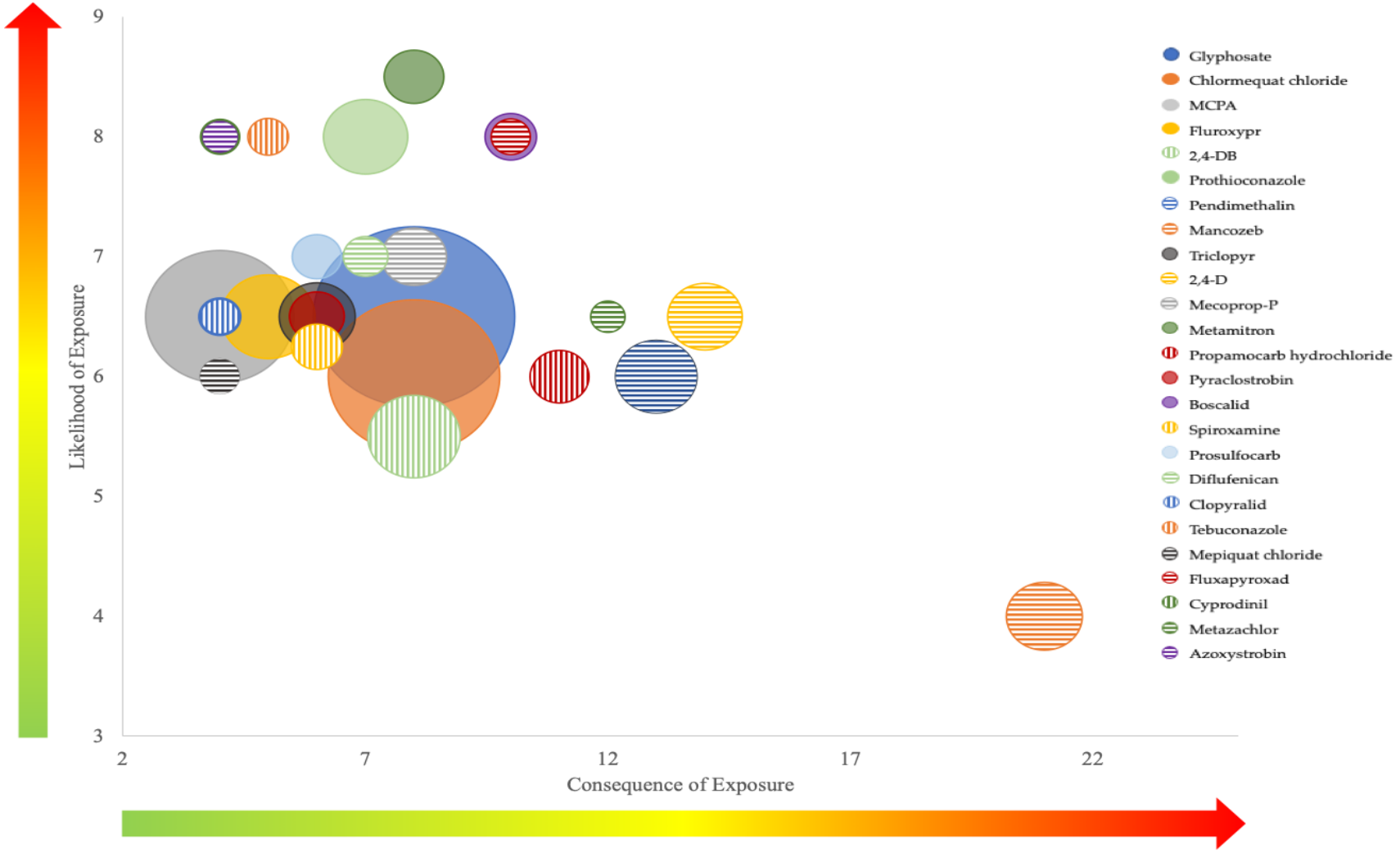


Figure 3.3: Likelihood of exposure vs consequence of exposure vs quantity of use in Dunleer catchment for 25 most used pesticides in Ireland. Area of bubble is proportional to the pesticide's quantity of use (kg).

3.4.2 Hazard Score and Quantity-Weighted Hazard Score

Figure 3.2 and Figure 3.3 provide information to rank pesticides based on their likelihood of exposure and consequence of exposure for the most widely used pesticides in Ireland (representing over 65% of the applied pesticides). However, pesticide use can be regionally variable, and therefore pesticides used in low quantities nationally may have regional significance, e.g. in a region where a specific pesticide is used in relatively large quantities due to the land-use in that area. Therefore, it can be important to consider the hazard score of less commonly used pesticides to provide risk information for pesticide users. These hazard scores can also be used to inform pesticide selection in future should the land-use be diversified requiring the use of alternative pesticides in order to avoid application of potentially harmful pesticides.

As a result, Figure 3.4 shows the top 30 pesticides hazard scores in Cregduff and Dunleer for all pesticides used in Ireland to enable comparison of pesticide risk scores for both widely used pesticides and lesser used pesticides, and the top 25 quantity-weighted hazard scores in an Irish context. Overall, prochloraz has the greatest hazard score with a score of 52.6 (out of a maximum of 144) in both catchments. Prochloraz's relatively high hazard score is due to the combination of its moderately high consequence of exposure score of 17 (of a maximum of 31), making it the second most toxic pesticide in this study and its high likelihood of exposure score of 8 (out of a maximum of 12) (Table A3.9). Prochloraz is highly mobile and is extremely persistent in surface water with a half-life of 359 days. Propyzamide has a hazard score of 43.5 (Figure 3.4), which is the second highest hazard score overall as it is as mobile as prochloraz but slightly less toxic and persistent.

Based on hazard score alone, prochloraz and propyzamide are the pesticides of greatest concern in this study. However, several pesticides have relatively high hazard scores and are used in high quantities. These include mancozeb, 2,4-dichlorophenoxyacetic acid (2,4-D), and pendimethalin, which have the 3rd, 5^{th,} and 9th highest hazard scores, respectively (Figure 3.4). These pesticides are as toxic, if not more in the case of mancozeb, than prochloraz and propyzamide, but are less mobile or persistent (Table A9). However, due to their high hazard scores and large national quantities, these pesticides may require more in-depth risk analysis and monitoring. The hazard scores of the pesticides used the most in Ireland, glyphosate and chlormequat chloride, are ranked in the top half of pesticides examined in this study (23rd of 63 and 28th/30th of

63 respectively); however, their hazard scores are relatively lower than the top ranked pesticides, with glyphosate scoring 21.7 compared to prochloraz's 52.6 in Dunleer (Table A10). Therefore, from their hazard score alone, further assessments may not be required, but incorporation of quantity of usage results in a high quantity-weighted score (Figure 3.4: inset), which would identify them as pesticides of concern for Irish drinking water.

As discussed previously, hazard scores are useful to compare the relative risk associated with pesticides at a site-level prior to application to select less risky pesticides. The quantity-weighted hazard score incorporates pesticide quantity into the calculated hazard score and therefore better represents the regional or national risk-profile from actual pesticide use. The national quantity-weighted hazard scores of pesticides used in Ireland over the study period were calculated using Dunleer as a representative site for Ireland to give a better insight into the national risk profile associated with the various pesticides used on a national scale. This mixed grassland/arable site with mixed soils was selected as it was regarded to be more typical of sites across Ireland. The inset in Figure 3.4 shows the top 25 quantity-weighted hazard scores for pesticides used in Ireland.

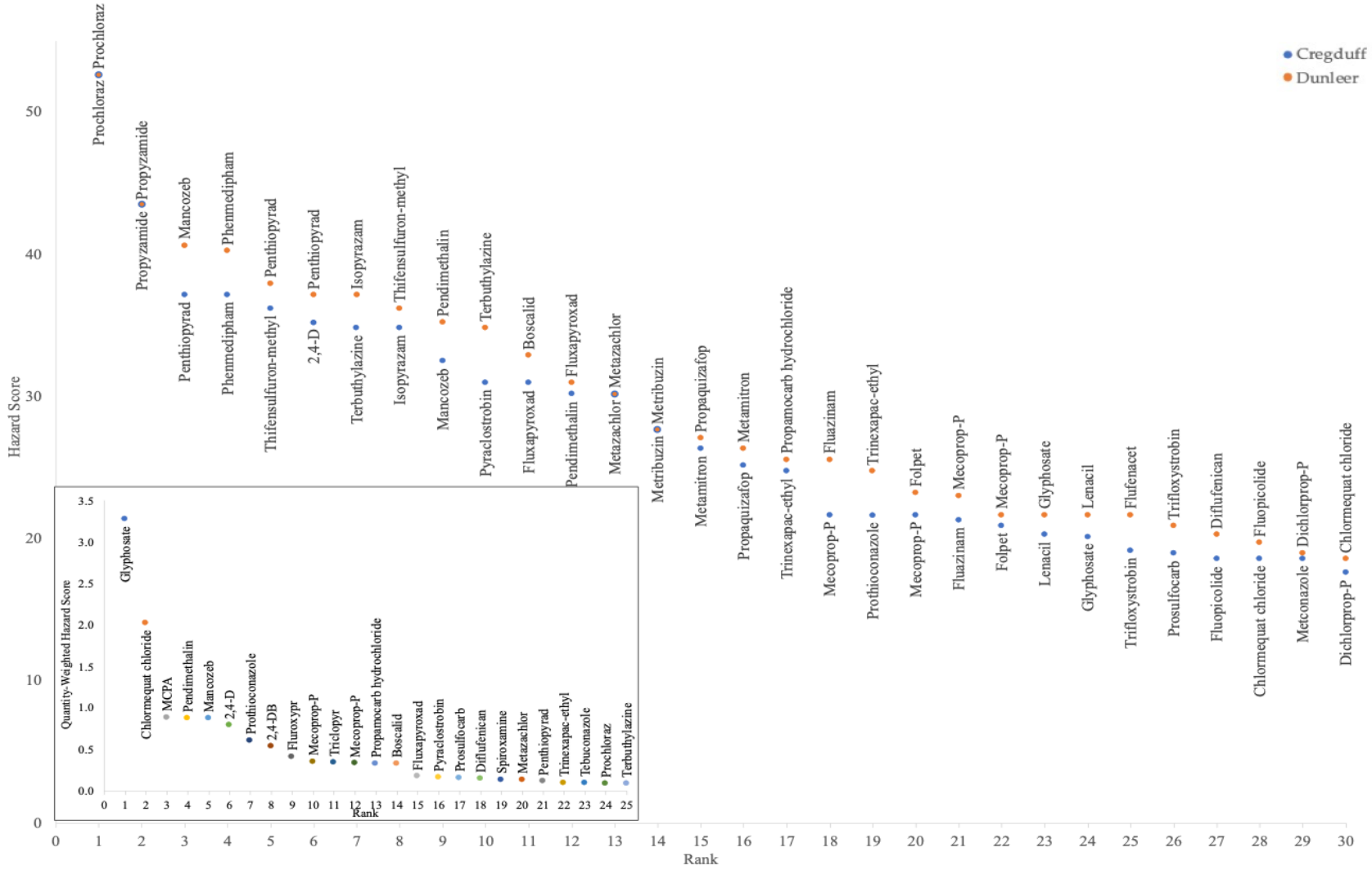


Figure 3.4: Top 30 pesticides of concern in Cregduff vs. Dunleer; Top 25 pesticide quantity-weighted hazard score (inset)

It is evident that quantity of use has a strong influence on the hazard score as the most used pesticides in Ireland, glyphosate and chlormequat chloride, are the highest ranked pesticides (Figure 3.4). The third most used pesticide over the study period MCPA, is ranked 55 of 63 for consequence of exposure and has the 10th lowest hazard score (Table A10). However, it has the third highest quantity-weighted hazard score due to the influence quantity has on the quantity-weighted hazard score. Conversely, prochloraz, is used in relatively low quantities (43rd out of the 63 pesticides) but is ranked second based on toxicity and has the highest hazard score (Tables A9 and A10). Even though prochloraz is used in relatively small quantities (0.2% of total pesticide use; (DAFM, 2020, 2021, 2024)), its moderately high quantity-weighted score ranks 24th. Hence highly toxic pesticides should not be discounted as a pesticide of concern, even if used in small quantities, and should be monitored closely to ensure they are not used in quantities that may increase this risk. Pendimethalin and mancozeb can be identified as the pesticides of greatest concern of the 63 examined in this study, as they score highly in all criteria examined, except for likelihood of exposure, and are 4th and 5th highest ranked pesticide respectively based on quantity-weighted hazard score, despite making up only 2% each of overall pesticide use. In the time since this analysis began, approval for mancozeb use in the EU has been withdrawn with a ban on mancozeb use coming into effect at the beginning of 2022 (European Commission, 2020). The upcoming ban on mancozeb confirms the findings of this study, that mancozeb poses a significant risk to Irish drinking water and further monitoring, detailed assessment, or, in this case, a ban is required.

3.4.3 METABOLITES

When metabolite data are included in the assessment, pesticides with key metabolites have increased risk scores. Some do not significantly change such as 2,4-D, as its metabolite is neither toxic nor persistent. Other pesticides experience a notable increase in either their likelihood of exposure score, consequence of exposure score or both, such as boscalid which has a very persistent metabolite, resulting in almost a doubling of its likelihood of exposure and triclopyr which has a very persistent and moderately toxic metabolite (Appendix A4). What is of most interest is the relative change in these scores and their rankings. Appendix A4 details the hazard and quantity-weighted scores of pesticides when metabolite data are included and shows how the ranking change when metabolites are considered. Parent compounds that were

classified as high concern such as mancozeb and 2,4-D become relatively lower concern when their non-persistent and non-toxic metabolites are considered, with their hazard score dropping from 3rd to 9th and 4th to 10th respectively. Others that are not priority pesticides, such as tribenuron-methyl and triclopyr, have much higher ranked hazard scores when metabolites are included, increasing by 12 and 13 places higher respectively. Regarding quantity-weighted hazard scores, both triclopyr and boscalid are ranked higher when metabolites are included but metamitron becomes a relatively lesser concern when its metabolite is considered in comparison to other pesticides with more harmful or persistent metabolites (Table A11).

3.4.4 Sensitivity Study

3.4.4.1 Uncertainty in Pesticide and Soil Data

A sensitivity study was carried out to evaluate how the variability and uncertainty related to pesticide and soil data can affect the output of the risk scoring tool. This was achieved by varying the value of several parameters in turn by a nominal value of 10%, while the values of the other parameters remained constant. The sensitivity study results are presented in Appendix A5.

The variation in pesticide data (i.e., half-life in groundwater, surface water, and soil, K_{OC} and solubility) had an impact on pesticide mobility and pesticide persistence, both impacting the hazard score (Table A12). Due to the banded nature of the scoring used in this methodology, less than half of the pesticides experienced any change when the values for pesticide data were varied. However, any resulting changes to hazard score were notable, with some of the pesticides experiencing up to a 20% change in hazard scores. For example, a reduction in soil half-life resulted in trifloxystrobin's leaching potential to change from low to very low, while its runoff potential reduced from moderate to low, therefore the pesticide is far less mobile resulting in an 18.2% reduction in its hazard score (Table A13). Both persistence and sorption are key factors in pesticide transport (Kumari and John, 2020), and therefore it is unsurprising that variation in this data would have a strong effect on pesticide risk scores. The variation of pesticide solubility had no impact on pesticide mobility or hazard scores, indicating variability associated with this parameter would not have significant impact on overall risk.

The sensitivity study also examined variability of soil data (i.e. horizon depth, soil organic matter (SOM), clay, sand and silt content) and found that SOM content was the only soil parameter to affect the pesticide mobility and the related hazard scores (Table A14). A 10% reduction of SOM content led to the sediment runoff potential to change from "Low" to "Moderate". This parameter is clearly an important source of uncertainty in this study as the majority of resulting pesticide hazard scores increased by 5% or more (Table A14). It is well established that pesticide sorption contributes significantly to pesticide transport as pesticides with high sorption potential tend to be less mobile (Motoki et al., 2014; Kumari and John, 2020) and that there is positive correlation between sorption and SOM content (López-Piñeiro et al., 2013; Dutta et al., 2015). This illustrates the importance of having relevant data, especially related to the organic contents of soil, for locations under assessment as variation in site data influences the results of the tool.

3.4.4.2 Uncertainty in the Scoring System

Scoring systems, similar to that used herein, have been developed and widely used by several authors (Sugeng et al., 2013; Dabrowski et al., 2014; Choi et al., 2020). A contentious point in this scoring method, however, is how missing or inconclusive data are dealt with. It is common in literature to score missing data higher than no/low effects which can lead to the uncertain conservative scoring of non-harmful pesticides or the underestimation of harmful pesticides. As 44 of the pesticides in the case study have missing or inconclusive data for one or more toxicological endpoints, a sensitivity study was carried out to investigate the effects missing toxicology data has on the output of this tool. Missing data were analysed as follows: (1) given the mid-range score for the relevant toxicological effect and (2) scored zero. As expected, the results of this study found that changing the "no data" score has a significant impact on the pesticide hazard scores and their risk ranking (Table A15). For example, if missing data are assigned a score of zero, the ranking of fluxapyroxad decreases by five as it has missing/inconclusive data for one health concern. Conversely, if missing data are given a mid-range score, fluxapyroxad moves from the 12th highest scored to the 10th most hazardous pesticide in this study for the same reason. Thus, the sensitivity study emphasises the need to continue to develop our understanding of the toxicological effects of pesticides on humans on a global level to improve the understanding and evaluation of pesticide risk.

3.5 CONCLUSION

The relative risk of pesticides can be scored and ranked from highest to lowest concern using the method developed and presented in this study. The approach presented allows for the comparison of pesticides based on several criteria: quantity of use, environmental fate, toxicity, overall hazard, and quantity-weighted hazard. The current study has expanded on existing methods to include the effects site data have on pesticide mobility through the use of a more comprehensive mobility indicator and is one of the first pesticide screening tools to address the impact metabolites have on overall pesticide risk pesticide risk. This study emphasises the need for a greater understanding of how metabolites persist in the environment and how they may cause harmful effects on humans. A sensitivity study, carried out to examine the limitations of the methodology, highlights the influence that variability in pesticide data can have on pesticide risks scores and identifies a need for future work pesticide toxicology studies. A simple screening method was developed as the first stage of detailed pesticide risk assessments to identify the main pesticides of concern in a given area. In the context of Irish drinking water, on both a national scale and in two different sites, mancozeb, 2,4-D, pendimethalin and glyphosate are some of the pesticides of greatest concern based on their combined quantity of use, toxicity, and exposure potential. This suggests that monitoring programmes should be considered in areas where these pesticides are used, and detailed risk assessments of these pesticides may be required on a national-scale based on their quantity-weighted hazard scores. This method can easily be adapted by pesticide users to examine the pesticide risk specific to their sites, allowing for the comparison of the relative risk of pesticides they may use and the selection of less risky pesticides. This method also allows risk managers and governmental departments to examine how pesticides may contribute to the health risks of a population on a regional or national-scale using quantity-weighted hazard scores.

CHAPTER 4

STOCHASTIC MODELLING OF PESTICIDE TRANSPORT TO DRINKING WATER SOURCES VIA RUNOFF AND RESULTING HUMAN HEALTH RISK ASSESSMENT

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ABSTRACT

A modelling framework was developed to facilitate a probabilistic assessment of health risks posed by pesticide exposure via drinking water due to runoff, with the inclusion of influential site conditions and in-stream processes. A Monte-Carlo based approach was utilised to account for the inherent variability in pesticide and population properties, as well as site and climatic conditions. The framework presented in this study was developed with an ability to integrate different data sources and adapt the model for various scenarios and locations to meet the users' needs. The results from this model can be used by farm advisors and catchment managers to identify lower risk pesticides for use for given soil and site conditions and implement risk mitigation measures to protect water resources. Pesticide concentrations in surface water, and their risk of regulatory threshold exceedances, were simulated for fifteen pesticides in an Irish case study. The predicted concentrations in surface water were then used to quantify the level of health risk posed to Irish adults and children. The analysis indicated that herbicides triclopyr and MCPA occur in the greatest concentrations in surface water, while mecoprop was associated with the highest potential for health risks. The study found that the modelled pesticides posed little risk to human health under current application patterns and climatic conditions in Ireland using international acceptable intake values. A sensitivity study conducted examined the impact seasonal conditions, timing of application, and in-stream processes, have on the transport of pesticides to drinking water.

4.1 INTRODUCTION

The global population is predicted to increase by 25% by 2050 (United Nations, 2019), and the resulting demand on food supplies is expected to more than double when compared to 2010 levels (Van Dijk et al., 2021). Pesticides are key in securing high crop yields, meaning agriculture has depended heavily on their use (Tudi et al., 2021). However, it has been suggested that as little as one percent of applied pesticides reach target organisms, resulting in potential contamination of surrounding environments and impacting non-target organisms (Ali et al., 2019). Pesticides have been found to be harmful to non-target terrestrial and aquatic organisms (Malaj et al., 2014; Wang et al., 2022), and it has been suggested that repeated ingestion of low doses of pesticides may cause chronic health effects in humans (Aloizou et al., 2020; Giambò et al., 2021; Kalyabina et al., 2021). Therefore, both the likelihood of exposure to pesticides via water supplies, and the consequence of this exposure should be assessed to help understand potential risks posed by pesticide usage.

Pesticide risk models have been widely used as a cost-effective method to provide information on the level of exposure to pesticides and resulting health implications, helping to limit potential risks to human health (Abreu-Villaça and Levin, 2017). However, there is extensive literature examining the large variability in factors that influence pesticide impacts and exposure to consumers, and how this affects model outputs (USEPA, 2004b; Lammoglia et al., 2018; EFSA and BfR, 2019; Troldborg et al., 2022). Therefore, probabilistic pesticide models are an important tool in higher-tier risk assessment, as they can quantify the uncertainty associated with model parameters and prediction, offer additional information to catchment and risk managers, and assist in making risk-informed management decisions (Asfaw, 2018). Probabilistic modelling is already widely used in assessing risks from pesticide exposure to humans via food to account for the variability in consumption patterns and the uncertainty associated with pesticide contamination and other contaminants (Bosgra et al., 2009; van der Voet et al., 2015; Stephenson and Harris, 2016; Liu et al., 2022).

Studies probabilistically modelling pesticide risks arising from drinking water are however relatively limited (Cantoni et al., 2021), when compared to the wide use of

probabilistic approaches in health risk via food. This is likely due to the reliance on pesticide transport model outputs in analysing likelihood of exposure within such models, for example Teklu et al. (2015) and Brodeur et al. (2023), which tend to adopt the traditional deterministic approach. Therefore, they rely on average values as input parameters to develop point estimate outputs, as highlighted by Gagnon et al. (2014) and Piffady et al. (2021). The use of average values, or point estimates, as input parameters means that the high level of uncertainty associated with input data and the resulting risks of exposure to pesticides cannot be fully accounted for (Troldborg et al., 2022). A number of studies have examined the suitability of adopting a stochastic approach to several process-based transport models (i.e. SWAT, PRZM, etc.) in order to address these limitations (Young and Carleton, 2006; Tasdighi et al., 2018; Winchell et al., 2018; Mentzel et al., 2022b). However, these process-based transport models are computationally complex, requiring significant processing power and data input for model parameterisation (Wang et al., 2019b). Therefore, attempts to apply probabilistic approaches to these process-based models tend to be limited to a handful of parameters, such as probabilistically modelling pesticide application scenarios only (Winchell et al., 2018; Rathjens et al., 2022) or rainfall and runoff parameters only (Tasdighi et al., 2018), with all other parameters modelled deterministically. While very insightful, this approach cannot fully account for variability and uncertainty associated with the broad range of parameters within the base models i.e. SWAT alone can require up to 60 user-defined parameters (Arnold et al., 2012a).

In order to apply a more fundamental probabilistic approach, with the majority of parameters considered modelled stochastically, a number recent of studies have combined Monte Carlo simulations or Bayesian belief networks with simpler computational models, which require less parameterisation and are thus more user-friendly. Monte Carlo risk assessment approaches have been applied by Clarke at al. (2016) to develop a health risk assessment posed by biosolids in surface water. Within the pesticide field, a similar approach was taken to assess pesticide risk from groundwater (Labite and Cummins, 2012), but this study did not consider more vulnerable surface water supplies. Both Cantoni et al. (2021) and Rezaei Kalantary et al. (2022) applied similar approaches to assess resulting health risks from treated water, however initial pesticide concentrations in raw water were obtained from monitoring data, which somewhat limits the application of these approaches to site

with available monitoring data. Troldborg et al. (2022) developed a comprehensive model to assess concentrations in both groundwater and surface water using Bayesian network beliefs, but resulting health risks were not considered. Additionally, the simpler computational models used in these studies could not account for the effects of natural processes, such as soil retention, and in-stream degradation, have on pesticide fate. All studies have contributed to the literature by offering more accessible probabilistic modelling approaches for pesticide risk assessment. However, the work in this paper seeks further contribute to this limited body of work and build on these existing studies in a number of ways.

This paper builds on current research through the modification of an existing pesticide transport model to be integrated into a quantitative health risk assessment. The study seeks to address identified shortcomings in the literature by (1) developing a probabilistic pesticide risk model based on a simple computational model resulting in a more user-friendly option for assessing pesticide risk probabilistically, (2) including model modifications, such as in-stream reduction process, which increases the models ability to better represent real-world scenarios while maintaining broad appeal, and(3) the progression of the framework beyond pesticide transport modelling, to include health risk by incorporating a widely used approach to quantify health risks, which may increase the user base for such a framework to include not just pesticide researchers and water quality managers, but also those interested in public health. The next section of this paper describes the development of a probabilistic modelling framework to assess pesticide health risks via drinking water. This framework is then applied to an Irish case-study in Section 4.3 to quantitatively assess the health risk, a comprehensive sensitivity study is presented in Section 4.4.4 which assesses overall model sensitivity, and the impact that seasonal conditions, timing of application, in-stream processes, and site location, have on the model output.

4.2 Methodology

4.2.1 Summary of Transport Model Selection

This sub-section provides a brief summary of the selection process used to identify the appropriate pesticide runoff model for probabilistically modelling a consumer's likelihood of exposure to pesticides via surface waterbodies. In this process several deterministic pesticide fate and transport models were examined for suitability for

probabilistic modelling. As the aim of this study was develop a fully quantitative risk assessment approach that is accessible to a range of users from different backgrounds, and can be easily adapted and to suit the user's needs, the models were assessed based on the balance between accuracy, complexity, required parametrisation and the practicality of adapting the model to facilitate representation of the majority of the model parameters probabilistically. Factors such as (1) balance between model complexity and proven realistic representation of pesticide transport process, (2) the level of expertise required for users of the framework to apply the model i.e. the mathematical complexity of the model, including number of equations and theoretical complexity of the equations, and (3) the availability of probabilistic data for the majority of the model parameters. A more detailed discussion of the model selection process is provided in Section 2.4 of Chapter 2.

In summary, a variety of models ranging from simple transport indicators and conceptual mathematical models to detailed, process-based models such as FOCUS modelling software and SWAT were considered. Indicator-based models are some of the most widely used methods to assess the likelihood of exposure to pesticides due to their easy application and low data requirement. They allow pesticide mobility to be scored using physio-chemical properties (e.g. California's SWPP approach (Luo et al., 2014)) or a site's vulnerability to pesticide pollution can be estimated based on geological features like DRASTIC (Aller et al., 1985). However, such methods cannot be used to assess health risks arising from pesticide exposure as they cannot provide probabilistic data on exposure concentrations. Conversely, a range of computational software has been developed to assess pesticide transport to surface waterbodies such as watershed models SWAT (Arnold et al., 2012a), AGNPS (Bingner and Theurer, 2001) or, SWASH, an edge-of-field assessment framework developed for use within the EU by FOCUS (Te Roller et al., 2015). Within the EU SWASH, which combines models PRZM, MACRO and TOXSWA, is widely used in pesticide regulation, while both SWAT and AGNPS are used internationally for pesticide research.

However, the application of models such as those in the SWASH framework and SWAT to individual sites or regions, outside of FOCUS surface water scenarios for example, requires a knowledge of hydrological processes, a high-level of programming competence and large resource and time demands (Wang et al., 2019b).

For example, using $PRZM_{SW}$ within the SWASH framework, may require up to 40 user-defined input parameters (FOCUS, 2010), while users may need to input up to 60 parameters to run SWAT depending on their site scenario (Arnold et al., 2012a). This makes model parameterisation for specific study sites time consuming and data intensive (Adu and Kumarasamy, 2018), and the limited availability of localised datasets can affect the model accuracy (Troldborg et al., 2022). Both the large data demands and the complex computational nature of the models also result in significant resource challenges when attempting to apply probabilistic approaches to the majority of the parameters for such models. The processing power required to run process-based models is significant, and can take a very long time to produce results if run for multiple scenario combinations, as may be required for probabilistic analysis (Bach et al., 2017). As a result, a relatively simple model, that could be more easily parameterised for a probabilistic approach, was selected herein to provide a practical compromise between comprehensive modelling and computational costs, and ease of use for users. The SFIL (OECD, 2000) was chosen as a suitable runoff model for the application of probabilistic methods. This model allows for the incorporation of a range of factors that influence pesticide transport and facilitates estimation of actual exposure concentrations, unlike simple environmental indicators. Despite this, it requires less data input (with only 22 input parameters in total), and expert knowledge than the more complex modelling (Troldborg et al., 2022). Its relatively simple theoretical basis also allows for modifications to be made to the model to improve its representation of study scenarios (Berenzen et al., 2005) and it has also been shown to compare well to observed data when used deterministically (Utami et al., 2020). The model used herein is not without its own limitations, however. In order to address some of these limitations, this study utilised a probabilistic approach to account for data uncertainty and variability. Additional pesticide processes were also integrated into the modelling framework to improve the representation of in-stream processes. The output of this model was then used to assess level of resulting health risk as described in Section 4.2.3.

4.2.2 Predicted Concentrations in Surface Water

A probabilistic model, in accordance with the framework outlined in Figure 4.1, was applied to predict the concentration of a single pesticide in a surface waterbody due to runoff. The theoretical model that forms the basis of this framework was adapted from

Berenzen et al's (2005) modified SFIL (Eq. 4.1 – 4.5 & 4.8) (OECD, 2000). This model allows factors that influence pesticide environmental fate and transport, such as pesticide physiochemical properties, rainfall and runoff volumes, site topography and agricultural processes, to be considered in estimations of concentration. It was further modified here by (1) the use of the SCS curve number method (Eq. 4.6 and 4.7) to assess runoff volume, and (2) the reduction of in-stream concentrations due to adsorption and degradation (Eq. 4.9 – 4.11). A probabilistic approach, detailed in Section 4.2.4, was then applied to this model utilising the statistical parameters described in Section 4.3. This methodology was adapted for an Irish case study, described in Section 4.3, to demonstrate how regional and national datasets may be applied to assess pesticide transport and resulting health risks in local areas. It is important to note in this context that water treatment processes that may reduce pesticide concentrations in drinking water were therefore not considered in this study, as effective pesticide removal processes are not currently available in water treatment plants within the Republic of Ireland (Uisce Eireann, 2021).

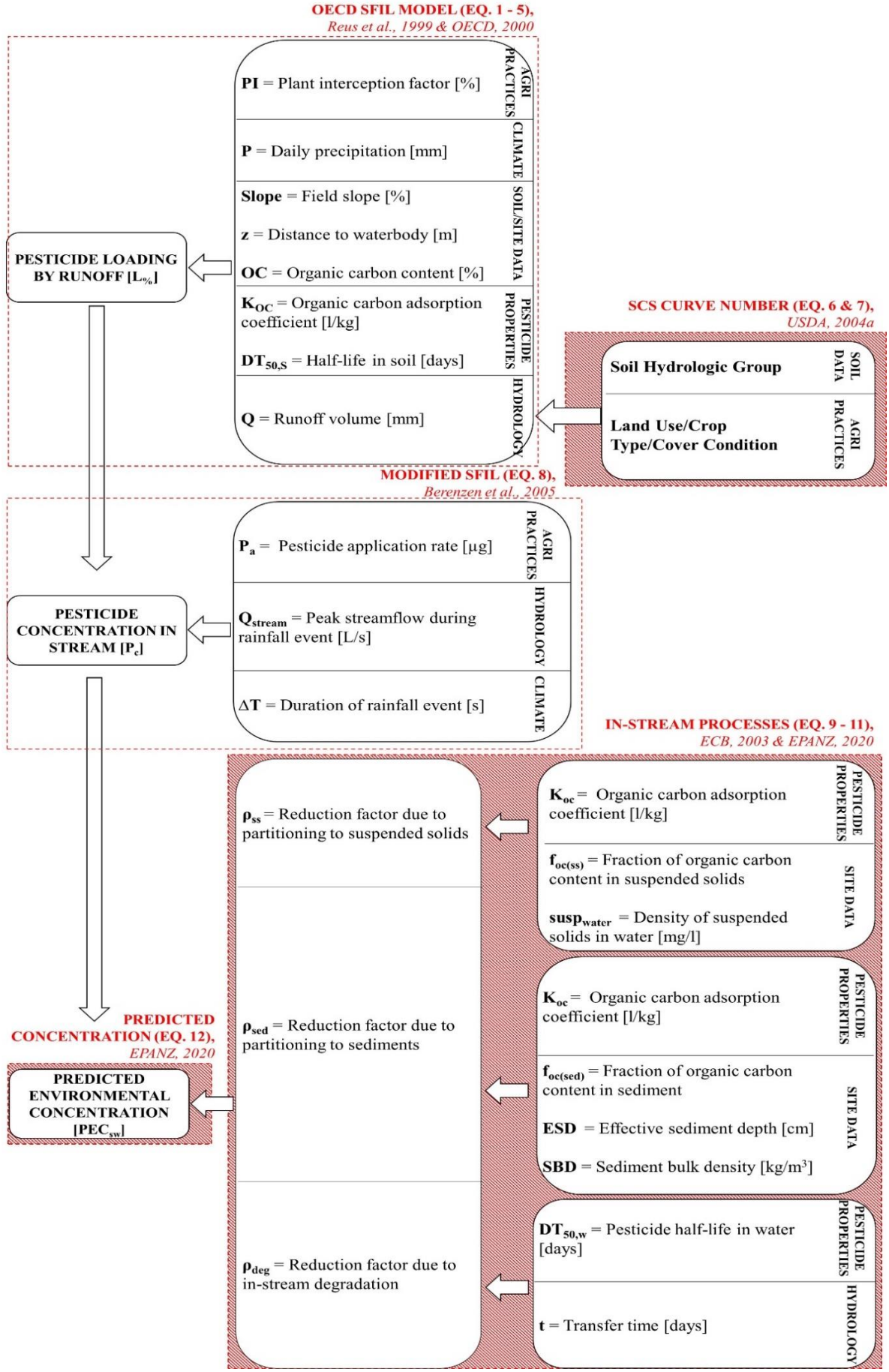


Figure 4.1: Modified surface runoff model framework; Modifications to existing model shown in hatched areas

The original SFIL estimates the percentage of the applied pesticide dose that will be lost to runoff. This was determined using the pesticide's physiochemical properties and several site conditions:

$$L_{\%} = \frac{Q}{P}\ x\ \frac{e^{\frac{-tln2}{DT_{50,s}}}\ x\ 100}{1 + K_d}\ x\ f_1\ x\ f_2\ x\ f_3 \tag{4.1}$$

where Q is the runoff volume (mm.day^{-1}), P is the daily average rainfall (mm.day^{-1}), t is the number of days between application and rainfall event. The SFIL model runs on the assumption that there will be three days between pesticide application and a rainfall event (OECD, 2000). In Ireland it is advised to ensure there is no rainfall forecast for 48 hours after pesticide application (Teagasc, 2020). $DT_{50,s}$ is the pesticide half-life in soil (days). K_d is the ratio of dissolved to adsorbed pesticide and is calculated as:

$$K_d = \frac{K_{oc}\ x\ OC}{100} \tag{4.2}$$

where K_{oc} is the pesticide adsorption coefficient (l.kg^{-1}), and OC is soil organic carbon content (%).

The correction factors f_1, f_2, f_3 account for the effects of site conditions and agricultural practices on pesticide loss. Correction factor f_1 considers how site slope affects potential runoff based on the relationship developed by Beinat and Van den Berg (1996), whereby:

$$f_1 = 0.02153slope + 0.001423slope^2; \text{ for slope} < 20\%$$
$$f_1 = 1; \text{ for slope} \geq 20\% \tag{4.3}$$

The effect that the distance between application site and closest waterbody has on pesticide loss is considered using the correction factor f_2 developed for the REXTOX model (OECD, 2000):

$$f_2 = 0.83^z \tag{4.4}$$

where z is the distance to the waterbody (m). In this study, a buffer zone of zero metres was assumed in line with findings in literature that this factor overrepresents the effects of buffer zones on pesticide mobility (Schriever and Liess, 2007).

The amount of applied pesticide intercepted by crop cover was included using factor f_3, whereby:

$$f_3 = 1 - \frac{PI}{100} \tag{4.5}$$

where PI is the plant interception factor (%), based on the crop type and its growth stage, as adapted for FOCUS (2002).

To date, runoff volume (Q) was obtained from methods described by Lutz and Maniak (1984; 1992), which were only available for two soil types: sandy and loamy, and only applied to three site scenarios: Scenario 1, bare soil (i.e. pre-emergence) with high moisture content; Scenario 2, bare soil with low moisture; and Scenario 3, covered soil (i.e. crops in growth stages) with low moisture. This limits the ability of the SFIL model to represent a variety of sites as there are various combinations of soil types, moisture content and crop cover not considered. Consequently, the current study applied an approach of obtaining runoff volume through the use of the SCS Curve Number method. The SCS Curve Number method is used by the USDA to estimate runoff volumes from small agricultural catchments (USDA, 2004b) in order to provide more site-specific estimations of runoff volumes. A curve number was obtained based on a specific combination of a site's hydrologic soil group, land use and crop type (USDA, 2009) (Appendix 4.1). The curve number (CN) was then used herein to assess the maximum potential soil retention (S) of a site before runoff occurs:

$$S = \frac{25400}{CN} - 254 \tag{4.6}$$

Runoff is expected to occur when precipitation exceeds 20% of the soil's maximum potential retention, and the resulting runoff volume was calculated as follows (USDA, 2004b):

$$Q = \frac{(P - 0.2S)^2}{(P + 0.8S)} \text{; for P} \geq 0.2\text{S}$$
$$Q = 0 \text{ ; for P} < 0.2\text{S} \tag{4.7}$$

Many of the more complex edge-of-field runoff models such as PRZM (Suárez, 2005), as well as catchment-scale models such as AGNPS and SWAT (Bingner and Theurer, 2001; Arnold et al., 2012a), use the SCS Curve Number method for their runoff estimations. This method was utilised herein for a more detailed representation of site conditions by considering soil texture, land use, and growth stage.

As shown in Figure 4.1, the pesticide loading by runoff ($L_{\%}$) obtained in Eq. 4.1 was then used to calculate P_c, the edge-of-field concentration ($\mu g.l^{-1}$) as per Berenzen et al. (2005):

$$P_c = L_{\%}\ x\ P_a\ x \frac{1}{Q_{stream}\ x\ \Delta t} \tag{4.8}$$

where P_a is the pesticide application rate to the site (µg), Q_{stream} is the flowrate of the stream during the rainfall event ($l.s^{-1}$), Δt is the duration of the rainfall event (s).

The SFIL is an edge-of-field model and cannot account for the fate or behaviour of a pesticide once it enters a waterbody. However, this study expands upon previous studies by considering the potential reduction in pesticide concentration resulting from in-stream processes. Adsorption of pesticides to suspended solids and sediment (Eq. 4.9 and 4.10), and in-stream degradation (Eq. 4.11) were considered as suggested by the European Chemical Bureau (ECB) (2003), and modified by the New Zealand EPA (2020). The reduction due to adsorption to suspended solids in the waterbody was calculated as follows:

$$\rho_{ss} = \frac{1}{1\ +\ \left(f_{oc(ss)}\ x\ K_{oc}\ x\ susp_{water}\right)\ x\ 10^{-6}} \tag{4.9}$$

where $f_{oc(ss)}$ is the fraction of organic carbon content in suspended solids, and $susp_{water}$ is the density of suspended solids in water ($mg.l^{-1}$) (ECB, 2003).

The reduction of pesticide concentration due to adsorption to sediment was accounted for as follows:

$$\rho_{sed} = \frac{z}{z\ +\ ESD\ x\ SBD\ x\ f_{oc(sed)}\ x\ K_{oc}} \tag{4.10}$$

where z is the depth of the waterbody (cm), ESD is the effective sediment depth (cm), SBD is the sediment bulk density ($kg.m^{-3}$) and $f_{oc(sed)}$ is the fraction of organic carbon in sediment in accordance with ECB (2003) and FOCUS (2015) guidelines.

Pesticide concentrations are also reduced through in -stream chemical and biotic degradation processes. These were considered in the following first-order degradation factor:

$$\rho_{deg} = e^{\frac{-ln2t_r}{DT_{50,w}}} \tag{4.11}$$

where $DT_{50,w}$ is the pesticide half-life in water (days) and t_r is the residence time (days). A residence time of five days was assumed based on FOCUS (2015).

These factors are combined with the edge-of-field pesticide concentration, P_c, so that the final predicted environmental concentration (PEC_{sw}) may be calculated:

$$PEC_{SW} = \rho_{ss} \, x \, \rho_{sed} \, x \, \rho_{deg} x \, P_c \tag{4.12}$$

where the reduction factors ρ_{ss}, ρ_{sed} and ρ_{deg} represent the reduction in pesticide concentration due to adsorption to suspended solids and sediment, and in-stream degradation, respectively (Eq. 4.9, 4.10 & 4.11), and P_c is the edge-of-field surface water concentration (Eq. 4.8).

4.2.3 Human Health Risk Assessment

Firstly, the estimated daily intake of a pesticide was obtained for adult and child population using FAO and WHO guidelines (FAO & WHO 1997):

$$EDI = \frac{PEC \, x \, WC}{BW \, x \, 1000} \tag{4.13}$$

where EDI is the estimated daily intake ($mg.kg^{-1}bw.day^{-1}$), PEC is the predicted environmental concentration ($\mu g.l^{-1}$) obtained from Eq. 4.12, WC is daily water consumption ($l.day^{-1}$), BW is body weight (kg) and 1000 is a conversion factor to convert micrograms to milligrams. A probabilistic approach, as described in Section 4.2.4, was applied to this model using statistical parameters presented in Section 4.3.

The calculated EDI was then compared to the acceptable daily intake (ADI; $mg.kg^{-1}bw.day^{-1}$) the level of daily pesticide exposure at which no adverse effects are expected which was obtained from EFSA reports for each pesticide (EFSA, 2021), to assess the risk quotient (RQ), or the likelihood of chronic human health risk associated with exposure to an individual pesticide, as recommended by both the EU and WHO (EFSA, 2019):

$$RQ = \frac{EDI}{ADI} \tag{4.14}$$

In order to quantify the risk resulting from pesticide mixtures, the concentration addition approach was applied as recommended by the EFSA (EFSA, 2019). In this study, it was conservatively assumed that all study pesticides were presented in the

mixture. The resulting total health risk posed by the mixture is calculated as the sum of risk quotients for individual pesticides (i):

$$RQ_{sum} = \sum_{i=1}^{n} RQ_i = \sum_{i=1}^{n} \frac{EDI_i}{ADI_i} \quad (4.15)$$

In either case, if the risk quotient is greater than one, the risk associated with the level of pesticide exposure was deemed unacceptable and adverse health effects may occur. If the risk quotient is less than one, there is no likelihood of health risk and therefore the level of exposure is deemed acceptable.

4.2.4 Probabilistic Model Methodology

A probabilistic approach was adopted using the Monte-Carlo technique, as it is recognised as a useful and reliable method for probabilistic assessments and uncertainty analysis. Monte-Carlo simulations involve random sampling of input parameters and successive model runs to produce statistical distributions of outputs. For each model iteration one value is randomly selected from the probability distribution of each input parameter and the model output results in a probability distribution, in this case a distribution of pesticide concentrations, and subsequently risk quotients. To ensure the statistical stability of the model's outputs, the 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 recorded data on MATLAB®, and a review of distributions used in literature to date for parameters. The distributions and statistical parameters used in the models are presented in Tables 4.1 and 4.2.

4.2.5 Sensitivity Analysis Methodology

Analysis was conducted to test the sensitivity of the model to variation in input parameters, thus identifying critical input parameters. In this study overall model sensitivity, as well as the influence of five important factors: rainfall pattern, timing between application, curve number, in-stream processes and seasonal conditions, were examined. Triclopyr was selected in this case as it had the highest modelled concentrations as discussed in Section 4.4 and the results were discussed in terms of the effects on its 95th percentile concentration. However, where the model results are

particularly affected by pesticide properties, additional analysis was included to highlight these effects. Model sensitivity was assessed using the simple approach of one-at-a-time sensitivity analysis (Dabrowski and Balderacchi, 2013). This involves varying each input parameter independently within a realistic range, and then observing the resulting impact on the model predictions. In this study a ±10% range was used, as has been used in literature (Probst et al., 2005; Faúndez Urbina et al., 2020) and its impact was observed. To investigate how the model may respond to different rainfall levels, the model was run using rainfall data from the west coast of Ireland, the wettest part of the country (μ = 4.1 mm.day^{-1}, σ = 5.89; 1187 mm.year^{-1}), in place of original rainfall data (μ = 2.7 mm.day^{-1}, σ = 5.28; 847 mm.year^{-1}). The impact of application timing has on pesticide runoff was examined by running the model for one, two and five days between application and rainfall. To assess the impact that different site conditions, and resulting curve numbers, have on the results, the model was run for a grassland site with alternative soil conditions. The effects of the additional in-stream processes were assessed by running the model with and without these in-stream processes. The model was also run for two climatic scenarios using annual rainfall (μ = 2.7 mm.day^{-1}, σ = 5.28) and the rainfall levels prevalent during the growing season, assumed to be March – October (μ = 2.4 mm.day^{-1}, σ = 5.19), to assess the impact on the modelled results.

4.3 Case Study

An Irish case study was used herein to illustrate how the proposed framework can be applied to estimate pesticide concentrations in waterbodies and assess resulting health risks due to pesticide use on an agricultural site. Site specific data was obtained from national pesticide, soil, and weather databases, while pesticide properties were obtained from European databases. A hypothetical site of a field with a stream running alongside was developed to represent an Irish agricultural scenario using dominant and/or average conditions for land use, soil properties, climate conditions and agricultural practices. Model simulations were carried out for a grassland site (pasture, rough grazing, silage, hay or any combination), as it makes up approximately 90% of Irish agricultural land (Cawkwell et al., 2017). Irish soil maps, reports and databases were used to identify the dominant soil hydrologic groups in Ireland (EPA, 2021b). Based on USDA classifications (USDA, 2009), approximately 48% of soils were found to be Group C soils, and 39% of soils were Group B soils (Description of soil

groups is available in Appendix A1, Table A4). Group C was selected for modelling as it was the more prevalent soil type in Ireland, and associated properties were identified based on analysis of the EPA Soils database (EPA, 2021b). However, as Group B is the second most prevalent soil group, (39% compared to 48%), and therefore is also widely representative of Irish soils additional analysis was carried out for this soil type in Section 4.4.3. Precipitation and hydrologic data were obtained from Met Éireann (Met Éireann, 2022), and EPA (EPA, 2021a) or GSI (GSI, 2021) databases, respectively and analysis of the rainfall data was carried out to assess the likelihood of runoff events for the selected site scenario.

Table 4.1: Statistical parameters for probabilistic model (current conditions)

Parameter	Symbol	Unit	Distribution	Values	Source
Half-Life (in soil)	$DT_{50,s}$	days	Normal*	Pesticide Specific (see Appendix B2)	
Application interval	t	days	Fixed	3	(OECD, 2000)
Adsorption coefficient	K_{OC}	$l.kg^{-1}$	Normal*	Pesticide Specific (see Appendix B2)	
Carbon content (soil)	OC	%	Normal*	$\mu = 2.36$; $\sigma = 2.79$	(Fay et al., 2007; EPA, 2021b)
Interception rate	PI	%	Uniform	min = 0; max = 70	(Labite and Cummins, 2012; FOCUS, 2015)
Precipitation	P	mm	Gamma*	a = 0.255; b = 10.457	(Mockler et al., 2016; Met Éireann, 2022)
Soil moisture retention	S	mm	Based on CN	-	(USDA, 2004b)
slope	-	%	Fixed	3	(Clarke et al., 2016)
Distance to waterbody	z	m	Fixed	0	(Berenzen et al., 2005)
Application rate	P_a	µg	Fixed	Pesticide Specific (see Appendix B2)	
Flowrate	Q_{stream}	$l.s^{-1}$	Lognormal*	$\mu = 6.602$; $\sigma = 1.562$	(WMO, 1989; EPA, 2021a)
Length of rainfall event	Δt	s	Fixed	3600	(APVMA, 2020)
Carbon content (suspended solids)	$f_{oc(ss)}$	kg	Fixed	0.1	(ECB, 2003)
Density of suspended solids	$susp_{water}$	$mg.l^{-1}$	Fixed	15	(ECB, 2003)
Carbon content (sediment)	$f_{oc(sed)}$	kg	Fixed	0.05	(ECB, 2003)
Effective sediment depth	ESD	cm	Fixed	0.8	(FOCUS, 2015)
Half-Life (in water)	$DT_{50,w}$	days	Normal*	Pesticide Specific (see Appendix B2)	
Retention time	t_r	days	Fixed	5	(FOCUS, 2015)

* *Distribution type has been selected based on recommendations from literature, distribution parameters developed from best-fit analysis to data*

The most recent pesticide usage surveys carried out by the Irish DAFM have identified over 100 pesticides used on grassland and fodder crops in Ireland (DAFM, 2020, 2021). Results of risk screening study of pesticides used in Irish agriculture were used to select 15 pesticides due to their mobility, potential impact on human health, quantity of use, or a combination of the three (Harmon O'Driscoll et al., 2022: Chapter 3). Relevant pesticide specific data used in the modelling process are presented in Appendix B2 (Table B3). Pesticide risk was assessed for both Irish adults and children. Statistical parameters and distributions for population data were obtained from the Irish Universities Nutritional Alliance (IUNA) and the USEPA to allow for this probabilistic approach to be applied (Table 4.2) (IUNA 2011, IUNA 2021, USEPA 2004).

Table 4.2: Population data and statistical parameters

Parameter	Symbol	Unit	Distribution	Statistical Parameters	Source
Adult Body Weight	BW_{adult}	kg	Normal	$\mu = 78.0$, $\sigma = 16.5$	(IUNA, 2011)
Child Body Weight	BW_{child}	kg	Normal	$\mu = 32.5$, $\sigma = 11.4$	(IUNA, 2021)
Adult Water Intake*	WC_{adult}	$l.day^{-1}$	Lognormal	$\mu = 1.2$, $\sigma = 0.68$	(USEPA, 2004a; IUNA, 2011)
Child Water Intake*	WC_{child}	$l.day^{-1}$	Lognormal	$\mu = 0.5$, $\sigma = 0.32$	(USEPA, 2004a; IUNA, 2021)

* *Includes water-based drinks such as tea and coffee*

4.4 Results and Discussion

4.4.1 Predicted Concentrations in Surface Water

As stated in Section 4.2.1, the incorporation of the SCS curve number method allows site properties to be accounted for in the rainfall-runoff relationship, i.e., the amount of rainfall required to result in a runoff event is dictated by a site's soil type and land use. The daily likelihood of rainfall exceeding required levels for runoff occurring for a number of site combination in the east of Ireland is presented in Figure 4.2.

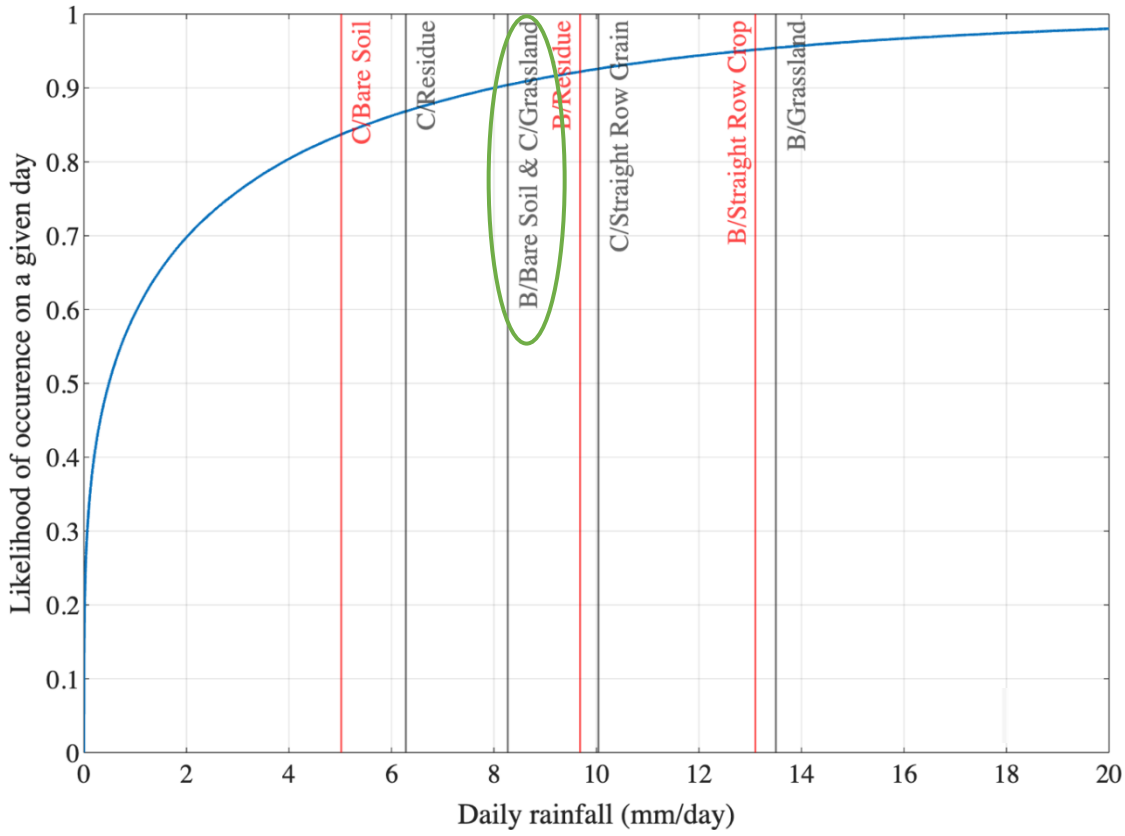


Figure 4.2: Likelihood required rainfall in East Ireland for different combinations of land use and soil groups common in Ireland. Site scenario used in case study highlighted.

The grassland site with group C soils selected for this study requires a minimum of 8.3 mm of rainfall for runoff to occur (Figure 4.2). 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, an average of 36 days each year. Consequently, the vast majority of modelled days will result in no runoff and, as a result, the model will predict a zero result for in-stream pesticide concentrations. However, there is a variation of pesticide concentrations predicted on the days where runoff will occur; this bimodal nature of modelled results is demonstrated for triclopyr in Figure B1 in Appendix B3. The likelihood of no runoff, and as a result no pesticide detection, is very high in Figure B1. This is consistent with monitoring programmes of Irish rivers carried out by the EPA over a five-year period, which detected pesticides in 4.1% of 16,069 measurements (EPA, 2019).

The pesticides have been ranked based on their predicted 95th and 99th percentile concentrations in Table 4.3 for 1 million model runs, as is the likelihood of exceeding the 0.1 µg.l^{-1} legal limit. Only the 95th and 99th percentile values are presented as there are no predicted concentrations below the 90th percentile due to rainfall not exceeding

8.3 mm for 90% of model runs (see Figure 4.2). Triclopyr was found to have the highest concentration of 8.7 µg.l^{-1}, followed by MCPA (7.56 µg.l^{-1}), and mecoprop (5.13 µg.l^{-1}). All three pesticides have very low K_{oc} values – in fact they have the second, third and sixth lowest, respectively, of the 15 pesticides. Therefore, they are unlikely to adsorb to soil, making them more available to surface runoff. Mecoprop is not very persistent in soil but is very persistent once in water, with an average half-life of approximately 155 days, and has a relatively high legal application dose. Hence it ranks higher than more mobile pesticides like 2,4-D, which rapidly breaks down in water with a half-life of 9.4 days, or clopyralid which is applied at a much lower dose than mecoprop. Conversely, the two lowest ranked pesticides, prothioconazole and phenmedipham, have 99th percentile concentrations of 7.7e-4 µg.l^{-1} and 2.1e-8 µg.l^{-1}, respectively. Both are relatively immobile as they readily adsorb to soil with high K_{OC} values. Prothioconazole is the least persistent pesticide in soil and is also non-persistent in water, while phenmedipham rapidly degrades in water with an average $DT_{50,W}$ of less than 5 hours. It is to be expected that concentrations of such immobile and non-persistent pesticides would be nearly undetectable in surface water, as has been found in monitoring studies (Aamlid et al., 2021). The modelled ranking of the pesticides is in broad agreement with the ranking of pesticides detected in Irish EPA monitoring. Of 14 pesticides monitored in 144 rivers in Ireland over a five-year period found that MCPA was the most widely detected pesticide in Irish rivers, followed by mecoprop and 2,4-D (EPA, 2019). The ranking of the modelled pesticides agrees with most commonly detected pesticides in this nationwide monitoring programme, whereby MCPA, mecoprop and 2,4-D were also predicted to have three of the four highest concentrations in this study.

Table 4.3: Ranking based on predicted concentration in surface water (including zero-runoff days)

Pesticide	95th Percentile (µg.l-1)	99th Percentile (µg.l-1)	Likelihood of exceedance (%)	Rank
Triclopyr	0.49	8.7	7.2	1
MCPA	0.38	7.56	6.8	2
Mecoprop	0.27	5.13	6.4	3
2,4-D	0.27	4.85	6.4	4
Clopyralid	0.21	3.48	6.1	5
Fluroxypyr	0.1	1.76	5.0	6
2,4-DB	0.04	1.13	3.6	7
Terbuthylazine	0.036	0.72	3.4	8
Penthiopyrad	4.3e-3*	0.095	0.95	9
Propyzamide	2.2e-3*	0.06	0.63	10
Prochloraz	1.2e-4*	4.0e-3*	0.05	11
Glyphosate	5.5e-5*	2.6e-3*	0.07	12
Pendimethalin	3.1e-5*	7.7e-4*	0.005	13
Prothioconazole	1.8e-5*	5.7e-4*	0.003	14
Phenmedipham	1.3e-12*	2.1e-8*	0	15

* *Predicted concentration less than the limit of detection (LOD) (Appendix B4)*

Pesticide detections in Irish surface water are relatively infrequent and the majority of model runs in this study result in no pesticide runoff. However, it is important to recognise that pesticide runoff can still occur with concentrations exceeding legal limits for drinking water. The legal limits set within the EU were not based on toxicological studies, and are therefore not significantly relevant in terms of health risk assessments (Dekant et al., 2010). However, these threshold values are important in assessing water quality due to their practical application within the EU in a legislative context. To better investigate potential pesticide transport, and allow for comparisons between pesticides, the model results were truncated to only include runoff events i.e. the distribution shown in the inset of Figure B1. Henceforth only the pesticide concentrations from rainfall events exceeding the required level to result in runoff are assessed, and the resulting concentration distributions of the 15 pesticides modelled in this study are presented in Figure 4.3. It is important to keep in mind the context of likelihood of exposure when examining the predicted concentrations of the selected pesticide. The 90th percentile concentrations of several pesticides presented in Figure 4.3 are relatively high when compared to the EU's legal limit of 0.1 µg.l^{-1} for individual pesticides in drinking water (European Commission, 1998), and even

the limit of 0.5 $\mu g.l^{-1}$ for total pesticide concentration set out by the original drinking water quality directive 75/440/EEC (European Commission, 1975) which is still in place today. However, these limits were derived using the lowest limit of detection at the time, rather than actual pesticide toxicology, and are perceived by some to represent the EU's desire to have no level of pesticides in drinking water (Dolan et al., 2013). Additionally, Figure 4.3 relates only to simulations when runoff occurs i.e. approximately 10% of days annually, as stated above. In that context, a 9.37 $\mu g.l^{-1}$ concentration of triclopyr is predicted to occur less than four times a year. These concentrations will be further investigated in terms of their toxicity in Section 4.4.3.

Only one of the fungicides selected for this study, penthiopyrad, is predicted to reach the legal limit of 0.1 $\mu g.l^{-1}$ at the 90^{th} percentile concentration, the resulting health implication of these exceedances will be discussed in Section 4.4.2. In general, fungicides are relatively immobile with moderate to high adsorption coefficients (Zubrod et al., 2019), while the herbicides selected in this study tend to be very mobile. Penthiopyrad has a comparatively low adsorption coefficient of 796.8 $l.kg^{-1}$ for a fungicide and is also significantly persistent in both soil ($DT_{50,s}$ of 122 days) and water ($DT_{50,W}$ of 279 days). The other fungicides selected for this study either rapidly breakdown in soil and water, such as prothioconazole (14^{th} of 15) (Figure 4.3), or are very immobile, such as prochloraz. This is also reflected in data from monitoring programmes of European surface waters from 2007 to 2017, which found that herbicides were the cause of the majority of pesticide exceedances, with 5-15% of herbicide detections resulting in an exceedance, while fungicides exceeded limits in less than 1% of cases (Mohaupt et al., 2020). This suggests that fungicides tend to be of lesser concern in surface water despite being used in similar quantities as herbicides within the EU (McGinley et al., 2023a).

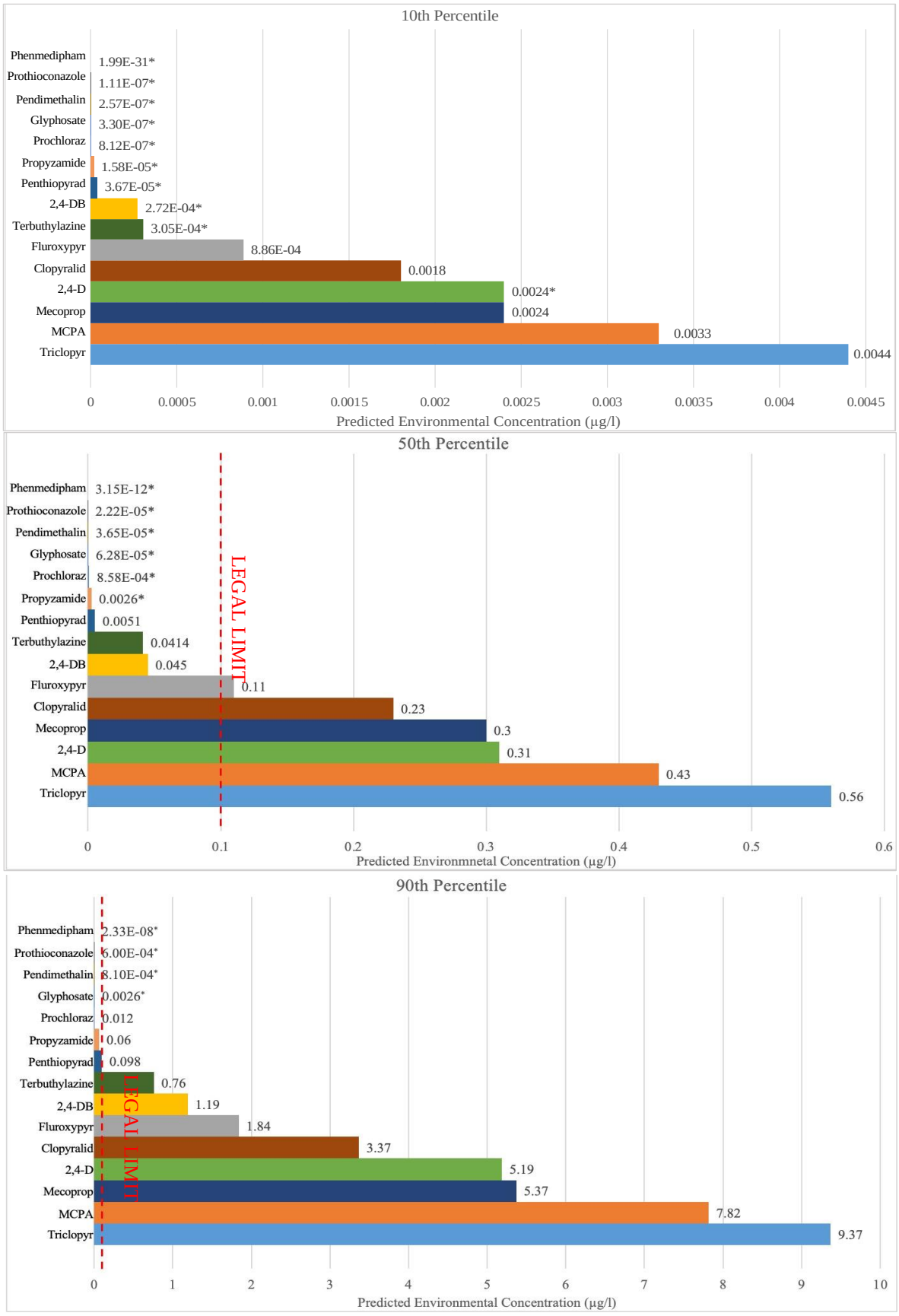


Figure 4.3: a) 10th, b) 50th, and c) 90th percentile concentrations on days when rainfall exceeds 8.3 mm (denotes less than LOD (Appendix B4)).*

4.4.2 Comparison of Predicted Concentrations with Measured Data

In order to assess whether the model produced realistic results, the predicted environmental concentrations were compared to monitoring data from a two-year long field study (McGinley et al., 2023b). These field studies were carried out at two locations in the north and east of the country, monitoring surface waterbodies for some of the most widely used pesticides in Ireland: MCPA, fluroxypyr, triclopyr, 2,4-D, mecoprop and clopyralid. The monitoring sites were predominately grassland, with moderate-to-poor draining soils, similar to the hypothetical site developed for the case study. Passive water samplers were in-situ for two weeks every month during the monitoring periods of April to November, inclusive, for the years 2021 and 2022. For each month a 14-day time-weighted average concentration was obtained for the monitored pesticides. In order to compare the predicted surface water concentrations in this study to the measured data, 14 day-average concentrations were obtained from the predicted concentrations. This was achieved by finding an average concentration for every 14 model runs, whereby 14 model runs represent 14 days in the model, over the 1,000,000 model iterations to produce over 70,000 14-day time-weighted average predicted concentrations. As these adjusted modelled data points and the monitored data were now on the same time-series, these values could then be compared directly. The 14-day average concentrations obtained from the field studies and the modelled results were compared in Figure 4.4 to assess whether the model produced realistic results for Irish agricultural sites.

It is noted that this comparison is intended as a form of ‘reality check’ on the model output, rather than a direct comparison. The hypothetical modelled site used was developed based on the most common features of Irish agriculture land (soil conditions, crop type, etc), so that it could be widely representative of many agriculture sites in Ireland, rather than a single localised monitored location. Direct comparison between the modelled and measured concentrations cannot made as the modelled site conditions are not an exact replica of the conditions present at the monitored sites. Comparison with real monitoring data within Ireland is still however useful. Overall the modelled concentrations showed broad agreement with the monitored concentrations, with both the monitoring programme and the model

detecting relatively high 95th percentile concentrations of MCPA, 2,4-D and triclopyr compared to the legal limit in drinking water.

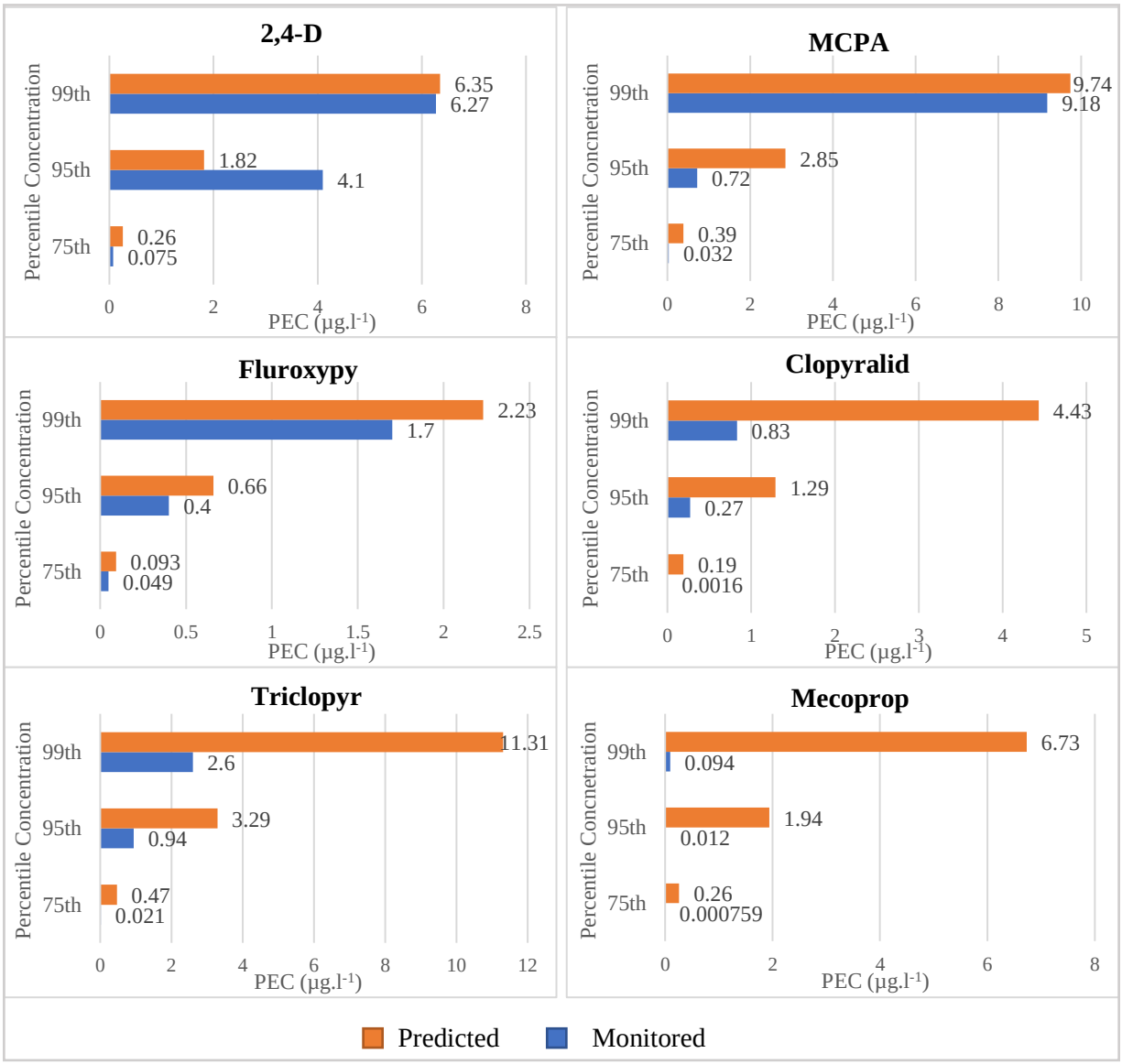


Figure 4.4: Predicted vs monitored concentrations of pesticides in runoff

Agreement between the monitored and modelled concentrations of the other three pesticides was not as good, this may reflect the extent of usage of these pesticides in the field studies, and modelling assumptions. All pesticides were modelled for their full recommended doses, which may not be the case in reality. Mecoprop and clopyralid made up only 8% and 10% of detections, compared to MCPA and fluroxypyr's 25% and 22%, suggesting that the pesticides with poorer agreement are not widely used in the areas where the monitoring was carried. Additionally, some disparity between the model results and measured concentrations are to be expected due to the differences in site conditions and model limitations. These limitations

include the lack of consideration of some factors that may further influence pesticide transport, including alternative degradation pathways and volatilisation, have not been included. However, the comparison presented here suggests that the model can produce relatively realistic results for the modelled conditions, while remaining simple enough to encourage adoption across a broad user base.

4.4.3 Human Health Risk Assessment

For the sake of brevity only the 99th percentile EDIs, the fixed ADI values obtained from the EFSA and risk quotient values are presented in Table 4.4. Triclopyr has the highest EDI for adults and children. Overall children have a higher rate of exposure to pesticides in drinking water due to their 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 are predicted to be well below the acceptable daily intake for all pesticides, even at the most extreme concentrations.

As was the case for the modelled EDIs, the risk quotient for children's health is higher than adults for example, exposure to mecoprop results in a 99th percentile risk quotient of 0.015 for adults but 0.019 for children. From Table 4.4, the pesticides with the highest potential to harm human health due to exposure via surface water were mecoprop, triclopyr and 2,4-D (risk quotients of 0.023, 0.013 and 0.011, respectively). It is interesting to note that despite terbuthylazine's relatively low concentrations in drinking water (8th out of 15, Table 4.3), it has the 4th highest risk quotient. This may be explained by its very low ADI of 0.004 mg.kg^{-1}.day^{-1}, compared to pesticides such as mecoprop (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 3% that of the quantity of applied MCPA, therefore it is unlikely to be a major risk to the health of the general public in Ireland. Of the most widely used pesticides in Ireland, both fluroxypyr and glyphosate are ranked very low (8th and 14th lowest). MCPA, however, has a much higher risk quotient score due to its mobility to water supplies, and as a result ranks in the top five pesticides in terms of risk quotient. However, as no EDIs exceed their respective ADIs, even the 99th percentile risk quotients are well below an unacceptable level of risk of one. The total level of risk posed by exposure to all pesticides is also well below one for both adults and children at the 99th percentile, with total risk quotients of 0.023 and 0.066 respectively. This suggests that despite concentrations occurring at levels higher than the EU legal limit

of 0.1 µg.l^{-1}, the results indicate that there is currently a very low level of risk to human health 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 concentrations (0.1 µg.l^{-1}) of terbuthylazine, the most toxic pesticide in the study, and fluroxypyr, the least toxic, the resulting risk quotients would be 3.85e-4 and 1.92e-6, respectively. Conversely, in order to be exposed to an unacceptable level of risk, a child would have to be exposed to a concentration of terbuthylazine of 260 µg.l^{-1}, which is over 350 times the 99th percentile of modelled concentration (Table 4.2). 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 fifteen pesticides assessed, it suggests that there is little risk associated with the level of pesticide contamination of Irish drinking water sources. 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 pose no risk to human health. Additionally, a fundamental issue with pesticide health risk assessment lies with classification of pesticide toxicity. It has been suggested that some pesticides have been incorrectly classified as low-risk due to misreporting of some pesticides' neurotoxicity by the pesticide industry (Mie and Rudén, 2023), and contradicting reports on the toxicity of pesticides (Kalofiri et al., 2021). Conversely, restrictions on the use of other pesticides may be overprotective, as they have been found to have overly conservative exposure limits (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, in addition to the issues associated with assessments on a site-specific level, and modelling limitations.

Table 4.4: 99th percentile EDI (mg.kg^{-1}.day^{-1}) for adults and children, pesticides' ADI (mg.kg^{-1}.day^{-1}), and 99th percentile RQ.

EDI Ranking					Health Risk Ranking		
Pesticide	**Rank**	**EDI$_{adult}$**	**EDI$_{child}$**	**ADI**	**Rank**	**RQ$_{adult}$**	**RQ$_{child}$**
Mecoprop	3	1.50e-4	1.92e-4	0.01	1	0.008	0.023
Triclopyr	1	1.17e-4	3.24e-4	0.03	2	0.005	0.013
2,4-D	4	1.34e-4	1.70e-4	0.02	3	0.004	0.011
Terbuthylazine	8	1.93e-5	2.42e-5	0.004	4	0.003	0.008
MCPA	2	2.02e-4	2.54e-4	0.05	5	0.002	0.007
2,4-DB	7	3.10e-5	3.94e-5	0.02	6	9.1e-4	0.003
Clopyralid	5	9.57e-5	1.20e-4	0.15	7	3.7e-4	0.001
Fluroxypyr	6	4.91e-5	6.27e-5	0.8	8	3.5e-5	9.6e-5
Propyzamide	10	1.59e-6	2.04e-6	0.05	9	1.9e-5	5.2e-5
Penthiopyrad	9	2.50e-6	3.14e-6	0.1	10	1.5e-5	4.2e-5
Prochloraz	11	9.98e-8	1.27e-7	0.01	11	6.0e-6	1.7e-5
Prothioconazole	14	1.91e-8	2.43e-8	0.05	12	1.8e-7	4.9e-7
Pendimethalin	13	2.06e-8	2.60e-8	0.125	13	9.7e-8	2.7e-7
Glyphosate	12	6.78e-8	8.52e-8	0.5	12	7.9e-8	2.2e-7
Phenmedipham	15	5.1e-13	6.5e-13	0.03	15	1.1e-5	3.0e-11
TOTAL						**0.023**	**0.066**

4.4.4 Sensitivity Analysis

The impact of variation in input parameter on the final output, risk quotient, was assessed in accordance with the ±10% of mean approach outlined in Section 4.2.5 above. The health risk model was most sensitive to variation to the pesticide's ADI (+15%, -11%). The in-stream concentration was found to be almost as influential (+15%, -10%), and was followed by body weight (+9%, -5%) and finally water consumption (+3%, - 1%). As the in-stream concentration was found to be a highly influential parameter, and involves a number of parameters and computational processes, further analysis of the influence of parameter variability and model sensitivity was carried out as presented in the following sections.

4.4.4.1 Model Sensitivity

The runoff model was most sensitive to a variation in rainfall (+22%, -25%), distance to waterbody (-16%), field slope (+14%, -10%), pesticide application rate, (+10%, -9%), and stream flowrate (+3%, -7%). Both distance to waterbody and slope were

identified as critical parameters by Probst et al. (2005), while Schriever et al. (2007) and Utami et al. (2020) found that daily average rainfall was one of the most influential parameters. Most of the influential parameters in this study are modelled as fixed variables due to their localised nature. This highlights the importance for obtaining site-specific data where possible for best representation of the modelled site.

4.4.4.2 Impact of Rainfall Data on Model Output

Rainfall was identified as the most important parameter for runoff. The change in rainfall data, using precipitation data from the west of the country, represented a 51% increase in daily average rainfall and, resulted in a 210% increase in 95th percentile concentration of triclopyr in surface water. This most likely due to an increase in days where rainfall exceeds the level required for runoff to take place in accordance with the SCS curve number approach (USDA, 2004b).

4.4.4.3 Impact of Timing of Application on Model Output

The resulting impact of varying application timing for one, two and five days on triclopyr's 95th percentile concentration was +6.1%, +4.1% and -4.1% respectively. Triclopyr is moderately persistent with a mean $DT_{50,s}$ of 35 days, therefore changing the number days between application and rainfall by a few days does not have as large an impact as it would for a pesticide that rapidly degrades such as prothioconazole with a half-life of 2.8 days (+11%, +50% and -40% impact on 95th percentile concentrations).

4.4.4.4 Impact of Curve Number on Model Output

The change in site scenario was found to have a significant impact on the modelled results, as much more rain is required for runoff to occur. Rainfall of 13.5 mm is required for group B soils, with only 4.5% of model runs exceeding this, compared to 8.3 mm or 10% of model runs for group C soils. As a result, triclopyr's 95th percentile concentration for the new scenario was zero, and there was a 78% decrease in the 99th percentile concentration. This highlights the importance of site-specific conditions in pesticide transport and illustrates the impact improvements made to the model developed with the addition of the curve number to the SFIL approach, may have to model results.

4.4.4.5 Impact of In-Stream Processes on Model Output

Overall, the inclusion of in-stream processes results in a 51% decrease in the 95th percentile concentration of triclopyr, with adsorption to sediment contributing most to the reduction in concentration (26% reduction) and adsorption to suspended solids contributing the least (0.4% reduction). However, in-stream processes would have a much greater impact on pesticides with very high adsorption coefficients such as prochloraz, or very short $DT_{50,W}$ such as prothioconazole. If they are removed, the 95th percentile concentrations for these pesticides increase by +3233% and 11011% respectively.

4.4.4.6 Seasonal Analysis

The variation of site conditions and agricultural practices due to seasonal effects can also impact pesticide transport. In Ireland, pesticides tend to be used in the greatest quantities shortly before and during the growing season, which begins in spring and extends until the end of autumn. However, Ireland can experience some of its most extreme periods of rainfall during the winter months, when pesticides are not in use. Therefore, it is important to consider the climatic conditions prevalent during the growing season and avoid including extremely heavy rainfall events that are less likely to occur during this period. As expected, the simulated concentrations of triclopyr were lower for the growing season than the annual conditions, with a 25% decrease in the 95th percentile concentration over the growing season. This is most likely due to the reduced number of rainfall events that will result in runoff during the growing season, with less than 8.5% of rainfall events during the growing season expected to result in runoff, compared to 10% annually.

4.5 Conclusions and Recommendations

A probabilistic modelling framework was developed, by adapting existing pesticide transport models and combining them with a quantitative health risk assessment approach, to improve the representation of real-world scenarios and quantitatively assess potential human health risks. This framework offers a useful step towards the use of probabilistic analysis in pesticide risk assessment. Although this modelling approach does not incorporate detailed considerations of some of the pesticide transport models, its comparative simplicity facilitates the integration of important

uncertainty. Thus, the model provides valuable insights into the relative risks of various pesticides, while using an accessible approach for a wide user base.

An Irish case study was developed to illustrate how the model may be applied and facilitate study of the potential health risks arising from contamination of drinking water by several pesticides used in Ireland. The modelled concentrations were shown to be in broad agreement with the measured concentrations of an Irish field study, and the modelled ranking of pesticides most likely to be detected in surface waters compares well with the findings of Irish and European monitoring studies. Triclopyr, MCPA and mecoprop were found to be the most mobile pesticides and predicted to occur in the highest concentrations. The three highest risk pesticides in terms of human health were found to be mecoprop, triclopyr and 2,4-D, however all pesticides were found to be well below an unacceptable level of risk currently and may only need increased monitoring in areas of high usage in Ireland to ensure levels of risk do not exceed acceptable level. The modelling framework in this study was developed in such a way to allow catchment managers and water quality monitors to adapt the model for their own use. The model was found to be sensitive to variation in localised parameters, suggesting a need for site-specific parameters when using the model. Additional factors such as site location, timing of pesticide application, and the addition of in-stream processes were all found to affect the modelled results.

The model may be improved through the incorporation of more health data from literature and lab studies, in addition to the use of regulatory thresholds, to allow for greater consideration of uncertainty associated with pesticide toxicity. Future works may include combining this model with environmental risk models to quantitatively assess pesticide risk to aquatic or terrestrial organisms, or the incorporation of geospatial datasets to develop a GIS-based tool. Additionally, input parameters may also be adapted to account for potential effects resulting from climate change.

CHAPTER 5

QUANTIFYING THE INFLUENCE OF CLIMATE CHANGE ON PESTICIDE RISKS IN DRINKING WATER

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ABSTRACT

This study investigated climate change impacts on pesticide concentrations and resulting health risks due to projected changes in precipitation, temperature, and growing seasons. Climate projections from bias-corrected, high-resolution climate models were integrated into a probabilistic modelling framework. A risk assessment was performed for three timeframes (current, 2050, 2100), under two different climate scenarios (RCP4.5 and RCP8.5) for locations in the north-east and the south-west of Ireland. This study found that exceedances of pesticide concentrations in drinking water will increase under all climate scenarios, approaching or exceeding legal limit by greater amounts than under baseline conditions, with health risks increasing by an average of 18% under RCP4.5 (2050), to 38% under RCP8.5 (2100). The model results also indicate significant regional variation in risk, with risks 48% higher in the south-west than the north-east under baseline conditions, and climate change effects intensifying these regional variances with risk up to 70% higher under RCP4.5 (2050), and 85% higher under RCP8.5 (2100). Despite these increases, overall pesticide health risks are likely to remain low in Ireland under future climates. This study presents a probabilistic framework that may be applied internationally to quantify the impact of climate change on pesticide risk at a local-scale and may be adapted for different site conditions and climate projections to suit users' needs. This approach can inform future pesticide management programmes by identifying vulnerable areas and key pesticides under changing climate conditions, emphasising the importance of incorporating climate change into pesticide risk mitigation and public health strategies.

5.1 INTRODUCTION

Climate change has emerged as one of the most pressing challenges of the 21st century and has already resulted in extensive changes to the atmosphere, natural resources, and aquatic and terrestrial ecosystems (IPCC, 2022). There is significant concern regarding the impacts that climate change-related flooding and droughts may have on the availability of drinking water (Chantal et al., 2023). In addition to these hydrologic effects, climate change also has great potential to affect drinking water quality due to increased agricultural pollutant loading, including pesticide contamination (Kaka et al., 2021). The extensive use of pesticides in modern agriculture has already resulted in the accumulation of pollutants in soil and water bodies (Li and Niu, 2021; Wolfram et al., 2021; McGinley et al., 2023a), posing significant threats to human health and the environment (Kalyabina et al., 2021; Wang et al., 2022). The intensification of food production required to meet a 60% increase in food demands by 2050 (UNEP, 2022), as well as the projected changes to climate variables (O'Brien et al., 2024), have the potential to exacerbate the likelihood of exposure to these chemicals in drinking water supplies and, in turn, pose greater health risks (Delcour et al., 2015; Saha et al., 2019). Therefore, the implementation of pesticide risk assessment and management measures for the future climate is a key factor in reducing the impact of climate change on water quality (Schäfer et al., 2019).

Pesticide risk assessment and management often relies on simulation models to assess pesticide transport, and resulting environmental and human health risks under current conditions, due to their effectiveness in representing the relationships between pesticide properties and site conditions (Li and Niu, 2021). Several studies have applied deterministic modelling approaches, models that produce a single outcome based on the assumption of fixed relationships between input variables and excluding any randomness, to predict pesticide concentrations for research and regulation under current climatic conditions (Luo et al., 2011; Pullan et al., 2016; Wang et al., 2019a). Probabilistic modelling approaches, models that incorporate variability and uncertainty through the use of probability distributions to represent likelihood of different variable combinations and resulting outcomes, are becoming more widely used in this field to account for the variability associated with pesticide behaviour, as well as the uncertainty associated with modelling soil, weather and pesticide data

(Cantoni et al., 2021; Troldborg et al., 2022). These deterministic and probabilistic simulation models are combined with effects models in order to quantify the risk arising from pesticide usage under current climatic conditions (Focks et al., 2014). However, it has been suggested that environment and human health risks arising from pesticide exposure are likely to change in the future due to climate change (Nadal et al., 2015; Tudi et al., 2021). Many studies have worked on identifying parameters which may change under future climates, and therefore may influence future pesticide risks i.e. changes to rainfall frequency and intensity, increasing temperatures and changes to growing seasons (Noyes et al., 2009; Delcour et al., 2015; Biswas et al., 2018). Despite there being considerable research identifying key climate change parameters, there is still limited work modifying fate and risk models to quantify the influence of these effects on pesticide risk to the environmental and human health risks (Hader et al., 2022; Bolan et al., 2024). Therefore, the majority of pesticide fate and risk models to-date only provide estimation of risk under current conditions, and therefore do not provide insight into future risk profiles or the need for climate adaptation strategies (Sperotto et al., 2017; Oldenkamp et al., 2024).

Although it is still a limited area of research, some studies have begun to integrate climate projections and pesticide fate/risk models (Moe et al., 2024). Initially work on applying probabilistic approaches to quantify climate change impacts on pesticide loss was limited to assessing changes in future environmental pesticide concentrations in groundwaters (Steffens et al., 2015) and surface water (Gagnon et al., 2016). More recently, this work has been advanced by researchers to analyse potential changes to pesticide environmental risks arising from future climate conditions using Bayesian Networks (Mentzel et al., 2022a; Martínez-Megías et al., 2023; Oldenkamp et al., 2024). Both Mentzel et al. (2022a) and Oldenkamp et al. (2024) adapted a pesticide exposure model (WISPE) using future climate projections for Norway to assess the influence climate change will have on pesticide risks in aquatic ecosystems. Similarly, Martínez-Megías (2023) applied Bayesian networks to another pesticide exposure model (RICEWQ) to probabilistically assess environmental risks arising from pesticide use in rice fields and resulting impacts of climate change on this risk in a Mediterranean climate. Despite the work carried out in these studies, research on adapting pesticide environmental risk assessments for climate change effects is still an emerging area of research (Martínez-Megías et al., 2023), and even less work has been

carried out in adapting human risk assessments for climate change (Gatto et al., 2016; Langreiter et al., 2023). Furthermore, although these studies have contributed significantly to the literature by advancing the work in the combination of global climate models with pesticide fate and risk models, these studies have been limited due to the climate models used in their assessments: The use of a small number of climate model ensembles can affect stochastic representation of climate change, as internal variation within the model can mask regional variability of climate change (Moe et al., 2022), and the use of global climate models that have not been downscaled to higher-resolution projections may not fully capture spatial variability of climate change effects (Kotamarthi et al., 2021). Additionally, developing risk assessments that use climate models that have not been bias-corrected may introduce errors into the model output, therefore they should be bias-corrected using observed historical data to improve robustness and reliability of projections (Navarro-Racines et al., 2020). The current study seeks contribute to this field of research by adapting a probabilistic human health risk model for future climatic conditions, utilising a large number of climate projections from high-resolution, bias-corrected climate models.

The aim of this study was to examine how future climatic conditions may influence pesticide concentrations in drinking water due to changes in pesticide runoff and assess resulting human health risk for future climatic conditions. This study presents a first-step towards quantifying climate change impacts on future risks posed to human health from pesticide exposure using probabilistic modelling. This will be achieved by (1) developing probability distributions for climate inputs using multi-ensemble, bias-corrected projections based on downscaled regional climate models, (2) adapting a previously developed, accessible probabilistic risk model for these climate scenarios using a Monte-Carlo approach, (3) illustrating the application of this model to predict future pesticide concentrations and resulting risk under future climatic conditions for Ireland. This study is one of first to assess the interaction between climate change and pesticide transport in terms of human health risks, and the approach developed may be used to inform pesticide-specific risk management schemes and climate adaptation strategies for the future.

5.2 METHODOLOGY

5.2.1 CLIMATE CHANGE PROJECTIONS

Standardised climate projections of daily precipitation and temperature data in Ireland were obtained from the TRANSLATE project (O'Brien et al., 2024). The TRANSLATE project has developed multi-ensemble and bias-corrected projections based on the post-processing of high-resolution regional climate models over discrete 30-year time periods using different emission scenarios for the quantitative assessment of climate change impacts within Ireland. Location-specific climate projections for two locations in the north-east (Dunleer, Co. Louth; 53° 50′ 09″ N, 6° 25′ 04″ W), and south-west (Causeway, Co. Kerry; 52° 24′ 48″ N, 9° 43′ 50″ W), of Ireland were used in pesticide risk modelling to represent the regional variability of climate change effects. Five climate scenarios were considered in the analysis: (1) baseline existing conditions, based on 1976 – 2005 climatic data, (2) the IPCC RCP4.5 scenario (intermediate emissions) for mid-century, (3) the IPCC RCP8.5 scenario (high emissions) for mid-century, (4) RCP4.5 for end-of-century, and (5) RCP8.5 for end-of-century. The two timeframes (mid-century and end-of-century) are based on 30-years of climate projections over the period of 2041 – 2070 and 2071 – 2100, respectively. The changes to the average precipitation and temperature based on these projections are given in Table 5.1, where the values represent the change under each climate scenario relative to the baseline conditions. In both locations daily precipitation is projected to increase, with the largest increase in both cases occurring at end of the century. Similarly, as daily temperature is projected to increase at both locations, growing seasons were found to be longer at both locations, beginning earlier in the year, as will be discussed in detail in Section 5.3.

Climate projections for Ireland were integrated into the probabilistic risk model framework (Section 5.2.2) in order to illustrate how the proposed framework can be applied using data from climate models for specific regions. However, other countries across the North Atlantic region (Northern Europe, Eastern Canada and North-Eastern USA) are likely to experience relatively similar climate effects to Ireland. IPCC projections for the region suggest that precipitation will experience a median increase of 12.2% and temperature by a median increase of 2.1 °C by 2100 relative to 1986 – 2005 levels (Gutiérrez et al., 2021). Precipitation and temperature in Ireland are

projected to increase by 10.8 - 12.2% and 2.2 – 2.4 °C (Table 5.1), which is in line with increases across the North Atlantic region. Therefore, while the projections used in this study are specific to two locations in Ireland, the results in this study may be indicative of changes to future pesticide risks across the region and may help inform the need for pesticide risk assessment under future climates.

Table 5.1: Changes to climate parameters under future climate scenarios relative to baseline conditions

Scenario	Daily precipitation		Daily mean temperature	
	Change to mean (%)	Change to standard deviation (%)	Change to mean (%)	Change to standard deviation (%)
Dunleer				
RCP4.5 (2050)	+ 3.1	+ 7.1	+ 10.2	+ 3.9
RCP8.5 (2050)	+ 5.4	+ 10.4	+ 14.7	+ 4.8
RCP4.5 (2100)	+ 6.8	+ 11.5	+ 14.4	+ 3.9
RCP8.5 (2100)	+ 12.2	+ 19.9	+ 26.9	+ 6.6
Causeway				
RCP4.5 (2050)	+ 2.0	+ 13.4	+ 8.7	- 1.0
RCP8.5 (2050)	+ 5.1	+ 19.6	+ 12.4	- 0.1
RCP4.5 (2100)	+ 5.8	+ 19.7	+ 12.6	- 0.7
RCP8.5 (2100)	+ 10.8	+ 21.7	+ 22.9	+ 1.2

Note: Change to mean = $\delta_{mean}(t)$ and Change to standard deviation = $\delta_{variance}(t)$ for Eqs. 5.4, 5.5 and 5.8 in Section 5.2.2

5.2.2 Pesticide Risk Assessment Methodology

This work builds on the authors' previous work in developing a user-friendly, probabilistic pesticide risk model (Harmon O'Driscoll et al., 2024: Chapter 4), through re-development to consider the influence of climate change using state-of-the-art climate projections. These modifications enabled the quantification of climate change impacts on future pesticide runoff to surface waters and resulting health risks arising from changes to pesticide exposure via drinking water. In brief, the authors' previous work developed a probabilistic pesticide risk assessment by building on the existing SFIL model (OECD, 2000; Berenzen et al., 2005). This base model allowed users to assess the influence of land use, soil and climate conditions, site data, and pesticide properties on exposure concentrations of pesticides in surface waters. The authors modified this base model by (1) incorporating a more detailed approach to assess the rainfall-runoff relationship using the SCS curve number method (USDA, 2004b), (2) including additional in-stream processes that may affect pesticide concentration, (3) combining this pesticide transport model with a widely used pesticide health risk assessment approach (FAO and WHO, 1997; EFSA, 2019), and (4) utilising a Monte

Carlo simulation approach to adapt the model for probabilistic assessment. For the work detailed herein, the authors adapted the model to facilitate incorporation of climate projections from a range of downscaled global climate models to account for the direct effects of climate change on pesticide transport and resulting health risks, thereby illustrating how the model may be adapted for future climates to inform climate adaption strategies. Figure 5.1 illustrates how the exposure component of the health risk assessment implemented in this study was modified for future climate scenarios.

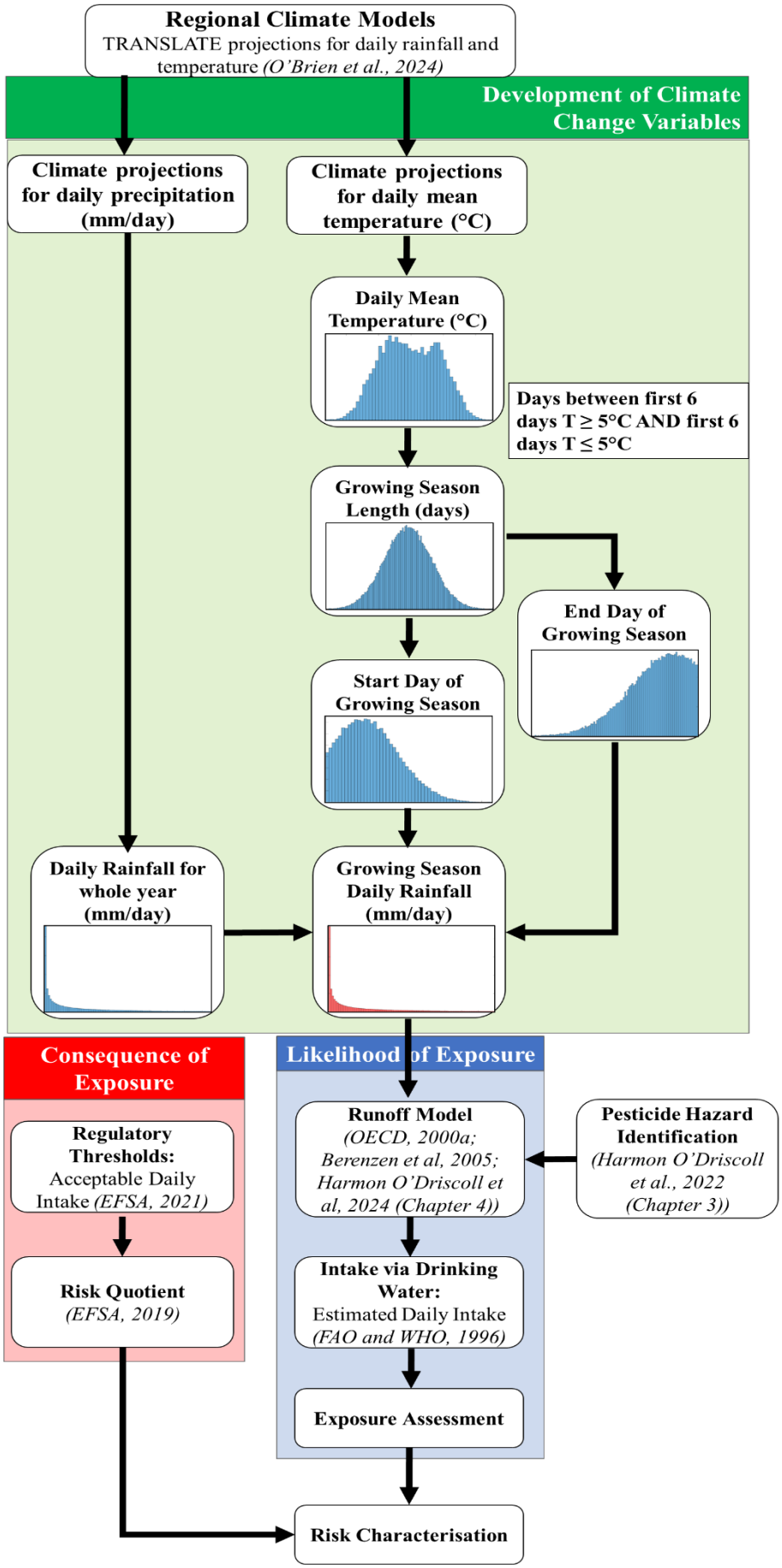


Figure 5.1: Health risk assessment framework adapted for climate change

The following discussion will focus on the elements of the model that will be adjusted to allow for the incorporation of climate change projections. For detailed discussion of the original model development see the authors' previous work (Harmon O'Driscoll et al., 2024: Chapter 4). Daily precipitation is the primary climatic parameter in the study's exposure model as it influences both the runoff volume (Eq. 5.1) and the percentage of applied pesticide available for runoff. Given that climate change is likely to have an impact on rainfall intensity and volume in Ireland (Nolan and Flanagan, 2020), there is significant potential for climate change to alter the level of risk associated with pesticide exposure.

First, daily runoff volume was calculated using model modifications adapted from the USDA's SCS Curve Number approach (USDA, 2004b):

$$Q = \frac{(R - 0.2S)^2}{(R + 0.8S)} \text{ ; for R} \geq 0.2\text{S}$$
$$Q = 0 \text{ ; for R} < 0.2\text{S} \quad (5.1)$$

where Q is the daily runoff volume (mm.day^{-1}), R is daily precipitation (mm.day^{-1}), and S is the maximum potential soil retention (mm). Based on Eq. 5.1, runoff will only occur when a rainfall event exceeds the threshold value of 20% of the maximum potential soil retention. The threshold value varies based on the interaction between a site's land-use, soil type and cover conditions as detailed in USDA (2004a). This highlights the importance of changes in rainfall patterns under future climates, as heavier rainfall periods are likely to result in more exceedances of this threshold and hence more frequent runoff events.

The gamma distribution was identified as the most appropriate for daily rainfall data based on distribution fitting to historical rainfall data and approaches taken in literature (Chandler and Wheater, 2002; Mockler et al., 2016; Ye et al., 2018). Daily rainfall under baseline conditions (R) was modelled as follows:

$$f(R) = \frac{(R^{\alpha-1}e^{-\frac{R}{\beta}})}{\beta^{\alpha}\Gamma(\alpha)}; \text{ for } 0 < \text{R} < \infty \quad (5.2)$$

where α and β are the shape and scale parameters of the gamma distribution, and the gamma function Γ(α) is defined as:

$$\Gamma(\alpha) = \int_0^{\infty} R^{\alpha-1}e^{-R}\, dR \quad (5.3)$$

In order to adapt Eq. 5.1 to account for the impacts of climate change on rainfall and resulting runoff, the shape and scale parameters (α and β) of Eq. 5.2 were modified to fit projected rainfall data (α_{cs} and β_{cs}, whereby cs is the different climate scenarios) as follows:

$$\alpha_{cs} = \frac{\mu^2}{\sigma^2} x \frac{\left(1 + \frac{\delta_{mean}(t)}{100}\right)^2}{\left(1 + \frac{\delta_{variance}(t)}{100}\right)^2} \tag{5.4}$$

$$\beta_{cs} = \frac{\sigma^2}{\mu} x \frac{\left(1 + \frac{\delta_{variance}(t)}{100}\right)^2}{1 + \delta_{mean}(t)} \tag{5.5}$$

where μ and σ are the mean and variance of baseline rainfall data, and $\delta_{mean}(t)$ and $\delta_{variance}(t)$ are timeframe-dependent percentage changes to the mean and variance value for each climate scenario (Table 5.1). Daily rainfall under future climate scenarios (R_{cs}) was then modelled based on Eq. 5.2 but using these adapted shape and scale parameters.

Eqs. 5.2 – 5.5 demonstrate how daily rainfall values for future climates were developed for the pesticide transport model. However, the resulting rainfall dataset is for the whole year, including months outside the growing season where there is little or no pesticide application. Previous work by the authors identified that predicted environmental concentration, and resulting health risk, decreased by up to 25% when modelling for conditions related to the growing season period, as opposed to the commonly modelled annual conditions, due to decreased levels of rainfall in the growing season compared to annual conditions in Ireland (Harmon O'Driscoll et al., 2024: Chapter 4). As a result, pesticide risk can be overstated when using annual climatic conditions in place of growing season conditions. Additionally, pesticide application timings are largely dependent on the timings of crop planting and growing during the growing season (Bareille et al., 2024). Therefore, this study only considered growing season conditions in the modelling of pesticide risk by limiting climate projections to the growing season period only, thereby better representing realistic climatic conditions during pesticide application. The thermal growing season for grassland was used to assess the period of pesticide application, as well as pesticide transport and resulting risks for this period, extrapolating growing season conditions from daily temperature projections as shown in Figure 5.1. The thermal growing

season for grassland (GSL (days)) is defined as the length of time between the first six successive days with an average temperature greater than five degrees, and the first six successive days with an average temperature less than five degrees (Dunn et al., 2020; Nolan and Flanagan, 2020), or as follows:

$$GSL = n - (i_2 - i_1) \quad (5.6)$$
$$where\ i_1 = \min[i|(T_i > T_c)\ and\ (T_{i+1} > T_c) and \ldots (T_{i+5} > T_c)]$$
$$\text{and } i_2 = \min[i|i > i_1 + 5\ and\ (T_i < T_c)\ and\ (T_{i+1} < T_c)\ and \ldots (T_{i+5} < T_c)]$$

where n is the number of days in the year, i_1 is the first day whereby the following five consecutive days have a mean temperature greater than T_C, the required growing temperature for a specific crop which is 5 °C for grassland, i_2 is the first day whereby the next five consecutive days have a mean temperature less than T_C, and T_i is the mean air temperatures (°C) on day i. Based on best-fit analysis of the observed daily mean temperature for baseline conditions, a normal distribution was used to obtain daily mean temperature:

$$f(T) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(T-\mu)^2}{2\sigma^2}} \quad (5.7)$$

where μ and σ, are the mean and standard deviation of the observed daily temperature data for baseline conditions. A modification was made to Eq. 5.7 to allow for climate-related effects to be incorporated into modelling daily temperature values for future scenarios (T_{cs}) as follows:

$$f(T_{cs}) = \frac{1}{\sqrt{2\pi\left(\sigma\left(\frac{(1+\delta_{variance}(t))}{100}\right)\right)^2}} e^{-\frac{\left(T_{cs}-\left(\mu\left(\frac{1+\delta_{mean}(t)}{100}\right)\right)\right)^2}{2\left(\sigma\left(\frac{(1+\delta_{variance}(t))}{100}\right)\right)^2}} \quad (5.8)$$

where $\delta_{mean}(t)$ and $\delta_{variance}(t)$ are timeframe-dependent percentage changes to the mean and variance value for each climate scenario (Table 5.1). For each climate scenario, the growing season length is calculated using Eq. 5.6, for future daily temperatures as obtained from Eq. 5.8, and distributions fitted to the resulting growing season length data. Additionally, distributions for the start and end day of growing seasons were extrapolated from growing season lengths, and these conditions were then used to truncate daily precipitation projections from annual conditions to growing season conditions as shown in Figure 5.1. The growing season conditions and resulting daily

rainfall during growing season for each climate scenario used in modelling are discussed in Section 5.3.1.

Eq. 5.1 was then modified for runoff volume under future climates (Q_{cs}) to account for the adaptations applied to rainfall data as follows:

$$Q_{cs} = \frac{(R_{cs} - 0.2S)^2}{(R_{cs} + 0.8S)} \text{ ; for } R_{cs} \geq 0.2S \quad (5.9)$$

$$Q_{cs} = 0 \text{ ; for } R_{cs} < 0.2S$$

Daily precipitation and daily runoff volume for the climate change scenario, as calculated in Eqs. 5.2 and 5.9, were then used to estimate the percentage of applied pesticide dose lost to runoff ($L_{\%}$), in combination with pesticide physiochemical properties and several site conditions as follows:

$$L_{\%} = \frac{Q_{cs}}{R_{cs}} \, x \frac{e^{\frac{-tln2}{DT_{50}}} \, x \, 100}{1 + K_d} x f_1 x f_2 x f_3 \quad (5.10)$$

where DT_{50} and K_d are input parameters based on pesticide properties (see Table C1), and f_1, f_2, and f_3 are correction factors to account for site conditions (Beinat and Van den Berg, 1996; OECD, 2000; FOCUS, 2002; Berenzen et al., 2005).

P_c, the pesticide concentration at the edge of field ($\mu g.l^{-1}$), was calculated as per Berenzen et al. (2005):

$$P_c = L_{\%} x P_a x \frac{1}{Q_{stream} x \, \Delta t} \quad (5.11)$$

whereby P_a is the application dose of the pesticide (µg), Q_{stream} is the flowrate of the waterbody ($l.s^{-1}$) and Δt is the length of the precipitation event (s), as defined by APVMA (2020).

The predicted pesticide concentration in drinking water was assessed as the product of the edge-of-field concentration (P_c) and several in-stream reduction factors (ρ_{ss}, ρ_{sed}, ρ_{deg}) (ECB, 2003; EPA NZ, 2020) that may reduce the concentration of pesticides over a retention period of five days (FOCUS, 2015):

$$PEC = P_c \, x \, \rho_{ss} \, x \, \rho_{sed} \, x \, \rho_{deg} \quad (5.12)$$

Finally, the human exposure rate to a pesticide was calculated according to FAO and WHO (1997) guidelines:

$$EDI = \frac{PEC\ x\ WC}{BW\ x\ 1000} \quad (5.13)$$

where EDI is the estimated daily intake ($mg.kg^{-1}.day^{-1}$), WC is the rate of water consumption ($l.day^{-1}$), BW is bodyweight (kg), and 1000 is a conversion factor. The estimated daily intake is the final output of the exposure component of the risk modelling framework described in Figure 5.1. To estimate the risk resulting from this exposure, it was then compared to the individual pesticide's ADI ($mg.kg^{-1}.day^{-1}$), the EFSA's regulatory thresholds for chronic health, in a risk quotient approach to provide a human health risk assessment (EFSA, 2019, 2021):

$$RQ = \frac{EDI}{ADI} \quad (5.14)$$

An additive approach, as recommended by the EFSA, was taken to assess the worst-case-scenario risk assuming exposure to a mixture of all modelled pesticides. Therefore, total health risk was calculated as the sum of risk quotients for each individual pesticide (i):

$$RQ_{total} = \sum RQ_i = \sum \frac{EDI_i}{ADI_i} \quad (5.15)$$

The proposed approach to facilitate adapting input variables in a probabilistic risk model for climate change projections may be applied using regional projections for any locations to suit users' needs. Section 5.3 presents results for two Irish locations to illustrate how the framework may be applied and to quantify climate change impacts to pesticide health risks in an Irish context. The use of the probabilistic approach described in Sections 5.2.3 enabled the model to consider the uncertainty and variability associated with the model, input parameters and importantly, climate projections for future scenarios.

5.2.3 Probabilistic Modelling Methodology

In developing the probabilistic approach used for the risk modelling framework in this study, input parameters, including climate variables under future scenarios, soil data, and pesticide properties, were fitted with probability distributions based on literature and best-fit analysis to available data. The probability distributions and statistical parameters developed for the input data are detailed in Section 5.2.4. A Monte-Carlo simulation method was then applied to allow the propagation of the model with randomly selected inputs from the defined distributions. For each iteration of the

model, one random sample was taken from each input distribution providing an iterative output. When all iterations are complete, distributions of model outputs were obtained. This approach was taken in developing distributions for growing season conditions (Section 5.3.1), as well as estimating pesticide concentrations in drinking water and resulting health risk (Section 5.3.2). The use on Monte-Carlo simulations allowed incorporation of input data uncertainty and variability into the model, providing a distribution of estimated pesticide concentrations and resulting pesticide risk quotients considering the effects of uncertainty and variability on model outputs. The model was run for 1,000,000 iterations for each location examined herein to ensure statistical stability.

5.2.4 Model Parameterisation

As previously mentioned, the modelling approach described above was applied for two different locations in Ireland: Dunleer in the north-east (NE) of Ireland, and Causeway in the south-west (SW), to assess the potential impact that climate change may have on pesticide transport to drinking water supplies and resulting health impacts. Comparison of the results from both sites will provides insights into climate change impact spatial variability, as highlighted by Nolan and Flanagan (2020). Both the NE site and the SW site have relatively similar site conditions, i.e. land-use and soil types, as they are predominately grassland (pasture, rough grazing, silage, hay or any combination) (EEA, 2021) with similar soil types (both sites classified as hydrologic group C soils (USDA, 2009; EPA, 2021b)). These site conditions are representative of the average Irish agricultural scenario, where 90% of agricultural land is grassland, and group C is the dominant soil group (Cawkwell et al., 2017; EPA, 2021b). A hypothetical agricultural site representing the average Irish conditions was developed by the authors in a previous study (Harmon O'Driscoll et al., 2024: Chapter 4), which is similar to the site conditions at both locations in the current study, and was herein used to represent soil and agricultural conditions in this study. Therefore, any differences in pesticide risks at the two locations will be a result of the regional variation of climate impacts as opposed to the influence of minor variations in site conditions. The statistical parameters used in assessing the influence of climate change on pesticide risk are discussed in Section 5.3.1. The Irish DAFM has lists 82 pesticides used on Irish grassland and fodder based on the most recent pesticide usage surveys (DAFM, 2020, 2021, 2024). A previous risk screening study of these pesticides

identified 15 key pesticides based on their mobility, toxicity to humans, quantity of use in Ireland, or a combination of three (Harmon O'Driscoll et al., 2022: Chapter 3). Details of the pesticide properties and their statistical parameters used in the modelling process are available in Table C1. National population data for body weight and water consumption rates were obtained from the IUNA national surveys and USEPA guidelines to probabilistically modelling pesticide exposure rates (USEPA, 2004a; IUNA, 2011, 2021). The statistical parameters developed for site and population data used in this study are presented in Table 5.2.

Table 5.2: Statistical parameters for probabilistic model (future conditions)

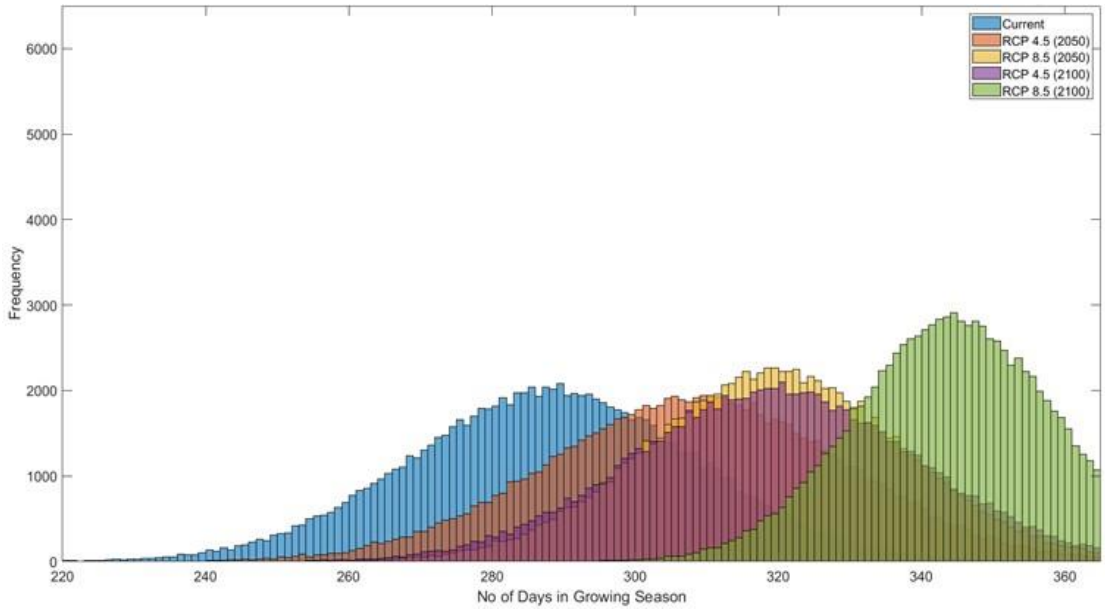
Parameter	Symbol	Unit	Distribution	Values	Source
Application interval	t	days	Fixed	3	(OECD, 2000)
Carbon content$_{soil}$	OC	%	Normal	$\mu = 2.36$; $\sigma = 2.79$	(Fay et al., 2007; EPA, 2021b)
Interception rate	PI	%	Uniform	min = 0; max = 70	(Labite and Cummins, 2012; FOCUS, 2015)
Soil moisture retention	S	mm	Based on CN	-	(USDA, 2004b)
slope	-	%	Fixed	3	(Clarke et al., 2016)
Distance to waterbody	z	m	Fixed	0	(Berenzen et al., 2005)
Flowrate	Q_{stream}	l.s^{-1}	Lognormal	$\mu = 6.602$; $\sigma = 1.562$	(WMO, 1989; EPA, 2021a)
Length of rainfall event	Δt	s	Fixed	3600	(APVMA, 2020)
Carbon content$_{ss}$	$f_{oc(ss)}$	kg	Fixed	0.1	(ECB, 2003)
Density of susp solids	$susp_{water}$	mg.l^{-1}	Fixed	15	(ECB, 2003)
Carbon content$_{sed}$	$f_{oc(sed)}$	kg	Fixed	0.05	(ECB, 2003)
Effective sediment depth	ESD	cm	Fixed	0.8	(FOCUS, 2015)
Retention time	t_r	days	Fixed	5	(FOCUS, 2015)
Adult Body Weight	BW_{adult}	kg	Normal	$\mu = 78.0$, $\sigma = 16.5$	(IUNA, 2011)
Child Body Weight	BW_{child}	kg	Normal	$\mu = 32.5$, $\sigma = 11.4$	(IUNA, 2021)
Adult Water Intake	WC_{adult}	l.day^{-1}	Lognormal	$\mu = 1.2$, $\sigma = 0.68$	(USEPA, 2004a; IUNA, 2011)
Child Water Intake	WC_{child}	l.day^{-1}	Lognormal	$\mu = 0.5$, $\sigma = 0.32$	(USEPA, 2004a; IUNA, 2021)

Distribution selected based on literature, distribution parameters developed from best-fit analysis to data. Ss = suspended solids, sed = sediment

5.3 Results and Discussion

5.3.1 Impact of Climate Change on Growing Season

Climate projections for Ireland indicate that daily temperatures will rise in the future, and this is likely to affect growing season conditions across the country. At both study locations daily temperatures are projected to increase, with temperatures increases in the NE site ranging from 10.2% for RCP4.5 (2050) to 26.7% for RCP8.5 (2100) relative to baseline conditions, and 8.7% - 22.8% at the SW site. All modelled future climate scenario showed that rising temperature resulted in a longer growing season that begins earlier in the year (Figure 5.2). Under baseline conditions, the average growing season length in NE site is around 280 days, but this increases substantially for all future scenarios, with season length increasing to 310 days under RCP4.5 (2050) and to 345 day under RCP8.5 (2100) conditions, equivalent to a 7 – 19% increase in growing season days. The same climate conditions result in an average 340 – 360-day long growing season in SW site, compared to the 320 days under baseline conditions (Figure 5.2). These changes suggest that climate change will have a slightly greater impact on growing season in the north-east compared to the south-west, which is due to the larger increase in projected temperatures (Table 5.1). Despite climate change having a greater overall impact on the growing season in the NE site, the SW site has the longer agricultural season under all scenarios due to baseline conditions, as shown in Figure 5.2.



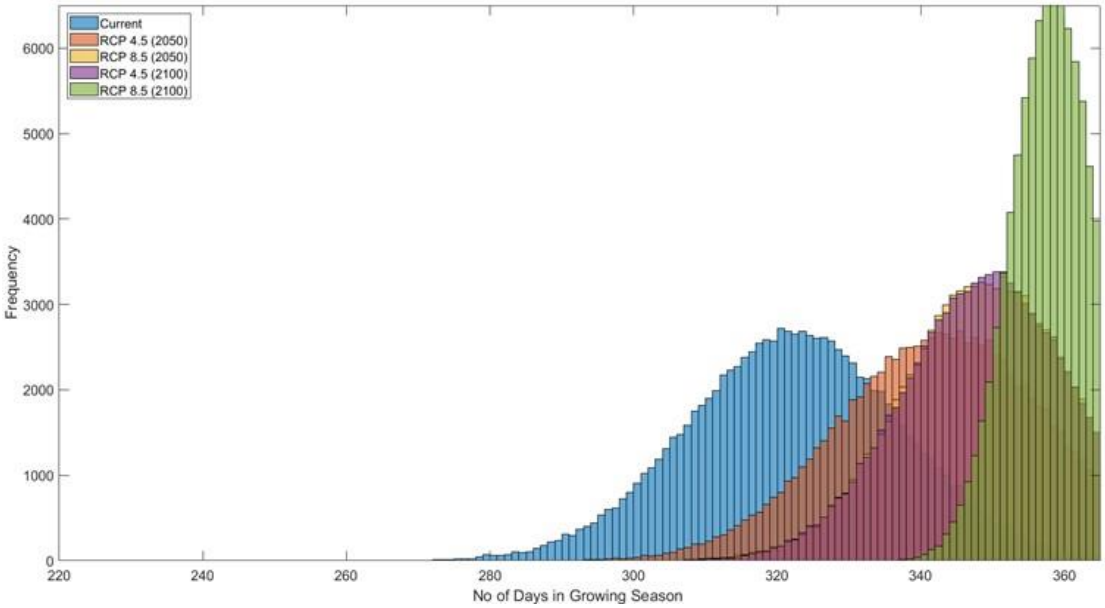


Figure 5.2: Distribution of growing season length for the five model scenarios in (i) Dunleer (NE) and (ii) Causeway (SW)

Changes to growing season are important when considering pesticide risks, as they define the period of the year when pesticides tend to be applied. In Ireland, under current climatic conditions, the growing season commonly starts in March and ends around November (Teagasc, 2017c), so pesticide application periods often avoid the heavier rainfall associated with winter months. However, as the growing season length increases, the beginning of the season starts earlier in the year. This can be clearly seen in the shift of the start date curves in Figure 5.3. In both locations, the growing season for all future climate scenarios begins much earlier in the year, with the start of the season shifting from the beginning of March in the north-east under baseline conditions, to mid-January under RCP8.5 (2100) conditions, and from the start of February to almost the beginning of the year in the SW site for the same scenarios. Therefore, the start of the agricultural season is projected to start and end in winter months. Future application periods are therefore likely to coincide with these heavier daily rainfall events as the growing season starts earlier and ends later in the year, given that future daily winter precipitation is projected to have the greatest increase of the four seasons (Nolan and Flanagan, 2020). This is particularly likely for RCP8.5 (2100) conditions associated with the longest growing season projections in both locations, where the 50th percentile start and end date have shifted to early/mid-January and mid/late December, respectively.

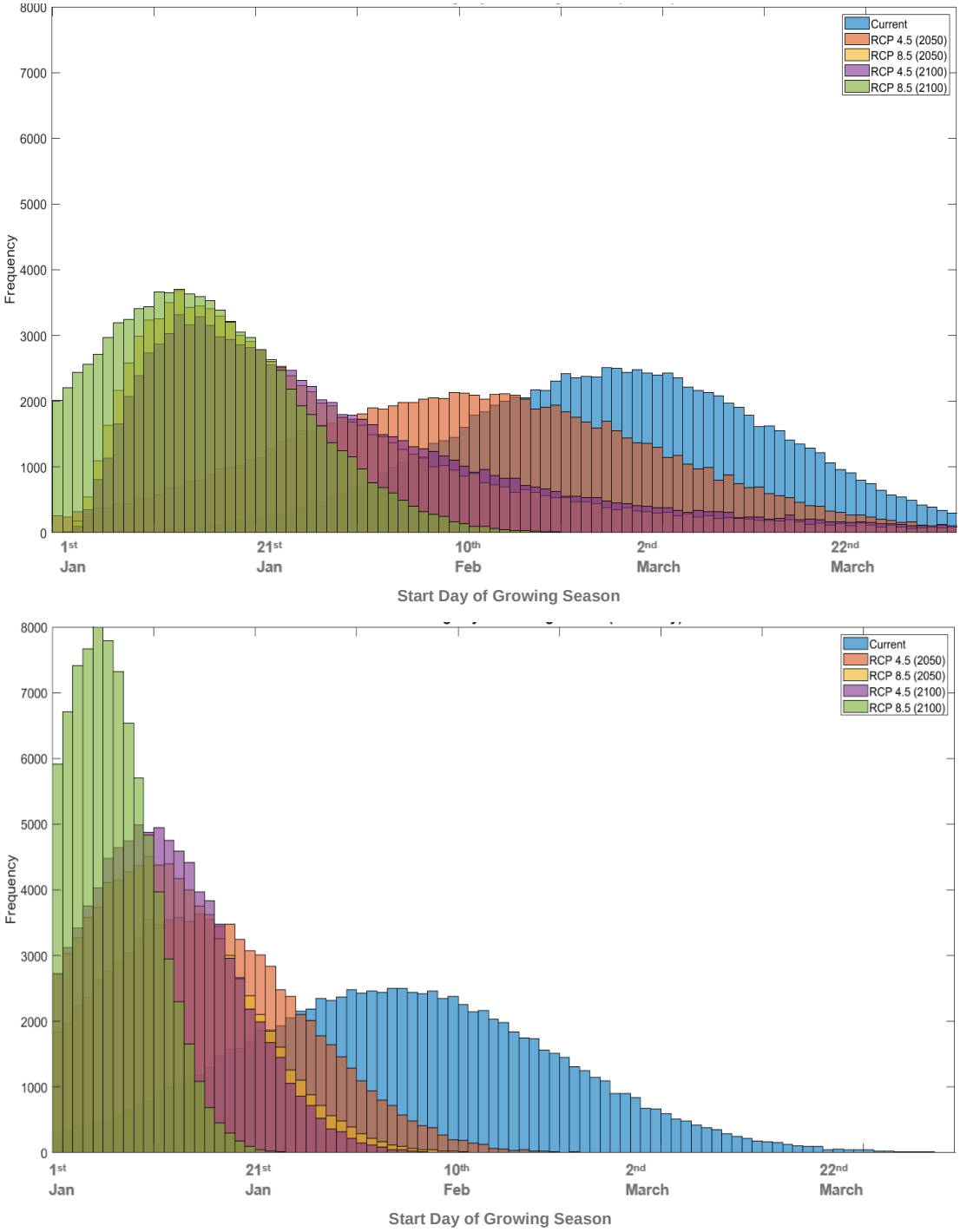


Figure 5.3: Distribution of growing season start date for five model scenarios in (i) Dunleer (NE), and (ii) Causeway (SW)

In the NE site, average rainfall across a growing season is projected to increase from 590 mm/season under baseline conditions to 653 mm/season for RCP4.5 (2050), and 788 mm/season for RCP8.5 (2100), corresponding to a 3.6% - 12% increase in daily rainfall over a growing season. Similarly, in the SW site daily average precipitation is projected to increase by 7.6% - 16.5% under the same climatic conditions relative to baseline conditions. This increase in rainfall intensity during periods of pesticide

application will lead to greater runoff volumes, higher rates of pesticide exposure in drinking water supplies, and therefore increases in health risks as is discussed in the following sections. Table 5.3 presents the climate parameters for each scenario, which were used in the models (Section 5.3.2).

Table 5.3: Statistical parameters for climatic parameters under the different climatic scenarios

Scenario	Start of Growing Season*			Growing Season Length (days)			Growing Season Daily Precipitation (mm.day^{-1})†		
	Distribution	μ	σ	Distribution	μ	σ	Distribution	a	b
Dunleer (North-East site)									
Baseline (1990)	Normal	55	16	Normal	288	20	Gamma	0.29	7.14
RCP4.5 (2050)	Normal	40	19	Normal	308	21	Gamma	0.27	7.76
RCP8.5 (2050)	Lognormal	26	22	Normal	319	18	Gamma	0.27	7.93
RCP4.5 (2100)	Lognormal	29	24	Normal	319	20	Gamma	0.27	8.14
RCP8.5 (2100)	Normal	12	11	Normal	344	14	Gamma	0.26	8.89
Causeway (South-West site)									
Baseline (1990)	Lognormal	33	16	Normal	322	15	Gamma	0.44	6.39
RCP4.5 (2050)	Lognormal	13	11	Normal	343	15	Gamma	0.37	8.05
RCP8.5 (2050)	Lognormal	9	9	Normal	349	12	Gamma	0.37	8.38
RCP4.5 (2100)	Lognormal	9	8	Normal	349	12	Gamma	0.37	8.43
RCP8.5 (2100)	Lognormal	4	5	Normal	358	6	Gamma	0.35	9.36

**Note: Day 1 = 1st January, †Statistical parameters for daily precipitation for growing season consider both the changes in growing season as a result of daily temperature projections, and the changes in daily rainfall due to projected precipitation for each climate scenario.*

5.3.2 Impact of Climate Change on Pesticide Exposure and Risk

The analysis of climate change impacts on pesticide risk was carried out for two locations in Ireland. However, to facilitate detailed discussion of the results, this section will be focus on one location only, Causeway in the south-west, and will compare 2100 conditions to baseline conditions. Section 5.3.3 will present results for both locations to compare the influence climate change has on pesticide risk in both sites, thus illustrating the regional variability of climate change impacts. However, the readers may find detailed results for 2050 climate scenarios, and more detail on changes to exposure/risk in the north-east in Appendix C2.

Simulated pesticide concentration in surface water due to runoff is strongly related to precipitation. However, precipitation must exceed 20% of the soil's maximum potential retention for runoff to occur (Eq. 5.1), which depends on a site's land-use and soil combination (USDA, 2004a, b). Therefore, based on the soil conditions and

land-use combination at study site, runoff will only occur when the precipitation threshold of 8.3 $mm.day^{-1}$ is reached (Harmon O'Driscoll et al., 2024: Chapter 4). Under baseline conditions, rainfall events that trigger runoff will occur on average 35 times a year. However, climate change is projected to increase daily rainfall intensity, with compounding effects due to the extension of the growing season. Therefore, the number of annual runoff events are projected to increase on average to 42 days under RCP4.5 and 44 days annually under RCP8.5 by 2100. While this will increase the rate of pesticide loss to drinking water supplies, it is important to note that 88 – 90% of simulated days are unlikely to receive sufficient rainfall to trigger a runoff event under any model scenario (i.e. reach the 8.3 $mm.day^{-1}$ threshold). As a result, the results in Figure 5.4 are the 95^{th} percentile pesticide concentrations only, as median values equate to zero runoff, and zero pesticide concentrations.

Triclopyr has the highest simulated concentration for all modelled scenarios, followed by MCPA, 2,4-D and mecoprop (Figure 5.4). These pesticides occur in the highest concentrations due to their very low adsorption coefficients, making them unlikely to adsorb to soil, and therefore more readily available for runoff. Additionally, these pesticides have relatively high application rates (EFSA, 2021) which increases the amount of pesticide available for transport. For both RCP4.5 and RCP8.5 projections, pesticide concentrations increase when compared to current climates, with the highest concentrations occurring under RCP8.5 conditions. The EU's limit of 0.1 $\mu g.l^{-1}$ for an individual pesticide in drinking water (European Commission, 2009b) is exceeded by five pesticides based on current climatic conditions. Under both RCP4.5 and RCP8.5 conditions half of the fifteen modelled pesticides are predicted to exceed this limit at the 95^{th} percentile concentration. The simulated total concentration of the modelled pesticides also exceeds the EU's legal limit of 0.5 $\mu g.l^{-1}$ total concentration in all modelled scenarios. However, under RCP8.5 conditions, the total concentration is predicted to be six times the legal limit, compared to 1.5 times the limit under current climatic conditions.

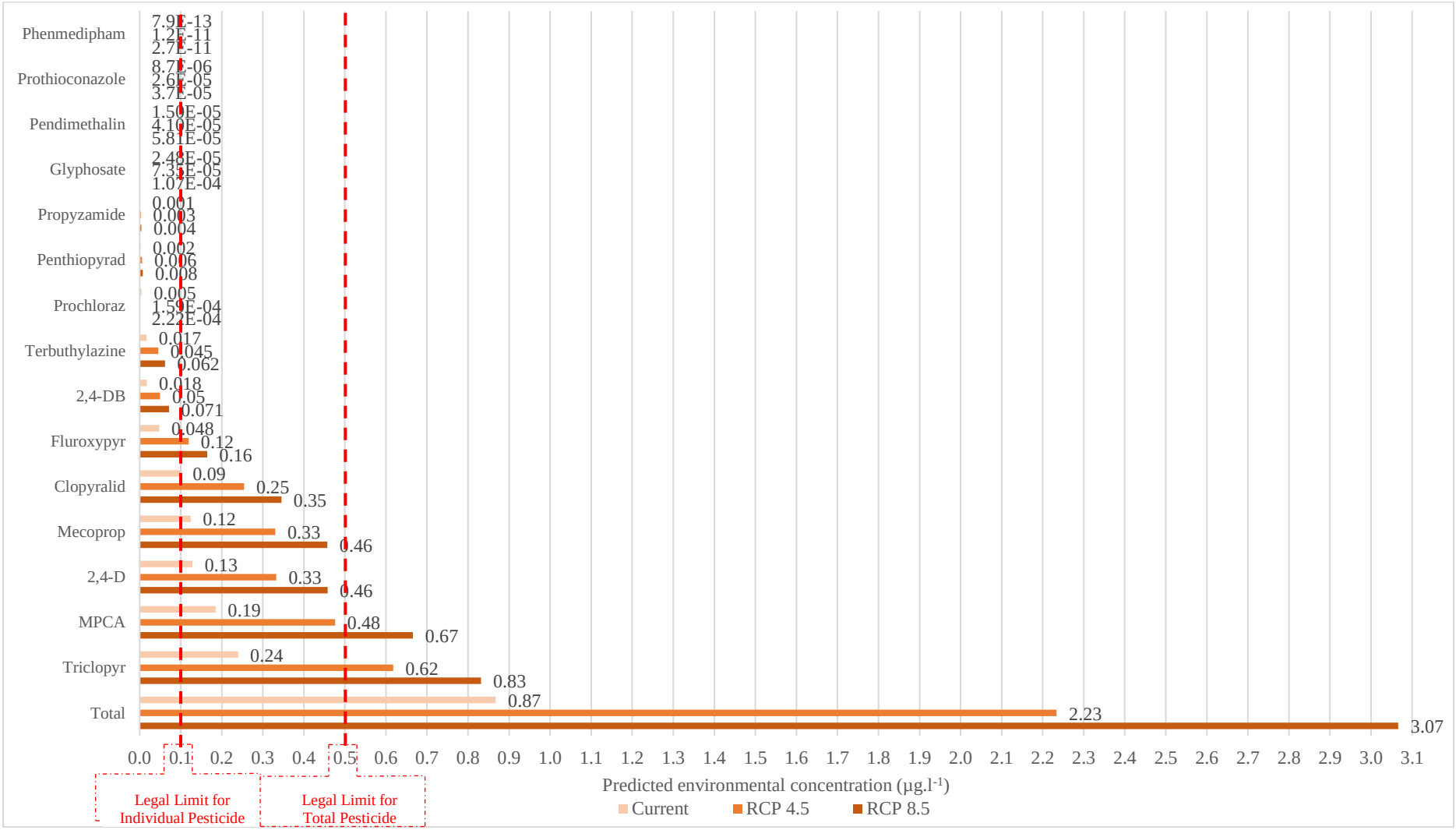


Figure 5.4: 95th percentile predicted environmental concentration (µg.l-1) for 2100 conditions in Causeway (SW)

The effect of climate change on simulated pesticide concentrations becomes more evident when the percentage changes to predicted concentrations are compared. Under RCP8.5 (2100), the worst-case climate scenario in this study, pesticide concentrations increased by an average of 36%, compared to 24% under RCP4.5 (2100) (Figure C2). This can be explained by the differences in climate change impacts on model climate variables: under RCP8.5 (2100) conditions mean daily rainfall during the growing season increases by over 16%, and the resulting number of days where runoff threshold (8.3 $mm.day^{-1}$) is exceeded increases by 9 days compared to baseline conditions (an increase of 26%). In comparison, mean rainfall increases by 11% and the number of runoff events only increase by 14% under RCP4.5 (2100). Therefore, under RCP 8.5 (2100) not only are there more runoff events than other modelled scenarios, but the resulting level of runoff is greater due to the projected increase in precipitation. As a result, the rate of exposure also increases substantially for both adults and children as can be seen in Table 5.4. Under RCP8.5 (2100), pesticide exposure rate in both adults and children more than doubles compared to current exposure rates (Table 5.4). This significant increase in exposure leads to higher levels of health risks in both adults and children under future climatic conditions as shown in Figure 5.5.

Table 5.4: 95th percentile adult and child estimated daily intakes ($mg.kg^{-1}.day^{-1}$) under baseline and RCP8.5 (2100) conditions, and acceptable daily intakes ($mg.kg^{-1}.day^{-1}$) as defined by the EFSA

Pesticide	Baseline Climate Conditions		RCP8.5 (2100)		ADI
	EDI_{adult}	EDI_{child}	EDI_{adult}	EDI_{child}	
Triclopyr	1.5e-4	2.2e-4	3.2e-4	4.6e-4	0.03
MPCA	1.3e-4	1.9e-4	2.7e-4	3.9e-4	0.05
Mecoprop	8.9e-5	1.3e-4	1.9e-4	2.8e-4	0.01
2,4-D	8.4e-5	1.2e-4	1.8e-4	2.6e-4	0.02
Clopyralid	6.0e-5	8.7e-5	1.3e-4	1.8e-4	0.15
Fluroxypyr	3.0e-5	4.5e-5	6.4e-5	9.3e-5	0.8
2,4-DB	1.9e-5	2.8e-5	4.4e-5	6.3e-5	0.02
Terbuthylazine	1.2e-5	1.8e-5	2.7e-5	3.8e-5	0.004
Penthiopyrad	1.0e-6	3.5e-6	3.5e-6	5.0e-6	0.1
Propyzamide	4.8e-7	2.2e-6	2.2e-6	3.3e-6	0.05
Prochloraz	6.2e-8	9.2e-8	1.5e-7	2.1e-7	0.01
Glyphosate	4.1e-8	6.0e-8	1.0e-7	1.5e-7	0.5
Pendimethalin	1.3e-8	1.9e-8	2.9e-8	4.2e-8	0.125
Prothioconazole	9.6e-9	1.4e-8	2.2e-8	3.1e-8	0.05
Phenmedipham	3.2e-13	4.7e-13	9.5e-13	1.4e-12	0.03

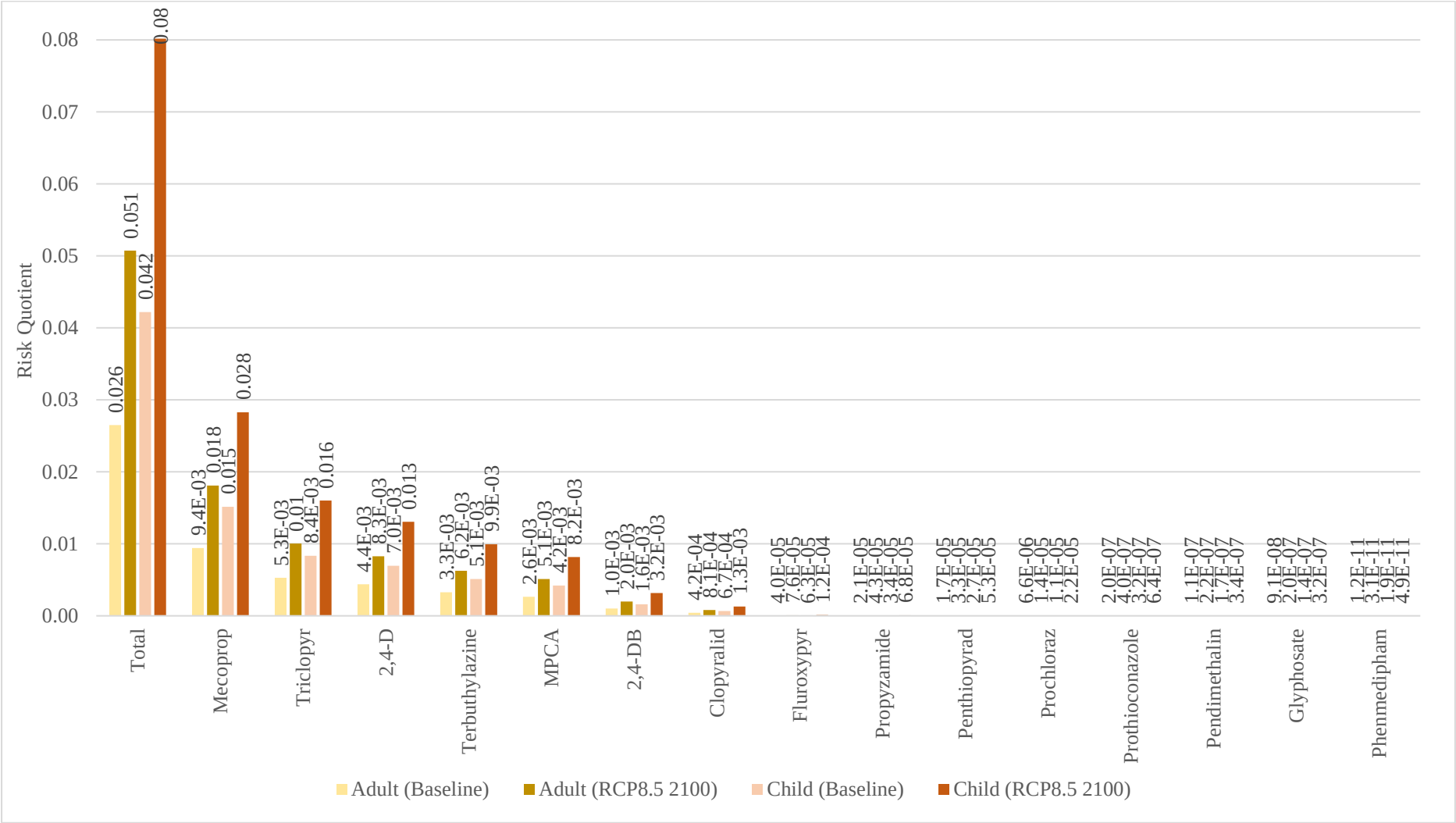


Figure 5.5: 99th percentile pesticide risk level for adults and children for baseline and RCP8.5 (2100) conditions in Causeway (SW)

Although many of the pesticides modelled were shown to have simulated pesticide concentrations which exceed EU drinking water quality limits, the resulting level of exposure was found to be well below the acceptable daily intake under future climate scenarios (Table 5.4). Therefore, health risks were found to be very low for all modelled pesticides. The 99th percentile risk quotients for the fifteen modelled pesticides, shown in Figure 5.5, are well below a risk quotient of one, therefore, based on this widely utilised metric, the risk of adverse health effects is extremely low for all modelled pesticides (EFSA, 2019). Mecoprop posed the highest risk to both adults and children as it has potential to cause developmental issues, and therefore has a low acceptable daily intake value (0.01 mg.kg^{-1}.day^{-1}) (EFSA, 2021). The second highest risk level was attributed to triclopyr, which has a higher allowable daily intake (0.03 mg.kg^{-1}.day^{-1}) than mecoprop but has much higher simulated concentrations (Figure 5.5). Despite the increasing likelihood of exposure to pesticides due to climate change effects, the resulting level of health risks posed to humans is still very low even under the most extreme climate scenario (RCP8.5 2100). Furthermore, the total risk from exposure to pesticides, assuming an additive effect of all modelled pesticides (EFSA, 2019), is also well below acceptable levels, ranging from a minimum of 0.026 for adults under baseline conditions to 0.080 for children under RCP8.5 (2100). In fact, it was found that there was a less than a 0.01% chance of exceeding an unacceptable level of risk, with 99.7% of model simulations for mecoprop, the pesticide with the highest risk quotient in Figure 5.5, producing a risk quotient less than 0.1.

Although levels of risks are relatively low for all climate scenarios (Figure 5.5), climate change will influence the level of risk arising from pesticide exposure as pesticide risk were found to increase by an average of 24% (RCP4.5 2100) to 37% (RCP8.5 2100) across the various pesticides, relative to current conditions (Figure 5.6). Due to the strong relationship between exposure rate and resulting health risk, RCP8.5 (2100) was shown to potentially have the greatest influence on pesticide health risk. Although the health risks posed by the modelled pesticides has been shown to be very low for the modelled scenarios, the impact that climate change has on both the rate of pesticide loss to runoff and resulting health risk highlights the need for awareness in terms of agricultural practices and behaviours. For example, it has been shown that climate change will likely extend the growing season period for crops. This may also increase the abundance of pests, such as insects and fungi, and therefore

cause an increase in pesticide usage, or change in active ingredient used in agriculture for more effective treatment (Gagnon et al., 2016). Therefore, it is important to factor in climate change impacts in risks assessments, especially when land use or pesticide use may change into the future.

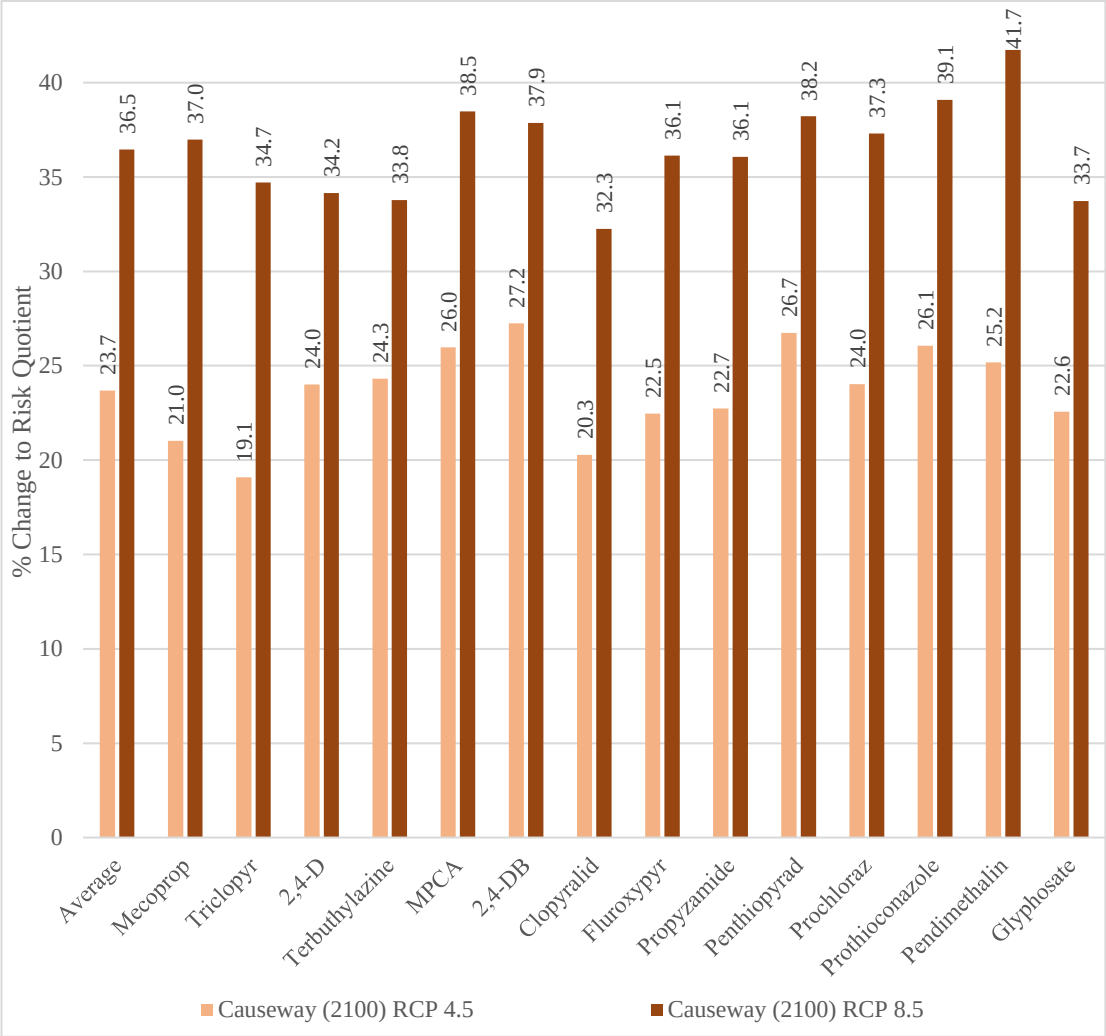


Figure 5.6: Percentage change 99th percentile risk quotient (child) for future scenarios relative to current climate in Causeway (SW)

5.3.3 Regional Variability in Climate Effects

In this section, results from both locations used in the current study are presented to illustrate the impact spatial variability in climate projections has on modelled results and highlight the need for localised/regional climate change risk modelling. Although climate change was shown to have a slightly larger impact on climate parameters at the NE site than the SW site (Sections 5.2.1 and 5.3.1), pesticide concentrations and resulting risks are much higher at the SW site for all climate scenarios. The percentage

increase in pesticide risk for five of the highest risk pesticides (Figure 5.5) under RCP4.5 and RCP8.5 (2100) are given in Figure 5.7.

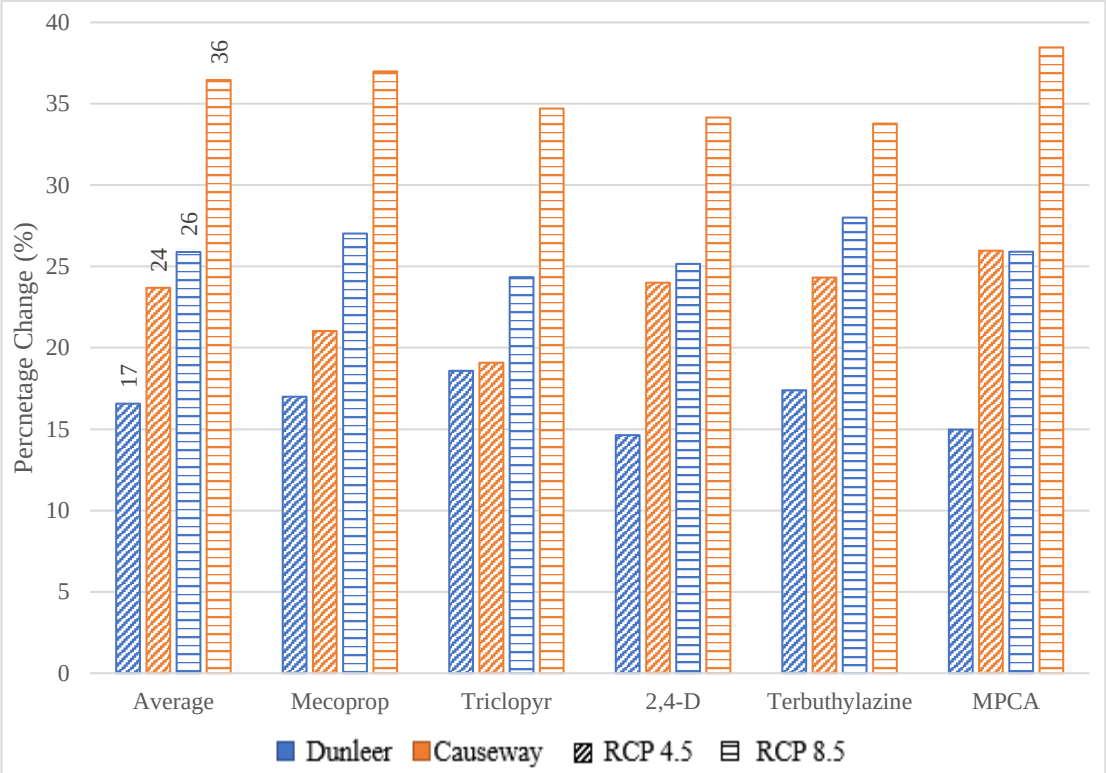


Figure 5.7: Percentage change to 99th percentile RQ (child) for 2100 relative to current in Dunleer (NE) and Causeway (SW)

In the NE site, the influence of climate change results in an average 17% increase in health risks under RCP4.5, and a 26% increase under RCP8.5 conditions by the end of the century across the five pesticides. However, health risks from pesticides in drinking water are on average 50% higher in the SW site than the NE site under baseline conditions and increase to almost 90% higher under RCP8.5 (2100) conditions (See Fig C10). The differences in climate impacts across the two locations can be partly explained by considering the influence of baseline conditions on the runoff model. Firstly, baseline daily temperatures are higher in the SW (μ = 10.6 °C) compared to the NE (μ = 9.9 °C), and as a result, the growing season is on average 34 days longer. Therefore, the likelihood of pesticide application during periods of wetter weather for baseline conditions is higher, as previously discussed. This impact is amplified under RCP8.5, whereby the growing season length is effectively the entire year in the SW site. More importantly, however, under baseline conditions, the south-west of Ireland experiences significantly more precipitation than the north-east (1074 mm.y^{-1} versus 785 mm.y^{-1}), as well as more heavy rainfall days. This regionally

variability is predicted to intensify in the future, with climate projections showing a greater increase in heavy rainfall periods along the west coast of Ireland (Causeway area) than in eastern regions (Dunleer area) (O'Loughlin and Mozafari, 2023; O'Brien et al., 2024). This is particularly important due to the bimodal relationship between rainfall and runoff, where runoff only occurs during periods of heavy rainfall i.e. 8.3 $mm.day^{-1}$ for the site conditions considered above. The projected changes to rainfall in the SW site result in an increase in the number of days where runoff may occur, rising from 35 days under baseline conditions to 42 and 44 days for RCP4.5 and RCP8.5, respectively. The NE site, however, experiences far fewer runoff events, with rainfall exceedances occurring only 24 times a year on average for baseline conditions, increasing to a maximum of 30 under RCP8.5 (2100). Additionally, the volume of runoff is also much less, as overall daily precipitation in the south-west is much greater than the north-east under baseline and future climatic conditions. Average daily precipitation during the growing season in the NE site increases from a baseline of 2.05 $mm.day^{-1}$ by a maximum of 11.7% (RCP8.5 (2100)). In the SW site, daily precipitation increases from an average of 2.78 $mm.day^{-1}$ by 16.5% (RCP8.5 (2100)). Therefore, although climate projections suggest that climate change has a slightly greater impact on climate variables in Dunleer (Table 5.3), it was found that pesticide runoff and resulting health risks increase at a higher rate at the SW site. Consequently, this analysis emphasises the need to carry out localised assessment of climate impacts on pesticide risks to account for the spatial variability of climate effects.

5.4 Conclusions

This study demonstrates how climate projections can be incorporated into existing risk models to quantify the projected impact that climate change may have on future risks arising from exposure to pesticides via drinking water. Climate projections for the study locations indicate an increase in average daily precipitation and temperature, in line with increases across the North Atlantic region, which will likely affect pesticide concentrations in surface waters. The case study of 15 pesticides in two locations in Ireland shows that health risks will increase in the future under all climate scenarios, with the greatest increase in health risks at both study sites occurring under RCP8.5 (2100), due to increases in growing season and heavy rainfall events. Climate change is projected to result in greater pesticide risks in the south-west due to significant projected increases in growing season and rainfall compared to the north-east.

However, the likelihood of exceedances of acceptable levels of risks based on EU regulatory thresholds are to remain low under future climatic conditions for the simulated pesticides at both locations.

Despite the low predicted risks, this study highlights the need to account for climate change impacts in pesticide risk assessments to inform adaptation and mitigation strategies for the future where necessary. Additionally, the results indicate that region-specific climate risk modelling is potentially significant to account for the localised variability in climate change effects. This study contributes to the literature quantifying the impacts of climate change on health risks by demonstrating how multi-ensemble, bias-corrected projections from downscaled regional climate models may be incorporated into probabilistic models, using a practical approach suitable for international users. However, there is also a need to expand the research to consider the indirect effects of climate change, such as changes to land-use and pesticide application rates, in future analysis as this will have compounding effects on future pesticide risk profiles.

CHAPTER 6

GENERAL CONCLUSIONS AND RECOMMENDATIONS

6.1 Overview

Pesticide use has growing steadily over the last century and is likely to continue to grow to ensure food supply demands are met in the future. At the same time, there are growing concerns among pesticide regulators and the general public regarding pesticide contamination of water supplies and resulting impacts to human health. Therefore, there is a need to quantify the health impacts of pesticides in drinking water through the use of risk assessment approaches. These approaches should enable decision-making around the need for risk management and mitigation of key pesticides in vulnerable locations under current conditions, but should also be able to incorporate climate change projections to enable future planning for a changing climate.

Therefore, the main objective of this thesis was to develop an efficient and practical risk assessment framework that follows a tiered approach, including risk screening, numerical assessment and risk characterisation, to enable effective use of time and data. An initial user-friendly, semi-quantitative risk screening approach was developed in Chapter 3 to identify priority pesticides for detailed analysis from a wide range of pesticides currently used in Ireland. A probabilistic risk model was developed in Chapter 4 to enable detailed health risk assessment of identified pesticides under current conditions. This approach was further adapted in Chapter 5 to enable quantification of climate change impacts on future pesticide risks. The work presented in this thesis developed an accessible and practical tiered risk assessment framework and illustrated its implementation in Irish case-studies.

6.2 Key Findings

- A new health risk-screening tool was developed building on identified limitations of existing approaches to provide users with a more comprehensive preliminary risk screening as a first stage of risk assessment. This tool integrates a broader range of factors than existing approaches that contribute to pesticide mobility, chronic health impacts, and risks from metabolites.

    - Over 100 pesticides used in Irish agriculture were screened using this approach at two locations (Dunleer with poorly-draining, clayey-loam soils, and Cregduff with a well-draining karst landscape) to identify those of highest

concern and illustrate application of the tool. The findings revealed higher overall risk scores in Dunleer, highlighting the significance of incorporating soil conditions into risk assessments, which is not done in the majority of published risk screening.

- Prochloraz and propyzamide were identified as high priority due to the combination of their toxicity and/or mobility, while commonly used pesticides like glyphosate, chlormequat chloride, and MCPA had high quantity-weighted hazard scores. The study underscored the importance of considering site conditions and metabolite properties in risk scoring.

- An accessible and practical probabilistic risk model was developed using the OECD's Simplified Formula for Indirect Loading from runoff (SFIL) model as a theoretical base model with novel modifications in order to address identified limitations of application of probabilistic modelling in existing approaches. This model provides a probabilistic assessment of pesticide concentrations and human health risks, and was applied as part of an Irish case study of 15 priority pesticides in Irish agriculture.
  - Triclopyr, MCPA, mecoprop and 2,4-D were predicted to occur in the highest concentrations for Ireland, often exceeding EU drinking water limits, in agreement with findings of local and national monitoring programmes.
  - Mecoprop was identified to pose the greatest risk to human health of modelled pesticides, however health risks were found to be well below regulatory thresholds suggesting that pesticide risks to human health in Ireland under current conditions are low.

- Adaptation of the proposed probabilistic risk assessment framework presented a first-step towards the integration of climate projections into probabilistic pesticide models to quantify climate impacts on future human health risks. The novel risk assessment framework was modified to enable the incorporation of bias-corrected, high-resolution climate projections from multiple ensembles to quantify climate change impacts on future pesticide health risks for the first time in the published literature.
  - The study showed that pesticide concentrations and health risks increase under all climate scenarios with RCP8.5 (2100) conditions producing greatest

increase runoff concentrations and resulting risks for all modelled pesticides. Despite these increases, the overall health risks remained low for all future climate scenarios, adhering to EFSA regulatory thresholds.

- Climate impacts on pesticide risks were found to vary at the two study locations (in the north-east and south-west of Ireland). Despite climate projections suggesting a smaller impact on climate variables in the south-west, pesticide risks were found to be higher, with a 36% increase in pesticide risks under RCP8.5 (2100) compared to baseline conditions in the south-west and a 26% increase in the north-east. These somewhat counterintuitive findings emphasise the need to consider spatial variability using localised climate projections when assessing pesticide risks under future climatic conditions.

- The developed risk assessment tools are designed to be adaptable for international user-base, aiding decision-making on pesticide risk management and mitigation. Specific-case studies were used to illustrate application of the framework and demonstrate how national and international databases may be accessed to inform model parameters to suit the users' needs. These tools enable users to make informed decisions regarding pesticide risk management and mitigation, climate adaptation strategies in the agriculture sector and public health policies for current and future climatic conditions.

- Existing approaches to quantify the impacts of climate change on future pesticide risks are constrained by the use of a limited number of low-resolution climate models that lack bias correction. This can lead to significant biases and poor representation of model uncertainty and localized variability. Improvement in this area can be achieved through the utilization of high-resolution, bias-corrected climate projections obtained from multiple ensembles, enhancing the accuracy and reliability of future risk predictions.

6.3 Implications for Stakeholders

Agricultural Policymakers

- As the study projects increased risks under future climate conditions, regulatory frameworks should evolve to consider climate change impacts on pesticide behaviour and risks.

- The findings of this study indicate low risks to human health under both current and future climates, however further work should be carried out to probabilistically model pesticide risks to vulnerable aquatic and terrestrial environmental receptors under current and future climates.
- It is important to note that findings for Ireland only represent a subset of the entire risk profile associated with pesticide exposure. While daily exposure levels for humans via drinking water are predicted to be below acceptable daily intake thresholds for chronic human health effects under both current and future climates, pesticide regulations should not be made less restrictive nor should application doses be allowed to increase without consideration of all major exposure pathways. Any changes to pesticide applications should only be made after a more extensive risk assessment accounting for additional exposure routes (e.g. dietary, groundwater, inhalation), as well as consideration of additional climate factors, and environmental receptors (i.e., terrestrial and aquatic vertebrates and invertebrates) as discussed in the previous section.
- Agricultural policymakers could encourage pesticide manufacturers to provide more detailed reporting of pesticide health studies to produce datasets of pesticide toxicological effects. This would enable more robust analysis of health risk impacts and facilitate assessment of targeted health concerns.

<u>Pesticides Users, Farm Advisors, Catchment Managers</u>

- Findings indicate that sites with poorly draining soils are particularly vulnerable to pesticide contamination via runoff, therefore highlighting the need to consider localised soil and environmental conditions in application practices, for example avoiding use of pesticides which are very prone to runoff at a site with clayey soils.
- Tiered risk assessment approach developed in order to provide an accessible risk analysis approach for stakeholders whereby the different steps can be used separately or altogether depending on the users' requirements and expertise.
- The first stage, human health risk screening approach enables the identification of high-risk pesticides or can facilitate informed selection of "safer" pesticides through the comparison of the relative risk without substantial time or resource demands. This approach can also be used in isolation by catchment managers to identify priority pesticides for assessment/monitoring at their specific locations.

Therefore, this can provide useful information to pesticide users, farm advisors and catchment managers without significant time/resource demands.

- Should stakeholders require more specific information regarding a pesticide's in-stream concentrations or health risk information, the results form risk screening can also be combined with the next steps of the detailed risk model to better inform risk management strategies, enable decision making regrading mitigation approaches, etc.

Water Utilities

- Despite predicted instream concentrations often exceeding EU drinking water quality limits for pesticides, the associated health risks are predicted to remain well below acceptable daily intakes for chronic human health concerns under both current and future conditions for the most commonly used pesticides in Ireland. This finding indicates that there is not currently a need for pesticide-specific removal processes at Irish water treatment plants.
- Pesticides should continue to be assessed and/or monitored in Irish waters to ensure risks do not begin to approach an unacceptable level of human health risk whereby mitigation may be required or to identify changes in pesticide use trends which may alter risk profiles. This will allow for preventative rather than reactive risk mitigation measures to be implemented.
- While findings indicate pesticide human health risks are to remain low under worst case climate scenarios, the results also highlight that climate change will have a significant impact on pesticide risks, and may also impact the risks associated with other contaminants. Therefore, water utilities should consider incorporating climate projections into their assessments to enable future-planning of water quality management and infrastructure investment plans.

Climate Change Policymakers

- Findings indicate that climate change has the potential to significantly influence future pesticide risks to human health. Within Ireland modelled risks increased by up to 26 – 36% under RCP8.5 2100 conditions. Although the modelled risk levels were found to remain below acceptable daily intake thresholds, additional factors associated with climate change e.g. changes to agricultural policy and land-use, may have a compounding effect on pesticides risks. Therefore, it is important that

influence on risks arising from agrochemicals be considered in climate adaptation strategies especially in terms of future public health and environmental health strategies.

- Although the 26 – 36% increase in future health risk levels did not correspond with an unacceptable risk to human health due to pesticide exposure under future climates, this significant increase in pesticide exposure levels may correspond to a detrimental impact on vulnerable aquatic and terrestrial organisms. Therefore, environmental risk assessment should also be adapted to incorporate climate change projections to account for future changes in environmental risk profiles as applied in this study.

- Despite Ireland being a relatively small country, it was found that there was a significant regional variation in in climate change impacts on pesticide risks (health risks up to 85% higher in the South-West compared to the North-East). This highlights the importance of considering regional specific climate change strategies to account for the spatial variation in climate change impacts.

6.4 Recommendations and Future Work

- Significant work was done in this thesis to improve representation of site conditions in risk-screening and numerical assessment. Furthermore, the thesis focused on improving incorporation of variability and uncertainty at the numerical assessment stage, in the development of exposure modelling. However, this study relied on the commonly used risk quotient at the risk characterisation stage to quantify health risk levels. Alternative exposure assessment methods for risk characterisation could also be investigated to identify suitable approaches to be incorporated into the proposed risk assessment framework developed in this thesis. This would improve representation of health impacts in detailed analysis. As different pesticides can result in different health impacts, risk assessments could be carried out for specific health concerns (i.e. pesticides that target kidneys, neurotoxic pesticides, etc.) in order to provide more precise information regarding health impacts arising from pesticide exposure.
- Metabolites were considered in the risk-screening stage of the purposed framework but not in the detailed risk assessment stage due to lack of quality data relating to degradation rates and specific health impacts of specific metabolites.

More work needs to be done on metabolite studies to enable development of probability distributions for metabolite parameters to facilitate detailed analysis of both parent compounds and their metabolites, allowing for a more realistic representation of overall risk.

- This thesis quantified the direct impacts of climate change on pesticide risk by considering changes to precipitation and temperature. However, climate change will likely have wider reaching impacts on the agricultural sector due to indirect impacts of climate change, for example changes to land productivity and pest prevalence. Additionally, national and international policies, e.g. the EU's Farm-to-Fork policy (EU, 2020), are being developed to reduce the environmental impact of pesticides in response to climate change. These factors will likely affect land-use, thereby changing types of pesticides in use, as well as increasing/decreasing pesticide application rates in response to pest prevalence and policy changes. As a result, further study assessing future pesticide risks should consider both the direct and indirect effects of climate change.

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APPENDICES

APPENDIX A: SUPPLEMENTARY INFORMATION FOR CHAPTER 3

APPENDIX A1: SITE CONDITIONS

Table A1: Parameters for implementation of methodology

Parameter	Unit	Source
Horizon Depth	cm	(EPA, 2021)
Organic Matter Content	%	(EPA, 2021)
Hydrologic Group	-	(EPA, 2021) (USDA, 2009)
Erodibility Factor	t ha h ha^{-1} MJ^{-1} mm^{-1}	(EPA, 2021) (Panagos et al., 2014)
DT_{50} in Soil	days	(EFSA, 2021) (Lewis et al., 2016)
K_{oc}	$ml.g^{-1}$	(EFSA, 2021) (Lewis et al., 2016)
Solubility in Water	$mg.l^{-1}$	(EFSA, 2021) (Lewis et al., 2016)
DT_{50} in Water	days	(EFSA, 2021) (Lewis et al., 2016)
Evidence of health effects	-	(EFSA, 2021) (Lewis et al., 2016)
Metabolite DT_{50} in Soil	days	(EFSA, 2021) (Lewis et al., 2016)
Metabolite ADI	$mg.kg^{-1}bw.days^{-1}$	(EFSA, 2021) (Lewis et al., 2016)
Pesticide Quantity of Use	kg	(DAFM, 2016, 2017)

Cregduff

Cregduff is a 32 km^2 karst catchment in County Mayo in the west of Ireland. Shallow brown earths and rendzinas are the dominant soil types which overlay limestone bedrock with numerous karstic features such as sink holes, torloughs, springs and dolines. The catchment is mainly used for grassland grazing (92% grassland) and is grazed by cattle and sheep seven to eight months of the year (Mellander et al., 2013).

Dunleer

Dunleer is a 9.5 km^2 river catchment in the east of the country in County Louth. The soil types vary across the catchment with a mix of typical and stagnic luvisols, typical and stagnic brown earths, surface-water and groundwater gleyic soils. Over 70% of the catchment has been classified as poorly draining although artificial drainage has been put in place to improve the land. Approximately half is used for grassland and a third use for tillage, with the remaining used for woodland and other used. (Teagasc, 2017b; McDonald et al., 2019).

Table A2: Soil properties in study sites

Property	**Cregduff Value**	**Dunleer Value**	**Reference**
Soil Subgroup	Typical Calcareous Brown Earths	Stagnic Brown Earths	(EPA, 2021b)
O.C. Content (%)	4.38	2.7	(EPA, 2021b)
O.M. Content (%)	7.53	4.64	1.72[a] x O.C Content
Sand Content (%)	51	29	(EPA, 2021b)
Silt Content (%)	25	37	(EPA, 2021b)
Clay Content (%)	24	34	(EPA, 2021b)
Horizon 1 Depth (cm)	20	28	(EPA, 2021b)
Structural Class	2	2	(Panagos et al., 2014)
Permeability Class	4	4	(Panagos et al., 2014)
K factor	0.126	0.17	(Panagos et al., 2014)
Hydrologic Group	B	C	(Goss, 1992)
Leaching Potential	High	Moderate	(Goss, 1992)
Sediment Runoff Potential	Low	Moderate	(Goss, 1992)
Direct Runoff Potential	Moderate	High	(Goss, 1992)

[a] = *van Bemmelen factor*

Table A3: Mobility of pesticides based on Goss analysis of physiochemical properties

Pesticide	Leaching Potential	Sediment Run-Off Potential	Direct Run-off Potential
Glyphosate	Low	Moderate	Moderate
Chlormequat chloride	Moderate	Low	High
MCPA	High	Low	High
Fluroxypyr	Moderate	Low	High
2,4-DB	Low	Low	High
Prothioconazole	Low	Moderate	Moderate
Pendimethalin	Very Low	High	Moderate
Mancozeb	Very Low	Low	Moderate
Triclopyr	High	Low	High
2,4-D	High	Low	High
Mecoprop-P	Moderate	Low	High
Metamitron	Moderate	Low	High
Propamocarb hydrochloride	Low	Low	High
Pyraclostrobin	Low	Moderate	High
Boscalid	High	Moderate	High
Spiroxamine	Low	Moderate	High
Prosulfocarb	Low	Moderate	Moderate
Diflufenican	Low	High	Moderate
Clopyralid	High	Moderate	Moderate
Tebuconazole	Low	Moderate	High
Mepiquat chloride	Low	Low	Moderate
Fluxapyroxad	Moderate	Moderate	High
Cyprodinil	Low	Moderate	High
Metazachlor	Moderate	Low	High
Azoxystrobin	Moderate	Moderate	High
Trinexapac-ethyl	Low	Low	High
Ethephon	Low	Moderate	Moderate
Metalaxyl-M	Moderate	Low	High

Table A3 Continued

Pesticide	Leaching Potential	Sediment Run-Off Potential	Direct Run-off Potential
Fluazinam	Very Low	High	Intermediate
Penthiopyrad	Moderate	Moderate	High
Bixafen	Low	High	Moderate
Fenpropidin	Low	High	High
Metribuzin	Moderate	Moderate	High
Terbuthylazine	Moderate	Moderate	High
Isopyrazam	Low	High	Moderate
Pinoxaden	Very Low	Low	High
Lenacil	High	Moderate	High
Metconazole	Low	High	High
Ethofumesate	High	Moderate	High
Cymoxanil	Low	Low	High
Mandipropamid	Low	Low	Moderate
Thifensulfuron-methyl	Moderate	Low	High
Prochloraz	Moderate	Moderate	High
Folpet	Low	Low	Moderate
Propyzamide	Moderate	Moderate	High
Aminopyralid	High	Low	High
Metrafenone	Low	High	Moderate
Metaldehyde	Low	Low	High
Dimethenamid-P	Moderate	Low	High
Cyazofamid	Low	Moderate	Moderate
Dicamba	Moderate	Low	High
Trifloxystrobin	Very Low	Moderate	Moderate
Fluopicolide	High	Moderate	High
Imidacloprid	High	Moderate	High
Dichlorprop-P	Moderate	Low	High
Quinmerac	High	Low	High

Table A3 Continued

Pesticide	Leaching Potential	Sediment Run-Off Potential	Direct Run-off Potential
Tribenuron-methyl	Moderate	Low	High
Phenmedipham	Low	Moderate	Moderate
Fluoxastrobin	Low	High	High
Cypermethrin	Very Low	Moderate	Moderate
Flufenacet	Moderate	Low	Low
Propaquizafop	Low	High	Moderate
Imazamox	High	Moderate	High

Table A4: Hydrologic Soil Groups (USDA, 2009)

Hydrologic Group	Characteristics
Group A	Low runoff potential. Less than 10% clay content and greater than 90% sand content. Tend to have gravel or sand textures. Some loamy sand, sandy loam, loam or silt loam if they contain greater than 35% rock fragment, have a low bulk density and/or are well aggregated.
Group B	Moderately low runoff potential. Clay content tends to be between 10% and 20%, sand content between 50% and 90%. Tend to have loamy sand and sandy loam textures. Some loam, silt loam, silt and sandy clay loam textures if they contain greater than 35% rock fragment, have a low bulk density and/or are well aggregated.
Group C	Moderately high runoff potential. Clay content tends to be between 20 and 40% and have less than 50% sand. Tend to have loam, silt loam, sandy clay loam, clay loam and silty clay loam textures. Some clay, silty clay and sand clay textures if they contain greater than 35% rock fragment, have a low bulk density and/or are well aggregated.
Group D	High runoff potential. Tend to have a clay content greater than 40% and a sand content of less than 50%. Clayey textures.

APPENDIX A2: PESTICIDE TOXICITY

Table A5: Categories used for scoring evidence of health effects in Table 3.4

Category	Evidence
No	Unlikely in humans/ unlikely disruptor Not carcinogenic/genotoxic/a disruptor No effects No evidence No significant potential No toxicity
No data	Inconclusive data/evidence Insufficient data/evidence No data
Possible	Possible Category 3 R40/R63/R62 Limited evidence Some concerns
Probable	Probable Category 2/1B H351/H361/H362

Table A6: WHO guidelines for acute toxicity classes (WHO, 2019)

	Toxicity Class	LD_{50} for rat ($mg.kg^{-1}bw$)	
		Oral	**Dermal**
Ia	Extremely Hazardous	< 5	< 50
Ib	Highly hazardous	5 - 50	50 – 200
II	Moderately hazardous	50 - 2000	200 – 2000
III	Slightly hazardous	Over 2000	Over 2000
U	Unlikely to present acute hazard	500 or higher	

Table A7: Evidence of chronic health effects from EFSA pesticide reports

Pesticide	Carcinogenicity	Genotoxicity	Teratogenicity	Endocrine Disruption	Reproductive Toxicant
Glyphosate	Inconclusive evidence	Not genotoxic	Possible	Not a disruptor	Possible
Chlormequat	Not carcinogenic	Not genotoxic	No effects	No data/No data	Probable
MCPA	Not carcinogenic[a]	Not genotoxic[a]	Possible	Unlikely disruptor	Insufficient data[a]
Fluroxypyr	No evidence	Inconclusive evidence	Some concerns	Not a disruptor[a]	Not a toxicant
2,4-DB	Inconclusive evidence	Not genotoxic	H361	Unlikely disruptor	Not a toxicant
Prothioconazole	Not carcinogenic	Not genotoxic	Possible	Not a disruptor[a]	Category 2
Pendimethalin	Unlikely in humans	Unlikely in humans	H361	Possible	Possible
Mancozeb	Category 2	Unlikely in humans	Cat 1B	Probable	No effects
Triclopyr	Not carcinogenic	Not genotoxic	Category 3	No data/No data[a]	No effects
2,4-D	Inconclusive evidence	Unlikely in humans	Possible	Evidence of thyroid disruption	Possible
Mecoprop-P	Unlikely in humans	Unlikely in humans	H361	Insufficient data	No effects
Metamitron	Not carcinogenic	Not genotoxic	Possible	No data/No data[a]	Possible
Propamocarb	Not carcinogenic	Not genotoxic	Possible	Possible[a]	Possible
Pyraclostrobin	Not carcinogenic[a]	Not genotoxic[a]	No data[a]	Not a disruptor[a]	Probable[a]
Boscalid	Inconclusive data[a]	Possible[a]	Inconclusive data[a]	Not a disruptor[a]	Inconclusive data[a]
Spiroxamine	Not carcinogenic	Not genotoxic	R63	No data/No data[a]	No effects
Prosulfocarb	Not carcinogenic	Not genotoxic	Possible	No data/No data[a]	No effects
Diflufenican	Not carcinogenic	No significant potential	No evidence	Possible	No effects
Clopyralid	Not carcinogenic	No significant potential	No evidence	Insufficient data	No effects
Tebuconazole	Not carcinogenic	No significant potential	H361	No evidence	No effects
Mepiquat chloride	Not carcinogenic	No significant potential	No evidence	Inconclusive data[a]	No effects
Fluxapyroxad	Category 3	No significant potential	No evidence	Inconclusive data[a]	No effects
Cyprodinil	Not carcinogenic	No significant potential	No evidence	Inconclusive data[a]	No effects
Metazachlor	Category 3	No significant potential	Possible	Inconclusive data[a]	No evidence
Azoxystrobin	Not carcinogenic	No significant potential	No evidence	Inconclusive data[a]	No evidence
Trinexapac-ethyl	Not carcinogenic	No significant potential	Possible	Insufficient data	Possible
Ethephon	Not carcinogenic	No significant potential	Possible	Inconclusive data[a]	No evidence
Metalaxyl-M	Unlikely in humans	No significant potential	Possible	Not a disruptor	No evidence
Fluazinam	Not carcinogenic	No significant potential	Category 3	Possible[a]	Possible

Table A7 Continued

Pesticide	Carcinogenicity	Genotoxicity	Teratogenicity	Endocrine Disruption	Reproductive Toxicant
Penthiopyrad	Category 2	No significant potential	No evidence	Inconclusive data[a]	No evidence
Bixafen	Not carcinogenic	No significant potential	No evidence	Inconclusive data[a]	No evidence
Fenpropidin	Not carcinogenic	No significant potential	No evidence	Inconclusive data[a]	No evidence
Metribuzin	Not carcinogenic	Not genotoxic	R63	Possible[a]	R62
Terbuthylazine	Category 3	No significant potential	No effects	Inconclusive data[a]	No effects
Isopyrazam	Category 3	Not genotoxic	Category 3	Inconclusive data[a]	No effects
Pinoxaden	Not carcinogenic	Not genotoxic	Category 2	Inconclusive data[a]	No effects
Lenacil	Category 3	Not genotoxic	No effects	Not a disruptor[a]	No effects
Metconazole	Not carcinogenic	Not genotoxic	Category 3	Inconclusive data[a]	No effects
Ethofumesate	Not carcinogenic	Not genotoxic	No effects	Inconclusive data	No effects
Cymoxanil	Not carcinogenic	Not genotoxic	Category 3	Inconclusive data[a]	No effects
Mandipropamid	Not carcinogenic	Not genotoxic	No effects	Not a disruptor[a]	No effects
Thifensulfuron-methyl	Unlikely in humans	Unlikely in humans	Possible	Possible	No effects
Prochloraz	Category 3	Not genotoxic	Category 3	Possible	Possible
Folpet	Category 3	Not genotoxic	Category 3	Inconclusive data[a]	No effects
Propyzamide	Category 2	Unlikely in humans	No effects	Possible	No effects
Aminopyralid	Unlikely in humans	No significant potential	Possible	Inconclusive data[a]	No effects
Metrafenone	Unlikely in humans	No significant potential	No effects	Inconclusive data[a]	No effects
Metaldehyde	Unlikely in humans	No significant potential	No effects	Inconclusive data[a]	No effects
Dimethenamid-P	Unlikely in humans	No significant potential	No effects	Inconclusive data	No effects
Cyazofamid	Unlikely in humans	No significant potential	No effects	Inconclusive data	No effects
Dicamba	Unlikely in humans	No significant potential	No effects	Inconclusive data[a]	No effects
Trifloxystrobin	Unlikely in humans	No significant potential	Category 2	Unlikely disruptor	H362
Fluopicolide	Unlikely in humans	No significant potential	Possible	Inconclusive data[a]	No effects
Imidacloprid	Unlikely in humans	No significant potential	No effects	Inconclusive data[a]	No effects
Dichlorprop-P	Inconclusive evidence	No significant potential	No effects	Inconclusive data	No effects
Quinmerac	Unlikely in humans	No significant potential	No effects	Inconclusive data[a]	No effects
Tribenuron-methyl	Unlikely in humans	No significant potential	No effects	Possible	No effects

Table A7 Continued

Pesticide	Carcinogenicity	Genotoxicity	Teratogenicity	Endocrine Disruption	Reproductive Toxicant
Phenmedipham	Category 2	Inconclusive evidence	Category 2	Inconclusive data	No effects
Fluoxastrobin	Unlikely in humans	No significant potential	No effects	Not a disruptor[a]	No effects
Cypermethrin	Unlikely in humans	Inconclusive evidence	No effects	Inconclusive data	Possible
Flufenacet	Not carcinogenic[a]	No significant potential	Possible	Inconclusive data[a]	Possible
Propaquizafop	Category 3	No significant potential	No effects	Inconclusive data[a]	No effects
Imazamox	Unlikely in humans	No significant potential	Category 2	Unlikely disruptor	No effects

Data from EFSA reports unless marked with [a] where evidence taken from PPDB due to lack of information in EFSA reports

Table A8: Pesticide LD_{50} and acute toxicity classes

Pesticide	LD_{50}	Toxicity Class	Pesticide	LD_{50}	Toxicity Class
Glyphosate	4230	III	Metribuzin	322	II
Chlormequat chloride	433	II	Terbuthylazine	2160	III
MCPA	700	II	Isopyrazam	~310	II
Fluroxypyr	>5000	U	Pinoxaden	>2000	III
2,4-DB	700	II	Lenacil	>10000	U
Prothioconazole	>6200	U	Metconazole	660	II
Pendimethalin	1050	II	Ethofumesate	>6400	U
Mancozeb	>8000	U	Cymoxanil	1196	II
Triclopyr	710	II	Mandipropamid	>5000	U
2,4-D	375	II	Thifensulfuron-m.	>5000	U
Mecoprop-P	1050	II	Prochloraz	1600	II
Metamitron	1183	II	Folpet	>10000	U
Propamocarb h.	8600	U	Propyzamide	5620	U
Pyraclostrobin	*2000*	*II*	Aminopyralid	>5000	U
Boscalid	>5000	U	Metrafenone	>5000	U
Spiroxamine	500	II	Metaldehyde	227	II
Prosulfocarb	1820	II	Dimethenamid-P	371	II
Diflufenican	>2000	III	Cyazofamid	>5000	U
Clopyralid	4300	III	Dicamba	1707	II
Tebuconazole	1700	II	Trifloxystrobin	>5000	U
Mepiquat chloride	1490	II	Fluopicolide	>5000	U
Fluxapyroxad	>2000	III	Imidacloprid	450	II
Cyprodinil	*>2000*	*II*	Dichlorprop-P	800	II
Metazachlor	2150	III	Quinmerac	>5000	U
Azoxystrobin	>5000	U	Tribenuron-methyl	>5000	U
Trinexapac-ethyl	>2000	III	Phenmedipham	>8000	U
Ethephon	>4000	III	*Fluoxastrobin*	*>2000*	*III*
Metalaxyl-M	670	II	Cypermethrin	~250	II
Fluazinam	*>4100*	*III*	Flufenacet	600	II
Penthiopyrad	>2000	III	Propaquizafop	>5000	U
Bixafen	*>5000*	*U*	Imazamox	>4000	III
Fenpropidin	1440	II			

Any data in Italics were not in the WHO document, the LD_{50} values were taken from EFSA and put into toxicity classes based on the WHO document.

APPENDIX A3: FULL PESTICIDE RANKING

Table A9: Pesticide (i) consequence of exposure score; and likelihood of exposure score in (ii) Cregduff, and (iii) Dunleer

Rank	Pesticide	CES	Rank	Pesticide	LES_C	Rank	Pesticide	LES_D
1	Mancozeb	21	1	Terbuthylazine	9	1	Terbuthylazine	9
2	Prochloraz	17	2	Metamitron	8.5	2	Prothioconazole	8.5
3	Phenmedipham	16	3	Thifensulfuron-methyl	8.5	3	Metamitron	8.5
4	Propyzamide	15	4	Prothioconazole	8	4	Boscalid	8.5
5	2,4-D	14	5	Boscalid	8	5	Thifensulfuron-methyl	8.5
6	Pendimethalin	13	6	Tebuconazole	8	6	Fluopicolide	8.5
7	Folpet	12	7	Fluxapyroxad	8	7	Imazamox	8.5
8	Isopyrazam	12	8	Cyprodinil	8	8	Tebuconazole	8
9	Metazachlor	12	9	Azoxystrobin	8	9	Fluxapyroxad	8
10	Penthiopyrad	12	10	Trinexapac-ethyl	8	10	Cyprodinil	8
11	Fluazinam	11	11	Penthiopyrad	8	11	Azoxystrobin	8
12	Metribuzin	11	12	Metconazole	8	12	Trinexapac-ethyl	8
13	Propamocarb hydrochloride	11	13	Prochloraz	8	13	Penthiopyrad	8
14	Thifensulfuron-methyl	11	14	Fluopicolide	8	14	Isopyrazam	8
15	Boscalid	10	15	Fluoxastrobin	8	15	Lenacil	8
16	Fluxapyroxad	10	16	Imazamox	8	16	Metconazole	8
17	Propaquizafop	10	17	Isopyrazam	7.5	17	Prochloraz	8
18	Terbuthylazine	10	18	Lenacil	7.5	18	Aminopyralid	8
19	Trifloxystrobin	9	19	Propyzamide	7.5	19	Fluoxastrobin	8
20	2,4-DB	8	20	Aminopyralid	7.5	20	Prosulfocarb	7.5
21	Chlormequat chloride	8	21	Mecoprop-P	7	21	Diflufenican	7.5
22	Cypermethrin	8	22	Prosulfocarb	7	22	Propyzamide	7.5
23	Flufenacet	8	23	Diflufenican	7	23	Imidacloprid	7.5
24	Glyphosate	8	24	Fenpropidin	7	24	Quinmerac	7.5
25	Mecoprop-P	8	25	Metaldehyde	7	25	Glyphosate	7

Table A9: Pesticide (i) consequence of exposure score; and likelihood of exposure score in (ii) Cregduff, and (iii) Dunleer

Rank	Pesticide	CES	Rank	Pesticide	LES_C	Rank	Pesticide	LES_D
26	Metamitron	8	26	Imidacloprid	7	26	MCPA	7
27	Pinoxaden	8	27	Quinmerac	7	27	Pendimethalin	7
28	Trinexapac-ethyl	8	28	Flufenacet	7	28	Triclopyr	7
29	Dichlorprop-P	7	29	Glyphosate	6.5	29	2,4-D	7
30	Diflufenican	7	30	MCPA	6.5	30	Mecoprop-P	7
31	Lenacil	7	31	Fluroxypr	6.5	31	Clopyralid	7
32	Tribenuron-methyl	7	32	Triclopyr	6.5	32	Fenpropidin	7
33	Prothioconazole	7	33	2,4-D	6.5	33	Ethofumesate	7
34	Aminopyralid	6	34	Pyraclostrobin	6.5	34	Metaldehyde	7
35	Cymoxanil	6	35	Clopyralid	6.5	35	Dichlorprop-P	7
36	Ethephon	6	36	Metazachlor	6.5	36	Flufenacet	7
37	Fluopicolide	6	37	Metribuzin	6.5	37	Propaquizafop	7
38	Metconazole	6	38	Ethofumesate	6.5	38	Bixafen	6.75
39	Prosulfocarb	6	39	Dicamba	6.5	39	Cyazofamid	6.75
40	Pyraclostrobin	6	40	Dichlorprop-P	6.5	40	Fluroxypr	6.5
41	Spiroxamine	6	41	Tribenuron-methyl	6.5	41	Pyraclostrobin	6.5
42	Triclopyr	6	42	Propaquizafop	6.5	42	Mepiquat chloride	6.5
43	Fluroxypr	5	43	Spiroxamine	6.25	43	Metazachlor	6.5
44	Imazamox	5	44	Bixafen	6.25	44	Metribuzin	6.5
45	Tebuconazole	5	45	Cyazofamid	6.25	45	Metrafenone	6.5
46	Azoxystrobin	4	46	Chlormequat chloride	6	46	Dicamba	6.5
47	Bixafen	4	47	Pendimethalin	6	47	Tribenuron-methyl	6.5
48	Clopyralid	4	48	Propamocarb hydrochloride	6	48	Phenmedipham	6.5
49	Cyazofamid	4	49	Mepiquat chloride	6	49	Spiroxamine	6.25
50	Cyprodinil	4	50	Metalaxyl-M	6	50	Chlormequat chloride	6
51	Dicamba	4	51	Metrafenone	6	51	Propamocarb hydrochloride	6
52	Ethofumesate	4	52	Dimethenamid-P	6	52	Metalaxyl-M	6

Table A9 Continued

Rank	Pesticide	CES	Rank	Pesticide	LES_C	Rank	Pesticide	LES_D
53	Fenpropidin	4	53	Phenmedipham	6	53	Fluazinam	6
54	Imidacloprid	4	54	2,4-DB	5.5	54	Dimethenamid-P	6
55	MCPA	4	55	Trifloxystrobin	5.5	55	Trifloxystrobin	6
56	Mepiquat chloride	4	56	Ethephon	5	56	2,4-DB	5.5
57	Metaldehyde	4	57	Fluazinam	5	57	Ethephon	5.5
58	Metrafenone	4	58	Cymoxanil	5	58	Mandipropamid	5.5
59	Quinmerac	4	59	Mandipropamid	5	59	Cypermethrin	5.5
60	Metalaxyl-M	3	60	Folpet	4.5	60	Mancozeb	5
61	Dimethenamid-P	1	61	Cypermethrin	4.5	61	Pinoxaden	5
62	Fluoxastrobin	1	62	Mancozeb	4	62	Cymoxanil	5
63	Mandipropamid	1	63	Pinoxaden	4	63	Folpet	5

CES: Consequence of exposure score; LES_C: Likelihood of exposure score in Cregduff; LES_D: Likelihood of exposure score in Dunleer

Table A10: Pesticide hazard score in (i) Cregduff; (ii) Dunleer; (iii) national weighted hazard score

Rank	Pesticide	HS_C	Rank	Pesticide	HS_D	Rank	Pesticide	WHS
1	Prochloraz	52.6	1	Prochloraz	52.6	1	Glyphosate	3.28
2	Propyzamide	43.5	2	Propyzamide	43.5	2	Chlormequat chloride	2.03
3	Penthiopyrad	37.2	3	Mancozeb	40.6	3	MCPA	0.88
4	Phenmedipham	37.2	4	Phenmedipham	40.3	4	Pendimethalin	0.879
5	Thifensulfuron-methyl	36.2	5	2,4-D	37.9	5	Mancozeb	0.877
6	2,4-D	35.2	6	Penthiopyrad	37.2	6	2,4-D	0.80
7	Terbuthylazine	34.8	7	Isopyrazam	37.2	7	Prothioconazole	0.61
8	Isopyrazam	34.8	8	Thifensulfuron-methyl	36.2	8	2,4-DB	0.54
9	Mancozeb	32.5	9	Pendimethalin	35.2	9	Fluroxypr	0.41
10	Pyraclostrobin	31.0	10	Terbuthylazine	34.8	10	Metamitron	0.35
11	Fluxapyroxad	31.0	11	Boscalid	32.9	11	Triclopyr	0.35
12	Pendimethalin	30.2	12	Fluxapyroxad	31.0	12	Mecoprop-P	0.34

Table A10 Continued

Rank	Pesticide	HS_C	Rank	Pesticide	HS_D	Rank	Pesticide	WHS
13	Metazachlor	30.2	13	Metazachlor	30.2	13	Propamocarb hydrochloride	0.331
14	Metribuzin	27.7	14	Metribuzin	27.7	14	Boscalid	0.331
15	Metamitron	26.3	15	Propaquizafop	27.1	15	Fluxapyroxad	0.18
16	Propaquizafop	25.2	16	Metamitron	26.3	16	Pyraclostrobin	0.17
17	Trinexapac-ethyl	24.8	17	Propamocarb hydrochloride	25.5	17	Prosulfocarb	0.16
18	Mecoprop-P	21.7	18	Fluazinam	25.5	18	Diflufenican	0.15
19	Prothioconazole	21.7	19	Trinexapac-ethyl	24.8	19	Spiroxamine	0.141
20	Flufenacet	21.7	20	Folpet	23.2	20	Metazachlor	0.14
21	Fluazinam	21.3	21	Prothioconazole	23.0	21	Penthiopyrad	0.12
16	Propaquizafop	25.2	16	Metamitron	26.3	16	Pyraclostrobin	0.17
17	Trinexapac-ethyl	24.8	17	Propamocarb hydrochloride	25.5	17	Prosulfocarb	0.16
18	Mecoprop-P	21.7	18	Fluazinam	25.5	18	Diflufenican	0.15
19	Prothioconazole	21.7	19	Trinexapac-ethyl	24.8	19	Spiroxamine	0.141
20	Flufenacet	21.7	20	Folpet	23.2	20	Metazachlor	0.14
21	Fluazinam	21.3	21	Prothioconazole	23.0	21	Penthiopyrad	0.12
22	Folpet	20.9	22	Mecoprop-P	21.7	22	Trinexapac-ethyl	0.103
23	Lenacil	20.3	23	Glyphosate	21.7	23	Tebuconazole	0.097
24	Glyphosate	20.1	24	Lenacil	21.7	24	Prochloraz	0.095
25	Trifloxystrobin	19.2	25	Flufenacet	21.7	25	Terbuthylazine	0.094
26	Prosulfocarb	19.0	26	Trifloxystrobin	20.9	26	Fluazinam	0.092
27	Fluopicolide	18.6	27	Diflufenican	20.3	27	Isopyrazam	0.09
28	Chlormequat chloride	18.6	28	Fluopicolide	19.7	28	Metribuzin	0.08
29	Metconazole	18.6	29	Dichlorprop-P	19.0	29	Cyprodinil	0.072
30	Dichlorprop-P	17.6	30	Chlormequat chloride	18.6	30	Propyzamide	0.0717
31	Tribenuron-methyl	17.6	31	Aminopyralid	18.6	31	Clopyralid	0.0714
32	Aminopyralid	17.4	32	Metconazole	18.6	32	Thifensulfuron-methyl	0.066
33	2,4-DB	17.0	33	Tribenuron-methyl	17.6	33	Mepiquat chloride	0.059

Table A10 Continued

Rank	Pesticide	HS_C	Rank	Pesticide	HS_D	Rank	Pesticide	WHS
34	Spiroxamine	16.3	34	Prosulfocarb	17.4	34	Azoxystrobin	0.056
35	Clopyralid	15.5	35	2,4-DB	17.0	35	Ethephon	0.050
36	Tebuconazole	15.5	36	Cypermethrin	17.0	36	Lenacil	0.044
37	Imazamox	15.5	37	Imazamox	16.5	37	Folpet	0.041
38	Propamocarb hydrochloride	15.1	38	Triclopyr	16.3	38	Metconazole	0.037
39	Triclopyr	15.1	39	Tebuconazole	15.5	39	Bixafen	0.0331
40	Boscalid	14.5	40	Pinoxaden	15.5	40	Fenpropidin	0.0330
41	Cypermethrin	13.9	41	Pyraclostrobin	15.1	41	Pinoxaden	0.032
42	Fluroxypr	12.58	42	Spiroxamine	14.5	42	Phenmedipham	0.031
43	Cyprodinil	12.4	43	Ethephon	12.8	43	Aminopyralid	0.028
44	Azoxystrobin	12.4	44	Fluroxypr	12.6	44	Metalaxyl-M	0.026
45	Pinoxaden	12.4	45	Cyprodinil	12.4	45	Trifloxystrobin	0.025
46	Ethephon	11.6	46	Azoxystrobin	12.4	46	Cymoxanil	0.022
47	Cymoxanil	11.6	47	Imidacloprid	11.6	47	Fluopicolide	0.022
48	Fenpropidin	10.8	48	Quinmerac	11.6	48	Ethofumesate	0.021
49	Imidacloprid	10.8	49	Cymoxanil	11.6	49	Dichlorprop-P	0.020
50	Metaldehyde	10.8	50	Clopyralid	10.8	50	Propaquizafop	0.018
51	Quinmerac	10.8	51	Fenpropidin	10.8	51	Metaldehyde	0.015
52	Ethofumesate	10.1	52	Ethofumesate	10.8	52	Tribenuron-methyl	0.0147
53	Diflufenican	10.1	53	Metaldehyde	10.8	53	Flufenacet	0.0147
54	Dicamba	10.1	54	MCPA	10.8	54	Metrafenone	0.0147
55	MCPA	10.1	55	Bixafen	10.5	55	Cyazofamid	0.013
56	Bixafen	9.7	56	Cyazofamid	10.5	56	Imidacloprid	0.0125
57	Cyazofamid	9.7	57	Mepiquat chloride	10.1	57	Cypermethrin	0.012
58	Mepiquat chloride	9.3	58	Metrafenone	10.1	58	Dicamba	0.0119
59	Metrafenone	9.3	59	Dicamba	10.1	59	Quinmerac	0.011
60	Metalaxyl-M	7.0	60	Metalaxyl-M	7.0	60	Imazamox	0.0108

Table A10 Continued

Rank	Pesticide	HS_C	Rank	Pesticide	HS_D	Rank	Pesticide	WHS
61	Fluoxastrobin	3.1	61	Fluoxastrobin	3.1	61	Mandipropamid	0.004
62	Dimethenamid-P	2.3	62	Dimethenamid-P	2.3	62	Dimethenamid-P	0.003
63	Mandipropamid	1.9	63	Mandipropamid	2.1	63	Fluoxastrobin	0.002

HS_C: Hazard score in Cregduff; HS_D: Hazard score in Dunleer; WHS: National quantity-weighted hazard score

APPENDIX A4: RISK RANKING INCLUDING METABOLITES

Table A11: (i) Consequence of exposure score (ii) likelihood of exposure score (iii) hazard score; (iv) national quantity weighted hazard score, for pesticides including metabolites

Rank	Pesticide	CES_M	Rank	Pesticide	LES_M	Rank	Pesticide	HS_M	Change	Rank	Pesticide	WHS_M	Change
1	Mancozeb	23	1	Terbuthylazine	13	1	Propyzamide	89.4	+1	1	Glyphosate	6.85	0
2	Prochloraz	19	2	Boscalid	12.5	2	Prochloraz	78.2	-1	*2*	*Chlormequat*	*2.40*	*0*
3	Phenmedipham	18	3	Imazamox	12.5	3	Terbuthylazine	71.3	+7	3	MCPA	2.05	0
4	Propyzamide	17	4	Isopyrazam	12	4	Isopyrazam	71.3	+3	4	Pendimethalin	1.60	0
5	2,4-D	15	5	Propyzamide	11.5	5	Phenmedipham	69.9	-1	5	Mancozeb	1.36	0
6	Pendimethalin	14	6	Fluopicolide	11.5	6	Boscalid	68.6	+5	6	2,4-D	1.16	0
7	Fluazinam	13	7	Imidacloprid	11.5	7	Penthiopyrad	65.4	-1	7	Prothioconazole	1.14	0
8	Folpet	13	8	Glyphosate	11	8	Pendimethalin	64.0	+2	8	2,4-DB	0.98	0
9	Isopyrazam	13	9	MCPA	11	9	Mancozeb	63.1	-6	9	Triclopyr	0.87	+2
10	Metazachlor	13	10	Triclopyr	11	10	Thifensulfuron-m	62.4	-2	10	Fluroxypr	0.77	-1
11	Metribuzin	13	11	Diflufenican	11	11	2,4-D	54.9	-6	11	Boscalid	0.69	+3
12	Penthiopyrad	13	12	Penthiopyrad	11	12	Fluazinam	53.5	+6	12	Metamitron	0.64	-2
13	Thifensulfuron-m.	13	13	Prothioconazole	10.5	13	Metribuzin	50.5	+1	13	Mecoprop-P	0.57	-1
14	Boscalid	12	14	Metamitron	10.5	14	Fluxapyroxad	50.3	-2	14	Pyraclostrobin	0.43	+2
15	Propaquizafop	12	15	Pyraclostrobin	10.5	15	Propaquizafop	49.4	0	*15*	*Propamocarb h.*	*0.39*	*-2*
16	Terbuthylazine	12	16	Thifensulfuron-m.	10.5	16	Metamitron	48.0	0	16	Diflufenican	0.36	+2
17	Cypermethrin	11	17	Tribenuron-m.	10.5	17	Diflufenican	47.3	+10	17	Prosulfocarb	0.32	0
18	Flufenacet	11	18	Pendimethalin	10	18	Glyphosate	45.3	+5	18	Fluxapyroxad	0.29	-3
19	Fluxapyroxad	11	19	Fluxapyroxad	10	19	Metazachlor	44.6	-6	19	Penthiopyrad	0.217	+2
20	*Propamocarb h.*	*11*	20	Trinexapac-e.	10	20	Prothioconazole	43.2	+1	20	Tebuconazole	0.21	+3
21	Mecoprop-P	10	21	Fluoxastrobin	10	21	Tribenuron-m.	43.2	+12	21	Metazachlor	0.203	-1
22	Metamitron	10	22	Quinmerac	9.5	22	Folpet	41.6	-2	22	Fluazinam	0.193	+4
23	Trifloxystrobin	10	23	Tebuconazole	9	23	Trinexapac-e.	41.1	-4	23	Terbuthylazine	0.192	+2
24	2,4-DB	9	24	Cyprodinil	9	24	Flufenacet	40.2	+1	24	Trinexapac-e.	0.17	-2
25	Diflufenican	9	25	Azoxystrobin	9	25	Triclopyr	40.2	+13	25	Isopyrazam	0.17	+2
26	Glyphosate	9	26	Fluazinam	9	26	Pyraclostrobin	38.4	+15	*26*	*Spiroxamine*	*0.17*	*-7*
27	Metconazole	9	27	Fenpropidin	9	27	Metconazole	37.0	+5	27	Propyzamide	0.15	+3
28	Pinoxaden	9	28	Lenacil	9	28	Fluopicolide	36.8	0	28	Cyprodinil	0.14	+1
29	Prosulfocarb	9	29	Metconazole	9	29	Mecoprop-P	36.6	-7	29	Prochloraz	0.14	-5
30	Tribenuron-m.	9	30	Prochloraz	9	30	Trifloxystrobin	36.6	-4	30	Metribuzin	0.14	-2
31	Trinexapac-e.	9	31	Propaquizafop	9	31	Prosulfocarb	35.0	+3	31	Thifensulfuron-m.	0.11	+1
32	Prothioconazole	9	32	Fluroxypr	8.5	32	Imazamox	34.3	+5	32	Azoxystrobin	0.093	+2

Table A11 Continued

Rank	Pesticide	CES_M	Rank	Pesticide	LES_M	Rank	Pesticide	HS_M	Change	Rank	Pesticide	WHS_M	Change
33	*Chlormequat c.*	*8*	33	Metribuzin	8.5	33	Lenacil	32.9	-9	*33*	*Clopyralid*	*0.084*	*-2*
34	Dichlorprop-P	8	34	Phenmedipham	8.5	34	Tebuconazole	32.9	+5	34	Fenpropidin	0.075	+6
35	Lenacil	8	35	2,4-D	8	35	Cypermethrin	32.7	+1	35	Metconazole	0.074	+3
36	Pyraclostrobin	8	36	Mecoprop-P	8	36	2,4-DB	30.9	-1	36	Folpet	0.074	+1
37	Tebuconazole	8	37	Prosulfocarb	8	*37*	*Propamocarb h.*	*30.2*	*-20*	*37*	*Mepiquat c.*	*0.07*	*-4*
38	Triclopyr	8	38	Metalaxyl-M	8	38	Dichlorprop-P	29.3	-9	38	Lenacil	0.07	-2
39	Cymoxanil	7	*39*	*Aminopyralid*	*8*	39	Pinoxaden	28.8	+1	39	Pinoxaden	0.06	+2
40	Fluopicolide	7	40	Dimethenamid-P	8	40	Imidacloprid	26.3	+7	*40*	*Ethephon*	*0.06*	*-5*
41	*Aminopyralid*	*6*	41	Trifloxystrobin	8	41	MCPA	25.1	+13	41	Metalaxyl-M	0.06	+3
42	Cyprodinil	6	42	Dichlorprop-P	8	42	Cyprodinil	24.7	+3	42	Phenmedipham	0.054	0
43	Dicamba	6	43	Flufenacet	8	43	Fenpropidin	24.7	+8	43	Trifloxystrobin	0.043	+2
44	*Ethephon*	*6*	44	Cyazofamid	7.75	44	Fluroxypr	23.3	0	44	Fluopicolide	0.041	+3
45	Fenpropidin	6	45	2,4-DB	7.5	*45*	*Chlormequat c.*	*21.9*	*-15*	*45*	*Bixafen*	*0.039*	*-6*
46	Fluroxypr	6	46	Metazachlor	7.5	*46*	*Aminopyralid*	*21.9*	*-15*	46	Cymoxanil	0.037	0
47	Imazamox	6	47	Dicamba	7.5	47	Quinmerac	21.7	+1	47	Tribenuron-m.	0.036	+5
48	*Spiroxamine*	*6*	*48*	*Clopyralid*	*7*	48	Dicamba	20.6	+11	48	Propaquizafop	0.033	+2
49	Azoxystrobin	5	49	Pinoxaden	7	49	Azoxystrobin	20.6	-3	*49*	*Aminopyralid*	*0.033*	*-6*
50	Cyazofamid	5	*50*	*Ethofumesate*	*7*	50	Cymoxanil	19.2	-1	50	Dichlorprop-P	0.031	-1
51	Imidacloprid	5	51	Folpet	7	51	Cyazofamid	17.7	+5	51	Imidacloprid	0.028	+5
52	MCPA	5	*52*	*Metaldehyde*	*7*	*52*	*Spiroxamine*	*17.1*	*-10*	52	Flufenacet	0.0273	+1
53	Quinmerac	5	*53*	*Bixafen*	*6.75*	*53*	*Ethephon*	*15.1*	*-10*	*53*	*Ethofumesate*	*0.025*	*-5*
54	*Bixafen*	*4*	*54*	*Mepiquat c.*	*6.5*	54	Metalaxyl-M	14.6	+6	54	Dicamba	0.024	+4
55	*Clopyralid*	*4*	55	Mandipropamid	6.5	*55*	*Ethofumesate*	*12.8*	*-3*	55	Cypermethrin	0.0229	+2
56	*Ethofumesate*	*4*	*56*	*Metrafenone*	*6.5*	*56*	*Clopyralid*	*12.8*	*-6*	56	Imazamox	0.022	+4
57	*Mepiquat c.*	*4*	57	Cypermethrin	6.5	*57*	*Metaldehyde*	*12.8*	*-4*	57	Cyazofamid	0.0223	-2
58	Metalaxyl-M	4	*58*	*Spiroxamine*	*6.25*	*58*	*Bixafen*	*12.3*	*-3*	58	Quinmerac	0.0202	+1
59	*Metaldehyde*	*4*	*59*	*Chlormequat c.*	*6*	*59*	*Metrafenone*	*11.9*	*-1*	*59*	*Metaldehyde*	*0.0182*	*-8*
60	*Metrafenone*	*4*	60	Mancozeb	6	*60*	*Mepiquat c.*	*11.9*	*-6*	*60*	*Metrafenone*	*0.017*	*-6*
61	Dimethenamid-P	2	*61*	*Propamocarb h.*	*6*	61	Fluoxastrobin	9.1	0	61	Mandipropamid	0.011	0
62	Fluoxastrobin	2	62	Cymoxanil	6	62	Dimethenamid-P	7.3	0	62	Dimethenamid-P	0.010	0
63	Mandipropamid	2	*63*	*Ethephon*	*5.5*	63	Mandipropamid	5.9	0	63	Fluoxastrobin	0.007	0

CES_M: Consequence of exposure score, including metabolites; LES_M: Likelihood of exposure score, including metabolites; HS_M: Hazard score, including metabolites; WHS_m: National quantity-weighted hazard score, including metabolites; Pesticides in italics do not have any key metabolites identified by the EFSA

APPENDIX A5: SENSITIVITY STUDY

Table A12: Results from sensitivity study investigating the effect variability in pesticide data has on mobility

Pesticide	Half-Life (-10%)			Half-Life (+10%)			K_{OC} (-10%)			K_{OC} (+10%)		
	Leaching	Sed Runoff	Direct Runoff	Leaching	Sed Runoff	Direct Runoff	Leaching	Sed Runoff	Direct Runoff	Leaching	Sed Runoff	Direct Runoff
Mancozeb	-	-	-	-	-	-	-	-	-	-	-	M→L
Metamitron	-	-	-	M→H	-	-	L→M	-	-	-	-	-
Propamocarb	-	-	-	L→M	-	-	L→M	-	-	-	-	-
Pyraclostrobin	-	-	-	-	M→H	-	-	-	-	L→ V.L.	-	-
Boscalid	H → M	-	-	-	-	-	-	-	-	H→ M	-	-
Spiroxamine	-	-	H→ M	-	M→H	-	-	-	-	-	-	-
Fluxapyroxad	-	-	-	-	-	-	-	-	-	-	M→H	-
Cyprodinil	-	H→ M	-	-	-	-	-	-	-	-	-	-
Tebuconazole	-	-	-	-	-	-	L→M	M→H	-	-	-	-
Metalaxyl-M	-	-	-	L→M	-	-	L→M	-	-	-	-	-
Pinoxaden	-	-	-	-	-	-	-	-	-	-	-	-
Thifensulfuron-methyl	-	-	-	-	-	-	-	-	-	-	L→M	-
Trifloxystrobin	L→ V.L.	M→L	-	-	-	-	-	-	-	-	-	-
Fluoxastrobin	H → M	-	-	-	-	-	-	-	-	H→ M	-	-
Propaquizafop	-	H→ M	-	-	-	-	-	-	-	-	-	-

V. L = Very Low, L = Low, M = Moderate, H = High

Table A13: Influence of pesticide data on hazard score

Pesticide		2,4-D	Mancozeb	Metamitron	Propamocarb	Pyraclostrobin	Boscalid	Spiroxamine	Fluzapyroxad	Cyprodinil	Tebuconazole
Half-Life (-10%)	**Original HS**	-	-	-	-	-	32.9	14.2	-	11.6	-
	New HS	-	-	-	-	-	31.0	14.2	-	11.6	-
	% Change	-	-	-	-	-	-6.3	0.0	-	0.0	-
Half-Life (+10%)	**Original HS**	-	-	26.3	25.6	15.1	-	14.5	-	-	-
	New HS	-	-	27.9	27.7	16.3	-	15.7	-	-	-
	% Change	-	-	+5.6	+7.7	+7.1	-	+7.4	-	-	-
K_{OC} (-10%)	**Original HS**	-	-	26.3	25.6	-	-	-	-	-	14.5
	New HS	-	-	21.7	27.7	-	-	-	-	-	12.6
	% Change	-	-	-21.4	+7.7	-	-	-	-	-	-15.4
K_{OC} (+10%)	**Original HS**	-	40.7	-	-	15.1	32.9	-	31.0	-	-
	New HS	-	36.6	-	-	15.1	31.0	-	32.9	-	-
	% Change	-	-11.1	-	-	0.0	-6.3	-	5.9	-	-
Half-$Life_{SW}$ (-10%)	**Original HS**	-	-	-	-	-	-	-	-	-	-
	New HS	-	-	-	-	-	-	-	-	-	-
	% Change	-	-	-	-	-	-	-	-	-	-
Half-$Life_{SW}$ (+10%)	**Original HS**	17.1	-	-	-	-	-	-	-	-	-
	New HS	18.6	-	-	-	-	-	-	-	-	-
	% Change	+8.3	-	-	-	-	-	-	-	-	-
Half-$Life_{GW}$ (-10%)	**Original HS**	-	-	-	-	-	-	-	-	-	-
	New HS	-	-	-	-	-	-	-	-	-	-
	% Change	-	-	-	-	-	-	-	-	-	-
Half-$Life_{GW}$ (+10%)	**Original HS**	-	-	-	-	-	-	-	-	-	-
	New HS	-	-	-	-	-	-	-	-	-	-
	% Change	-	-	-	-	-	-	-	-	-	-

HS = Hazard Score, SW = Surface Water, GW = Groundwater, - = No change to score

Table A13 Continued

	Pesticide	Metalaxyl-M	Terbuthylazine	Pinoxaden	Mandipropamid	Thifensulfuron-	Trifloxystrobin	Quinmerac	Tribenuron-methyl	Propaquizafop
Half-Life (-10%)	**Original HS**	-	-	-	-	-	22.7	11.6	-	27.1
	New HS	-	-	-	-	-	19.2	10.8	-	25.2
	% Change	-	-	-	-	-	-18.2	7.1	-	-7.7
Half-Life (+10%)	**Original HS**	7.0	34.8	-	-	-	-	-	-	-
	New HS	7.6	36.8	-	-	-	-	-	-	-
	% Change	+7.7	+5.3	-	-	-	-	-	-	-
K_{OC} (-10%)	**Original HS**	7.0	34.8	-	-	-	-	-	-	-
	New HS	5.8	29.0	-	-	-	-	-	-	-
	% Change	-20.0	-20.0	-	-	-	-	-	-	-
K_{OC} (+10%)	**Original HS**	-	-	-	2.1	-	-	11.6	-	-
	New HS	-	-	-	2.3	-	-	10.8	-	-
	% Change	-	-	-	+8.3	-	-	-7.1	-	-
Half-$Life_{SW}$ (-10%)	**Original HS**	-	-	-	-	36.2	-	-	3.1	-
	New HS	-	-	-	-	34.1	-	-	2.9	-
	% Change	-	-	-	-	-6.3	-	-	-6.7	-
Half-$Life_{SW}$ (+10%)	**Original HS**	-	-	15.5	-	-	-	-	-	-
	New HS	-	-	17.0	-	-	-	-	-	-
	% Change	-	-	+9.1	-	-	-	-	-	-
Half-$Life_{GW}$ (-10%)	**Original HS**	-	-	-	-	-	-	17.6	-	-
	New HS	-	-	-	-	-	-	16.3	-	-
	% Change	-	-	-	-	-	-	-8.3	-	-
Half-$Life_{GW}$ (+10%)	**Original HS**	-	-	-	-	-	-	-	-	-
	New HS	-	-	-	-	-	-	-	-	-
	% Change	-	-	-	-	-	-	-	-	-

HS = Hazard Score, SW = Surface Water, GW = Groundwater, - = No change to score

Table A14: Influence of soil data on pesticide hazard scores

Pesticide	Original HS	New HS	% Change	Pesticide	Original HS	New HS	% Change
Prochloraz	52.6	55.9	6.3	Trifloxystrobin	17.4	20.9	20.0
Propyzamide	43.5	46.5	6.7	2,4-DB	17.0	18.6	9.1
Penthiopyrad	37.2	39.5	6.3	Prosulfocarb	16.3	17.4	7.1
Phenmedipham	37.2	40.3	8.3	Imazamox	15.5	16.5	6.3
Thifensulfuron-methyl	36.2	38.3	5.9	Triclopyr	15.1	16.3	7.7
2,4-D	35.2	37.9	7.7	Pyraclostrobin	15.1	16.3	7.7
Terbuthylazine	34.8	36.8	5.6	Tebuconazole	14.5	16.5	13.3
Isopyrazam	34.8	37.2	6.7	Spiroxamine	14.5	15.7	8.0
Mancozeb	32.5	36.6	12.5	Cypermethrin	13.9	15.5	11.1
Boscalid	31.0	32.9	6.3	Fluroxypr	12.6	13.6	7.7
Fluxapyroxad	31.0	32.9	6.3	Azoxystrobin	12.4	13.2	6.3
Pendimethalin	30.2	32.7	8.3	Pinoxaden	12.4	13.9	12.5
Metazachlor	30.2	32.5	7.7	Cyprodinil	11.6	13.2	13.3
Metribuzin	29.8	29.8	0.0	Imidacloprid	11.6	12.4	6.7
Metamitron	26.3	27.9	5.9	Ethephon	11.6	12.8	10.0
Propamocarb	25.5	27.7	8.3	Cymoxanil	11.6	12.8	10.0
Propaquizafop	25.2	27.1	7.7	Fenpropidin	10.8	11.6	7.1
Trinexapac-ethyl	24.8	26.3	6.3	Metaldehyde	10.8	11.6	7.1
Prothioconazole	21.7	23.0	6.3	Quinmerac	10.8	11.6	7.1
Mecoprop-P	21.7	23.2	7.1	MCPA	10.1	10.8	7.7
Flufenacet	21.7	23.2	7.1	Clopyralid	10.1	10.8	7.7
Fluazinam	21.3	23.4	10.0	Ethofumesate	10.1	10.8	7.7
Folpet	20.9	23.2	11.1	Dicamba	10.1	10.8	7.7
Lenacil	20.3	21.7	6.7	Bixafen	9.7	10.5	8.0
Glyphosate	20.1	21.7	7.7	Cyazofamid	9.7	10.5	8.0
Diflufenican	9.0	20.3	7.1	Metrafenone	9.3	10.1	8.3
Chlormequat chloride	18.6	20.1	8.3	Mepiquat chloride	8.5	10.1	18.2
Metconazole	18.6	19.7	6.3	Metalaxyl-M	7.6	7.6	0.0

Table A14 continued

Pesticide	Original HS	New HS	% Change	Pesticide	Original HS	New HS	% Change
Fluopicolide	18.6	19.7	6.3	Fluoxastrobin	3.1	3.3	6.3
Dichlorprop-P	17.6	19.0	7.7	Dimethenamid-P	2.3	2.5	8.3
Tribenuron-methyl	17.6	19.0	7.7	Mandipropamid	1.9	2.1	10.0
Aminopyralid	17.4	18.6	6.7				

Table A15: Influence of scoring system uncertainty on pesticide risk ranking

Pesticide	Original Ranking	Rank Change *(ND = 0)*	Rank Change *(ND = Mid-range)*	Pesticide	Original Ranking	Rank Change *(ND = 0)*	Rank Change *(ND = Mid-range)*
Prochloraz	1	0	-1	Tribenuron-methyl	33	+8	-21
Propyzamide	2	0	-6	Prosulfocarb	34	-4	+7
Mancozeb	3	0	-6	2,4-DB	35	+2	+3
Phenmedipham	4	-8	+3	Cypermethrin	36	-8	+18
2,4-D	5	-2	-1	Imazamox	37	+13	-19
Penthiopyrad	6	-3	+2	Triclopyr	38	-1	+7
Isopyrazam	7	-1	+2	Tebuconazole	39	+12	-19
Thifensulfuron-m.	8	+3	-5	Pinoxaden	40	+5	+2
Pendimethalin	9	+5	-5	Pyraclostrobin	41	+11	-12
Terbuthylazine	10	-3	+3	Spiroxamine	42	-1	+7
Boscalid	11	-12	+8	Ethephon	43	-2	-1
Fluxapyroxad	12	-5	+2	Fluroxypr	44	+4	-6
Metazachlor	13	-2	+2	Cyprodinil	45	-3	+5
Metribuzin	14	+8	-6	Azoxystrobin	46	-1	+9
Propaquizafop	15	-5	0	Imidacloprid	47	-2	+6
Metamitron	16	-6	+4	Quinmerac	48	-2	+6
Propamocarb h.	17	+7	-12	Cymoxanil	49	+1	+11
Fluazinam	18	+7	-12	Clopyralid	50	-6	+4
Trinexapac-ethyl	19	-7	+3	Fenpropidin	51	-1	+4
Folpet	20	-1	-3	Ethofumesate	52	-3	+7
Prothioconazole	21	+7	-12	Metaldehyde	53	+0	+5
Mecoprop-P	22	-6	+1	MCPA	54	+12	-5

Table A15 continued

Pesticide	Original Ranking	Rank Change *(ND = 0)*	Rank Change *(ND = Mid-range)*	Pesticide	Original Ranking	Rank Change *(ND = 0)*	Rank Change *(ND = Mid-range)*
Glyphosate	23	-6	+4	Bixafen	55	-2	+6
Lenacil	24	+6	-12	Cyazofamid	56	+5	+13
Flufenacet	25	-6	-1	Mepiquat chloride	57	-5	0
Trifloxystrobin	26	+10	-8	Metrafenone	58	-1	+7
Diflufenican	27	+8	-12	Dicamba	59	+1	+7
Fluopicolide	28	-6	+6	Metalaxyl-M	60	+19	0
Dichlorprop-P	29	-31	+12	Fluoxastrobin	61	+7	0
Chlormequat chloride	30	-2	+2	Dimethenamid-P	62	+1	0
Aminopyralid	31	-5	+6	Mandipropamid	63	0	0
Metconazole	32	-5	+8				

ND = No data score in Table 3.4

APPENDIX B: SUPPLEMENTARY INFORMATION FOR CHAPTER 4

APPENDIX B1: SITE CONDITIONS

Table B1: Runoff curve numbers for agricultural lands (USDA 2004)

Crop Type	Cover Condition	Hydrologic Soil Group			
		A	B	C	D
Bare Soil	-	77	86	91	94
Crop Residue	Poor	76	85	90	93
	Good	74	83	88	90
Straight Row Crop	Poor	72	81	88	91
	Good	67	78	85	89
Contour Row Crop	Poor	70	79	84	88
	Good	65	75	82	86
Straight Row Grain	Poor	65	76	84	88
	Good	63	75	83	87
Contour Row Grain	Poor	63	74	82	85
	Good	61	73	81	84
Pasture & Grassland	Poor	68	79	86	89
	Good	39	61	74	80

APPENDIX B2: PESTICIDE PROPERTIES

Table B2: Pesticide risk screening information

Pesticide	Quantity of use (kg)[a]	Hazard Score Rank[b]	Weighted Hazard Score Rank[b]
Glyphosate	238230	22	1
MCPA	128560	57	5
Fluroxypyr	51761	44	9
2,4-DB	49908	34	8
Prothioconazole	41529	25	7
Pendimethalin	39271	8	4
Triclopyr	33915	39	12
2,4-D	33206	4	6
Mecoprop	24581	31	14
Clopyralid	10372	50	29
Penthiopyrad	5221	5	21
Terbuthylazine	4249	11	25
Prochloraz	2844	2	27
Propyzamide	2519	3	31
Phenmedipham	1219	6	43

[a] Annual quantity of use on grassland, fodder and arable crop land from most recent Irish surveys (DAFM, 2020, 2021), [b] Ranking out of 63 pesticides (Harmon O'Driscoll et al., 2022: Chapter 3)

Table B3: Pesticide properties and distribution parameters for transport models

Pesticide	**Family**	**K_{oc} (l.kg^{-1})**	**$DT_{50,s}$ (days)**	**$DT_{50,w}$ (days)**	**Max Legal Appl. Rate (g.ha^{-1})**	**ADI (mg.kg^{-1}.day^{-1})**
Glyphosate *N-(phosphonomethyl)glycine*	Organophosphate	Normally distributed $\mu = 14396.7; \sigma = 15102.9$	Normally distributed $\mu = 45.1; \sigma = 93.91$	Normally distributed $\mu = 64; \sigma = 62.51$	Fixed: 2160	Fixed: 0.5
MCPA *(2-methyl-4-chlorophenoxyacetic acid)*	Aryloxyalkanoic Acid herbicide	Normally distributed $\mu = 75.2; \sigma = 42.22$	Normally distributed $\mu = 21.4; \sigma = 12.66$	Fixed: 16.9	Fixed: 1800	Fixed: 0.05
Fluroxypyr *4-amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid*	Pyridine herbicide	Normally distributed $\mu = 68; \sigma = 10.9$	Normally distributed $\mu = 19.6; \sigma = 15.23$	Normally distributed $\mu = 27.8; \sigma = 31.3$	Fixed: 400	Fixed: 0.03
2,4-DB *4-(2,4-Dichlorophenoxy) butanoic acid*	Phenoxy herbicide	Normally distributed $\mu = 373.9; \sigma = 370.57$	Normally distributed $\mu = 23.9; \sigma = 33.46$	Normally distributed $\mu = 27.6; \sigma = 18.51$	Fixed: 1800	Fixed: 0.02
Triclopyr *3,5,6-trichloro-2-pyridyloxyacetic acid*	Pyridine herbicide	Normally distributed $\mu = 49.2; \sigma = 7.73$	Normally distributed $\mu = 35.1; \sigma = 20.09$	Normally distributed $\mu = 29.3; \sigma = 29.28$	Fixed: 1440	Fixed: 0.03
2,4-D *(2,4-dichlorophenoxyacetic acid)*	Phenoxy herbicide	Normally distributed $\mu = 41.7; \sigma = 18.63$	Normally distributed $\mu = 18.8; \sigma = 25.48$	Normally distributed $\mu = 26.4\ \sigma = 16.83$	Fixed: 750	Fixed: 0.02
Mecoprop *(RS)-2-(4-chloro-o-tolyloxy)propionic acid*	Phenoxypropionic herbicide	Normally distributed $\mu = 56.3; \sigma = 56.3$	Normally distributed $\mu = 6.4; \sigma = 10.12$	Normally distributed $\mu = 155.6; \sigma = 59.42$	Fixed: 1200	Fixed: 0.01

Table B3 continued

Pesticide	**Family**	**K_{oc} (l.kg^{-1})**	**$DT_{50,s}$ (days)**	**$DT_{50,w}$ (days)**	**Max Legal Appl. Rate (g.ha^{-1})**	**ADI (mg.kg^{-1}.day^{-1})**
Clopyralid *3,6-dichloropyridine-2-carboxylic acid*	Pyridine herbicide	Normally distributed $\mu = 4.9$; $\sigma = 3.38$	Normally distributed $\mu = 42.9$; $\sigma = 47.06$	Normally distributed $\mu = 155$; $\sigma = 20.89$	Fixed: 200	Fixed: 0.15
Prothioconazole *(RS)-2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-1,2,4-triazole-3-thione*	Conazole fungicide	Fixed: 1765	Normally distributed $\mu = 2.4$; $\sigma = 2.6$	Normally distributed $\mu = 1.8$; $\sigma = 0.75$	Fixed: 200	Fixed: 0.05
Pendimethalin *N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine*	Dinitroaniline herbicide	Normally distributed $\mu = 17121.1$; $\sigma = 6986.6$	Normally distributed $\mu = 150.4$; $\sigma = 150.4$	Normally distributed $\mu = 92.2$; $\sigma = 68.29$	Fixed: 1600	Fixed: 0.125
Penthiopyrad *(RS)-N-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)pyrazole-4-carboxamide*	Carboxamide fungicide	Normally distributed $\mu = 796.8$; $\sigma = 130.2$	Normally distributed $\mu = 122$; $\sigma = 129.34$	Normally distributed $\mu = 279.8$; $\sigma = 26.82$	Fixed: 500	Fixed: 0.1
Terbuthylazine *N2-tert-butyl-6-chloro-N4-ethyl-1,3,5-triazine-2,4-diamine*	Triazine herbicide	Normally distributed $\mu = 231.3$; $\sigma = 56.9$	Normally distributed $\mu = 73$; $\sigma = 40.67$	Normally distributed $\mu = 75.6$; $\sigma = 27.41$	Fixed: 570	Fixed: 0.004

Table B3 continued

Pesticide	**Family**	**K_{oc} ($l.kg^{-1}$)**	**$DT_{50,s}$ (days)**	**$DT_{50,w}$ (days)**	**Max Legal Appl. Rate ($g.ha^{-1}$)**	**ADI ($mg.kg^{-1}.day^{-1}$)**
Prochloraz *N-propyl-N-[2-(2,4,6-trichlorophenoxy)ethyl]imidazole-1-carboxamide*	Amide fungicide	Normally distributed $\mu = 4423.6; \sigma = 3784.5$	Normally distributed $\mu = 130.9; \sigma = 198.8$	Normally distributed $\mu = 321.3; \sigma = 36.46$	Fixed: 450	Fixed: 0.01
Propyzamide *3,5-dichloro-N-(1,1-dimethylprop-2-ynyl)benzamide*	Amide herbicide	Normally distributed $\mu = 1855.1; \sigma = 1274.7$	Normally distributed $\mu = 73.8; \sigma = 66.4$	Normally distributed $\mu = 98.9; \sigma = 16.4$	Fixed: 1500	Fixed: 0.05
Phenmedipham *Methyl 3-(3-methylcarbaniloyloxy)carbanilate*	Carbanilate herbicide	Normally distributed $\mu = 1356.7; \sigma = 221.2$	Normally distributed $\mu = 37.7; \sigma = 29.47$	Normally distributed $\mu = 0.18; \sigma = 0.15$	Fixed: 320	Fixed: 0.03

APPENDIX B3: PREDICTED ENVIRONMENTAL CONCENTRATION

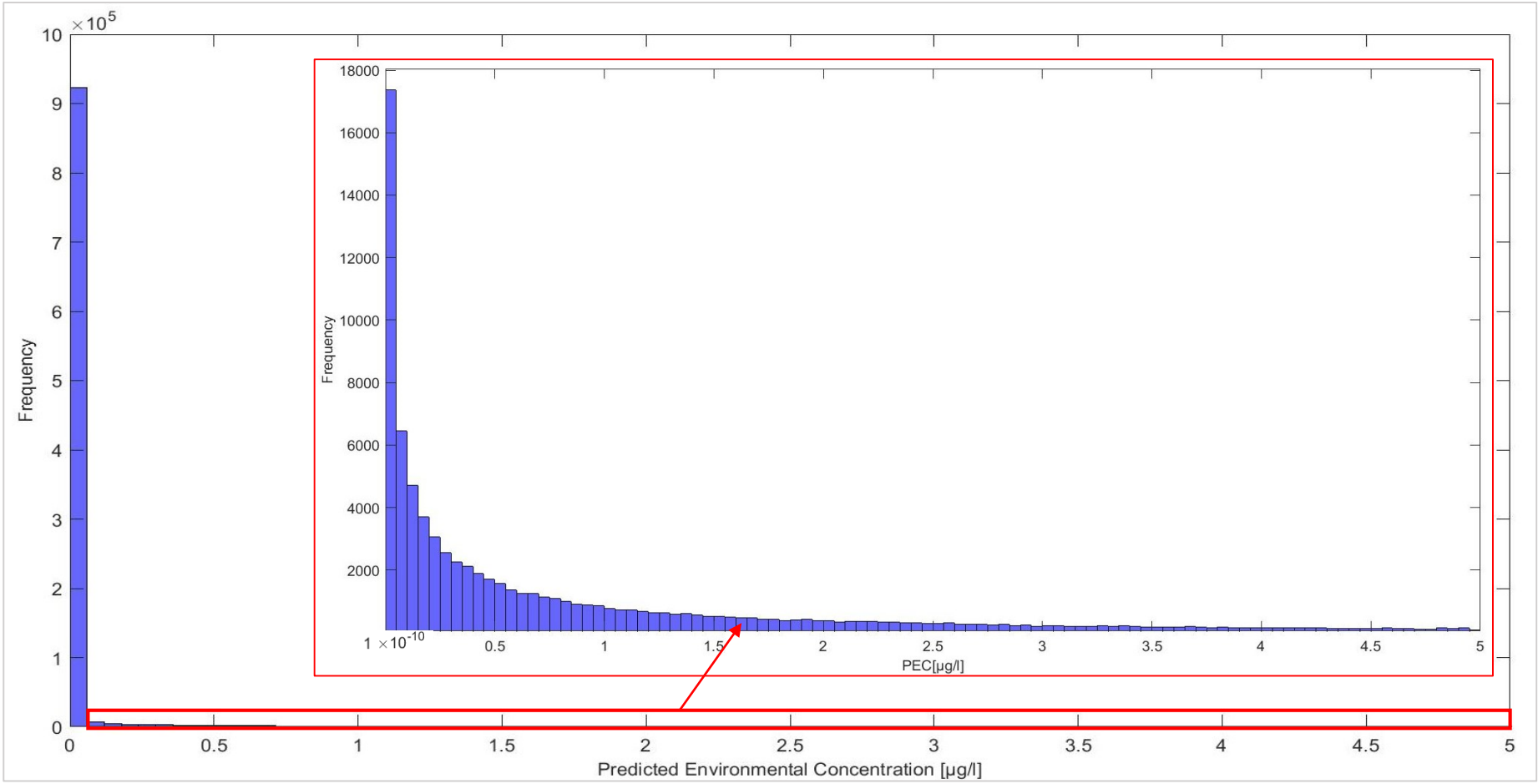


Figure B1: Distribution of predicted environmental concentrations of triclopyr for 1,000,000 model runs, truncated at 5 µg.l^{-1} for clarity; Distribution of predicted environmental concentration for runoff days only (Inset), truncated from 1e-10 to 5 µg.l^{-1} for clarity

APPENDIX B4: LIMIT OF DETECTIONS

Table B4: Limit of detection of pesticides using passive samplers

Pesticide	**Limit of Detection (µg.l^{-1})**	**Source**
Glyphosate	0.019	(Coble et al., 2022)
MCPA	0.0002	(Farrow et al., 2022)
Fluroxypyr	0.0004	(Farrow et al., 2022)
2,4-DB	0.003	(Townsend et al., 2018)
Triclopyr	0.0002	(Farrow et al., 2022)
2,4-D	0.007	(Townsend et al., 2018)
Mecoprop	0.0002	(Farrow et al., 2022)
Clopyralid	0.001	(Townsend et al., 2018)
Prothioconazole	0.002	(Ahrens et al., 2015)
Pendimethalin	0.005	(Ahrens et al., 2015)
Penthiopyrad	0.005	(Murcia-Morales et al., 2021)
Terbuthylazine	0.002	(Ahrens et al., 2015)
Prochloraz	0.005	(Ahrens et al., 2015)
Propyzamide	0.001	(Ahrens et al., 2015)
Phenmedipham	0.001	(Ahrens et al., 2015)

APPENDIX C: SUPPLEMENTARY INFORMATION FOR CHAPTER 5

APPENDIX C1: PESTICIDE PROPERTIES

Table C1: Pesticide properties and distribution parameters for transport models

Pesticide	**Family**	**K_{oc} (l.kg^{-1})**	**$DT_{50,s}$ (days)**	**$DT_{50,w}$ (days)**	**Max Legal Appl. Rate (g.ha^{-1})**	**ADI (mg.kg^{-1}.day^{-1})**
Glyphosate *N-(phosphonomethyl)glycine*	Organophosphate	Normally distributed $\mu = 14396.7; \sigma = 15102.9$	Normally distributed $\mu = 45.1; \sigma = 93.91$	Normally distributed $\mu = 64; \sigma = 62.51$	Fixed: 2160	Fixed: 0.5
MCPA *(2-methyl-4-chlorophenoxyacetic acid)*	Aryloxyalkanoic Acid herbicide	Normally distributed $\mu = 75.2; \sigma = 42.22$	Normally distributed $\mu = 21.4; \sigma = 12.66$	Fixed: 16.9	Fixed: 1800	Fixed: 0.05
Fluroxypyr *4-amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid*	Pyridine herbicide	Normally distributed $\mu = 68; \sigma = 10.9$	Normally distributed $\mu = 19.6; \sigma = 15.23$	Normally distributed $\mu = 27.8; \sigma = 31.3$	Fixed: 400	Fixed: 0.03
2,4-DB *4-(2,4-Dichlorophenoxy) butanoic acid*	Phenoxy herbicide	Normally distributed $\mu = 373.9; \sigma = 370.57$	Normally distributed $\mu = 23.9; \sigma = 33.46$	Normally distributed $\mu = 27.6; \sigma = 18.51$	Fixed: 1800	Fixed: 0.02
Triclopyr *3,5,6-trichloro-2-pyridyloxyacetic acid*	Pyridine herbicide	Normally distributed $\mu = 49.2; \sigma = 7.73$	Normally distributed $\mu = 35.1; \sigma = 20.09$	Normally distributed $\mu = 29.3; \sigma = 29.28$	Fixed: 1440	Fixed: 0.03
2,4-D *(2,4-dichlorophenoxyacetic acid)*	Phenoxy herbicide	Normally distributed $\mu = 41.7; \sigma = 18.63$	Normally distributed $\mu = 18.8; \sigma = 25.48$	Normally distributed $\mu = 26.4\ \sigma = 16.83$	Fixed: 750	Fixed: 0.02

Table C1 continued

Pesticide	**Family**	**K_{oc} (l.kg^{-1})**	**$DT_{50,s}$ (days)**	**$DT_{50,w}$ (days)**	**Max Legal Appl. Rate (g.ha^{-1})**	**ADI (mg.kg^{-1}.day^{-1})**
Mecoprop *(RS)-2-(4-chloro-o-tolyloxy)propionic acid*	Phenoxypropionic herbicide	Normally distributed $\mu = 56.3$; $\sigma = 56.3$	Normally distributed $\mu = 6.4$; $\sigma = 10.12$	Normally distributed $\mu = 155.6$; $\sigma = 59.42$	Fixed: 1200	Fixed: 0.01
Clopyralid *3,6-dichloropyridine-2-carboxylic acid*	Pyridine herbicide	Normally distributed $\mu = 4.9$; $\sigma = 3.38$	Normally distributed $\mu = 42.9$; $\sigma = 47.06$	Normally distributed $\mu = 155$; $\sigma = 20.89$	Fixed: 200	Fixed: 0.15
Prothioconazole *(RS)-2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-1,2,4-triazole-3-thione*	Conazole fungicide	Fixed: 1765	Normally distributed $\mu = 2.4$; $\sigma = 2.6$	Normally distributed $\mu = 1.8$; $\sigma = 0.75$	Fixed: 200	Fixed: 0.05
Pendimethalin *N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine*	Dinitroaniline herbicide	Normally distributed $\mu = 17121.1$; $\sigma = 6986.6$	Normally distributed $\mu = 150.4$; $\sigma = 150.4$	Normally distributed $\mu = 92.2$; $\sigma = 68.29$	Fixed: 1600	Fixed: 0.125
Penthiopyrad *(RS)-N-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)pyrazole-4-carboxamide*	Carboxamide fungicide	Normally distributed $\mu = 796.8$; $\sigma = 130.2$	Normally distributed $\mu = 122$; $\sigma = 129.34$	Normally distributed $\mu = 279.8$; $\sigma = 26.82$	Fixed: 500	Fixed: 0.1
Terbuthylazine *N2-tert-butyl-6-chloro-N4-ethyl-1,3,5-triazine-2,4-diamine*	Triazine herbicide	Normally distributed $\mu = 231.3$; $\sigma = 56.9$	Normally distributed $\mu = 73$; $\sigma = 40.67$	Normally distributed $\mu = 75.6$; $\sigma = 27.41$	Fixed: 570	Fixed: 0.004

Table C1 continued

Pesticide	**Family**	**K_{oc} (l.kg^{-1})**	**$DT_{50,s}$ (days)**	**$DT_{50,w}$ (days)**	**Max Legal Appl. Rate (g.ha^{-1})**	**ADI (mg.kg^{-1}.day^{-1})**
Prochloraz *N-propyl-N-[2-(2,4,6-trichlorophenoxy)ethyl]imidazole-1-carboxamide*	Amide fungicide	Normally distributed $\mu = 4423.6$; $\sigma = 3784.5$	Normally distributed $\mu = 130.9$; $\sigma = 198.8$	Normally distributed $\mu = 321.3$; $\sigma = 36.46$	Fixed: 450	Fixed: 0.01
Propyzamide *3,5-dichloro-N-(1,1-dimethylprop-2-ynyl)benzamide*	Amide herbicide	Normally distributed $\mu = 1855.1$; $\sigma = 1274.7$	Normally distributed $\mu = 73.8$; $\sigma = 66.4$	Normally distributed $\mu = 98.9$; $\sigma = 16.4$	Fixed: 1500	Fixed: 0.05
Phenmedipham *Methyl 3-(3-methylcarbaniloyloxy)carbanilate*	Carbanilate herbicide	Normally distributed $\mu = 1356.7$; $\sigma = 221.2$	Normally distributed $\mu = 37.7$; $\sigma = 29.47$	Normally distributed $\mu = 0.18$; $\sigma = 0.15$	Fixed: 320	Fixed: 0.03

APPENDIX C2: FULL MODEL RESULTS FOR CAUSEWAY (2050) AND DUNLEER (2050 AND 2100)

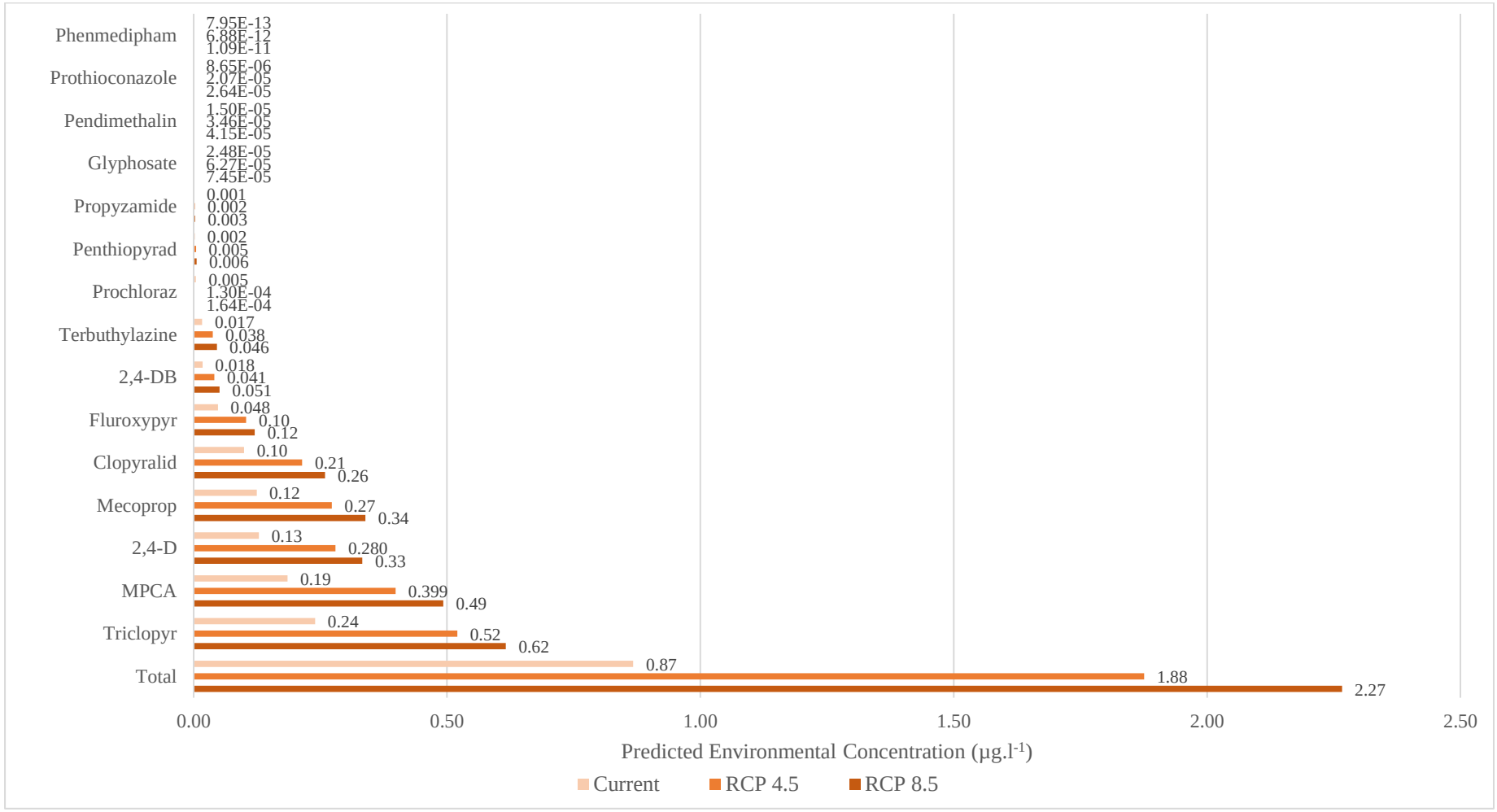


Figure C2: 95th percentile predicted environmental concentration for current and 2050 conditions in Causeway (SW)

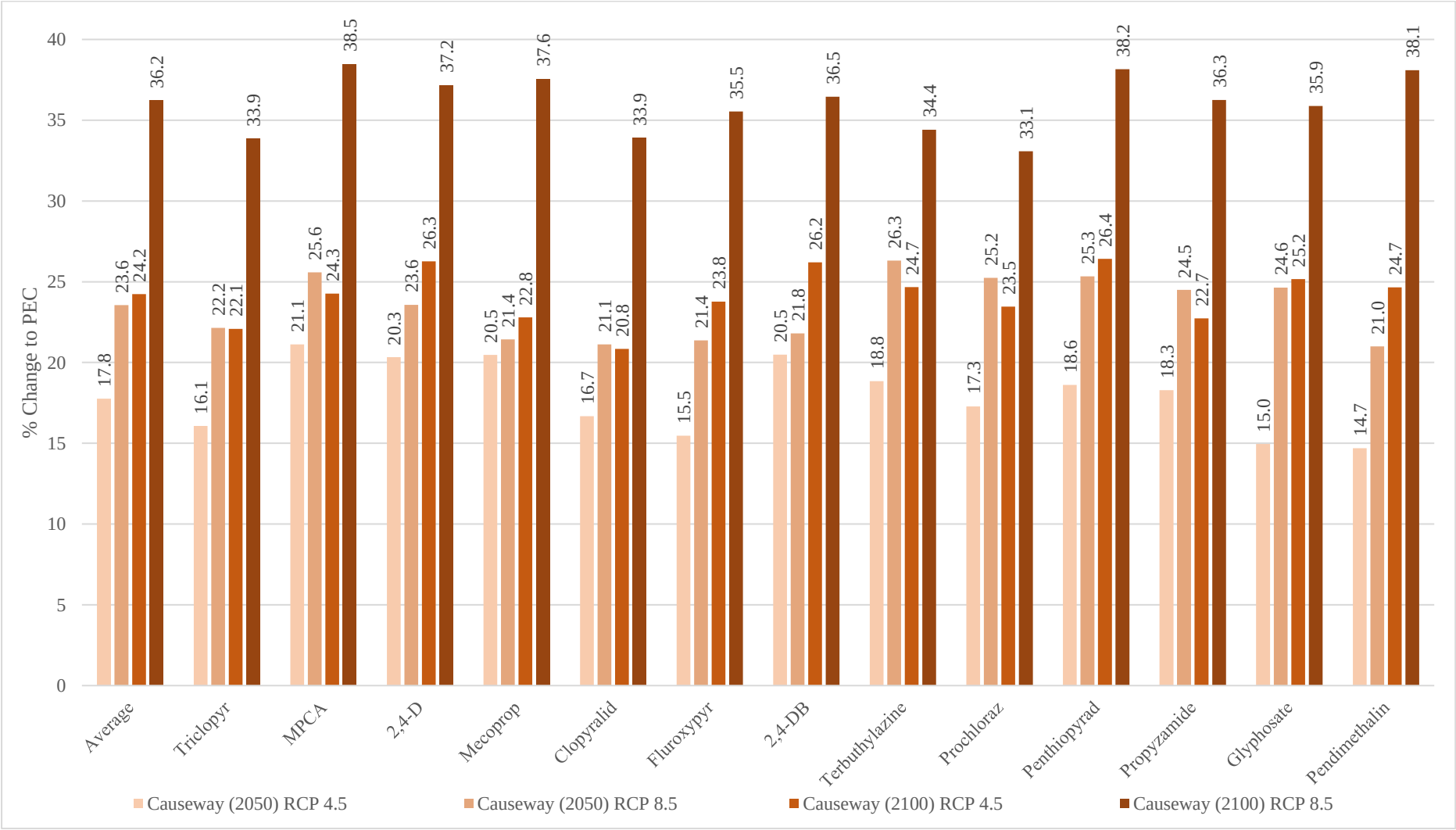


Figure C2: Percentage increase to 95th percentile predicted environmental concentrations in Causeway (SW) for future climate scenarios relative to current condition

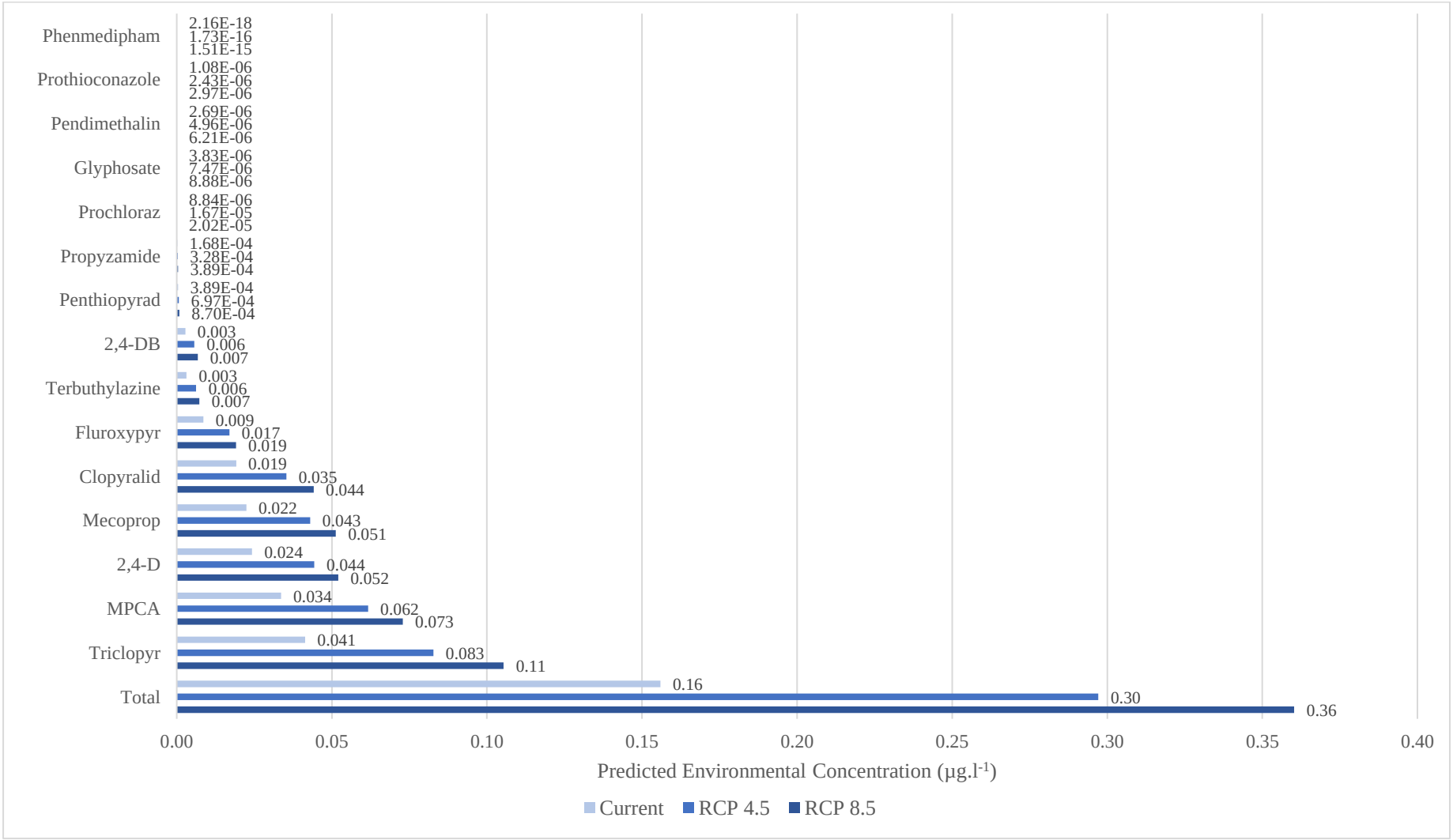


Figure C3: 95th percentile predicted environmental concentration for current and 2050 conditions in Dunleer (NE)

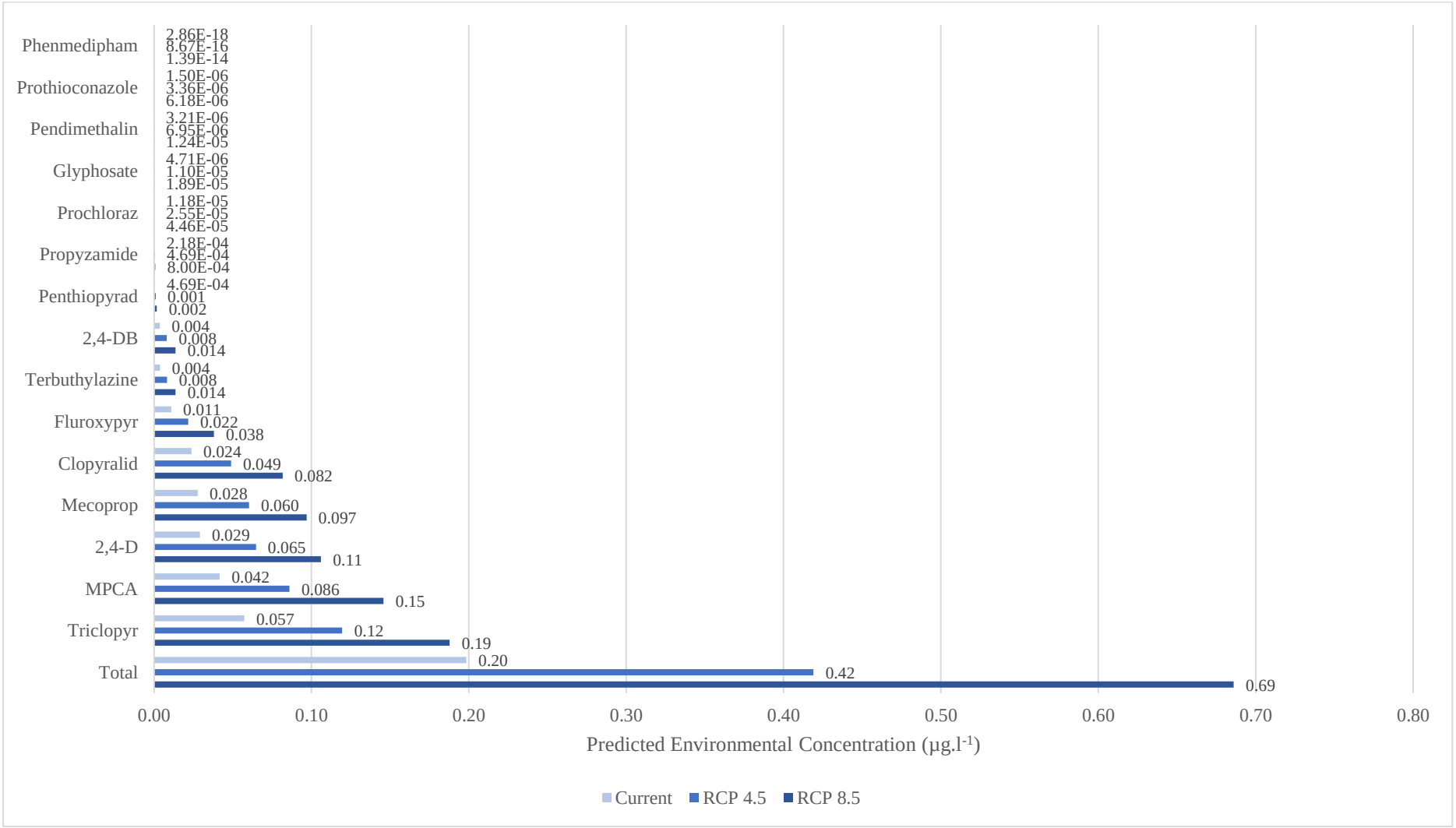


Figure C4: 95th percentile predicted environmental concentration for current and 2100 conditions in Dunleer (NE)

Table C2: 95th percentile adult and child estimated daily intake (mg.kg^{-1}.day^{-1}) for modelled scenarios in Dunleer (NE)

Pesticide	Baseline		RCP4.5 (2050)		RCP8.5 (2050)		RCP4.5 (2100)		RCP8.5 (2100)	
	EDI_{adult}	**EDI_{child}**	**EDI_{adult}**	**EDI_{child}**	**EDI_{adult}**	**EDI_{child}**	**EDI_{adult}**	**EDI_{child}**	**EDI_{adult}**	**EDI_{child}**
Triclopyr	1.04e-4	1.51e-4	1.28e-4	1.85e-4	1.36e-4	1.99e-4	1.44e-4	2.07e-4	1.66e-4	2.56e-4
MPCA	8.70e-5	1.27e-4	1.06e-4	1.54e-4	1.12e-4	1.61e-4	1.19e-4	1.72e-4	1.41e-4	2.18e-4
Mecoprop	6.13e-5	8.90e-5	7.47e-5	1.08e-4	7.81e-5	1.13e-4	8.13e-5	1.20e-4	9.88e-5	1.44e-4
2,4-D	5.73e-5	8.37e-5	7.00e-5	1.02e-4	7.36e-5	1.09e-4	7.83e-5	1.14e-4	9.04e-5	1.39e-4
Clopyralid	4.22e-5	6.23e-5	5.19e-5	7.62e-5	5.47e-5	7.98e-5	5.71e-5	8.6e-5	6.72e-5	1.04e-4
Fluroxypyr	2.08e-5	3.07e-5	2.60e-5	3.81e-5	2.71e-5	4.01e-5	2.84e-5	4.12e-5	3.40e-5	5.14e-5
2,4-DB	1.24e-5	1.81e-5	1.48e-5	2.14e-5	1.58e-5	2.31e-5	1.65e-5	2.42e-5	2.08e-5	3.12e-5
Terbuthylazine	8.29e-6	1.22e-5	1.04e-5	1.51e-5	1.11e-5	1.61e-5	1.17e-5	1.69e-5	1.33e-5	2.03e-5
Penthiopyrad	1.11e-6	1.63e-6	1.33e-6	1.95e-6	1.39e-6	2.05e-6	1.49e-6	2.21e-6	1.81e-6	2.70e-6
Propyzamide	6.44e-7	9.45e-7	8.11e-7	1.20e-6	8.55e-7	1.24e-6	9.07e-7	1.33e-6	1.09e-6	1.62e-6
Prochloraz	3.89e-8	5.74e-8	5.04e-8	7.43e-8	5.24e-8	7.57e-8	5.79e-8	8.36e-8	6.83e-8	1.02e-7
Glyphosate	2.40e-8	3.50e-8	3.01e-8	4.37e-8	3.20e-8	4.65e-8	3.59-e8	5.16e-8	4.45e-8	6.58e-8
Pendimethalin	8.70e-9	1.28e-8	1.05e-8	1.53e-8	1.16e-8	1.69e-8	1.18e-8	1.76e-8	1.43e-8	2.20e-8
Prothioconazole	5.91e-9	8.73e-9	7.74e-9	1.14e-8	8.09e-9	1.17e-8	8.54e-9	1.25e-8	1.04e-8	1.56e-8
Phenmedipham	1.27e-13	1.88e-13	1.83e-13	2.71e-13	2.05e-13	2.98e-13	2.09e-13	3.09e-13	3.08e-13	4.34e-13

Table C3: 95th percentile adult and child estimated daily intake (mg.kg^{-1}.day^{-1}) for modelled scenarios in Causeway (SW)

Pesticide	RCP4.5 (2050)		RCP8.5 (2050)		RCP4.5 (2100)	
	EDI_{adult}	**EDI_{child}**	**EDI_{adult}**	**EDI_{child}**	**EDI_{adult}**	**EDI_{child}**
Triclopyr	2.38e-4	3.44e-4	2.66e-4	3.86e-4	2.61e-4	3.76e-4
MPCA	2.02e-4	2.97e-4	2.26e-4	3.29e-4	2.25e-4	3.25e-4
Mecoprop	1.41e-4	2.05e-4	1.58e-4	2.28e-4	1.58e-4	2.29e-4
2,4-D	1.35e-4	1.94e-4	1.46e-4	2.13e-4	1.45e-4	2.11e-4
Clopyralid	9.68e-5	1.40e-4	1.03e-4	1.50e-4	1.05e-4	1.51e-4
Fluroxypyr	4.81e-5	6.97e-5	5.34e-5	7.77e-5	5.26e-5	7.65e-5
2,4-DB	3.07e-5	4.47e-5	3.51e-5	5.13e-5	3.42e-5	2.01e-5
Terbuthylazine	1.94e-5	2.79e-5	2.16e-5	3.16e-5	2.18e-5	3.18e-5
Penthiopyrad	2.65e-6	3.85e-6	2.91e-6	4.18e-6	2.94e-6	4.25e-6
Propyzamide	1.63e-6	2.37e-6	1.82e-6	2.65e-6	1.85e-6	2.68e-6
Prochloraz	1.04e-7	1.51e-7	1.20e-7	1.76e-7	1.20e-7	1.74e-7
Glyphosate	7.31e-8	1.06e-7	8.29e-8	1.22e-7	8.09e-8	1.19e-7
Pendimethalin	2.15e-8	3.12e-8	2.36e-8	3.45e-8	2.34e-8	3.42e-8
Prothioconazole	1.54e-8	2.26e-8	1.74e-8	2.52e-8	1.80e-8	2.61e-8
Phenmedipham	3.25e-13	4.72e-13	7.50e-13	1.09e-12	7.28e-13	1.05e-12

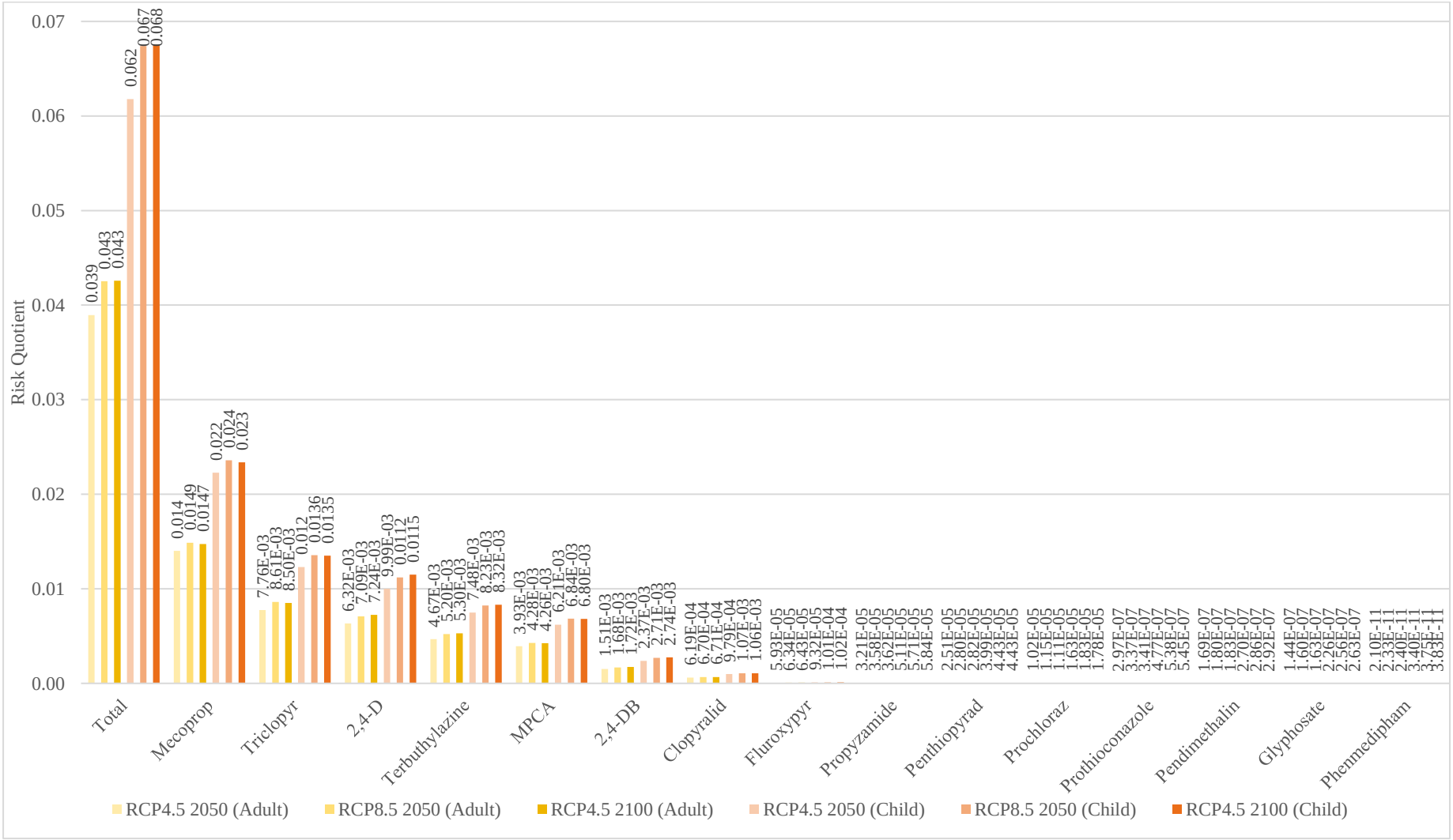


Figure C.5: 99th percentile risk quotient in Causeway (SW) for future climates

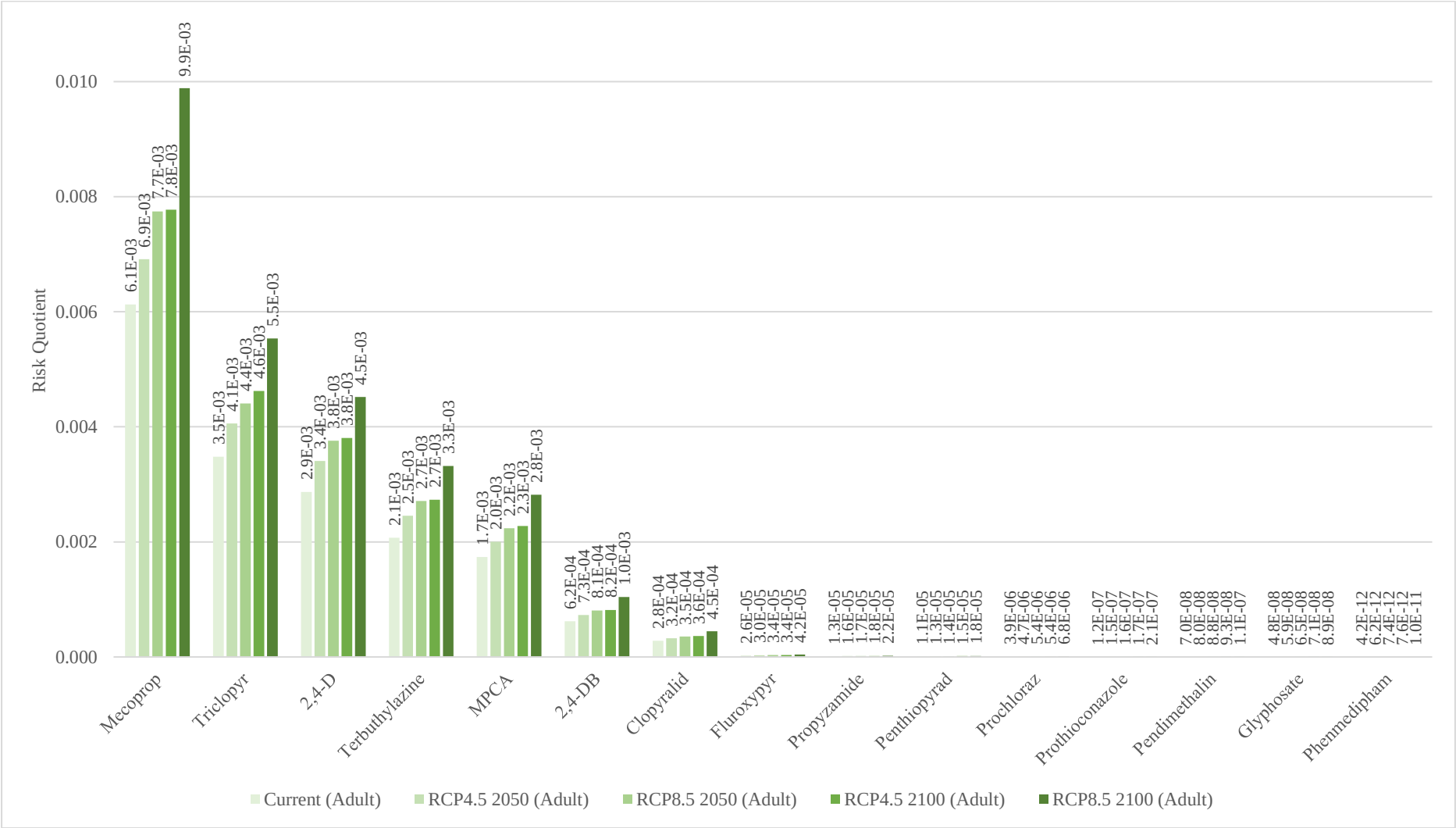


Figure C6: 99th percentile risk quotient for adults in Dunleer (NE) for modelled scenarios

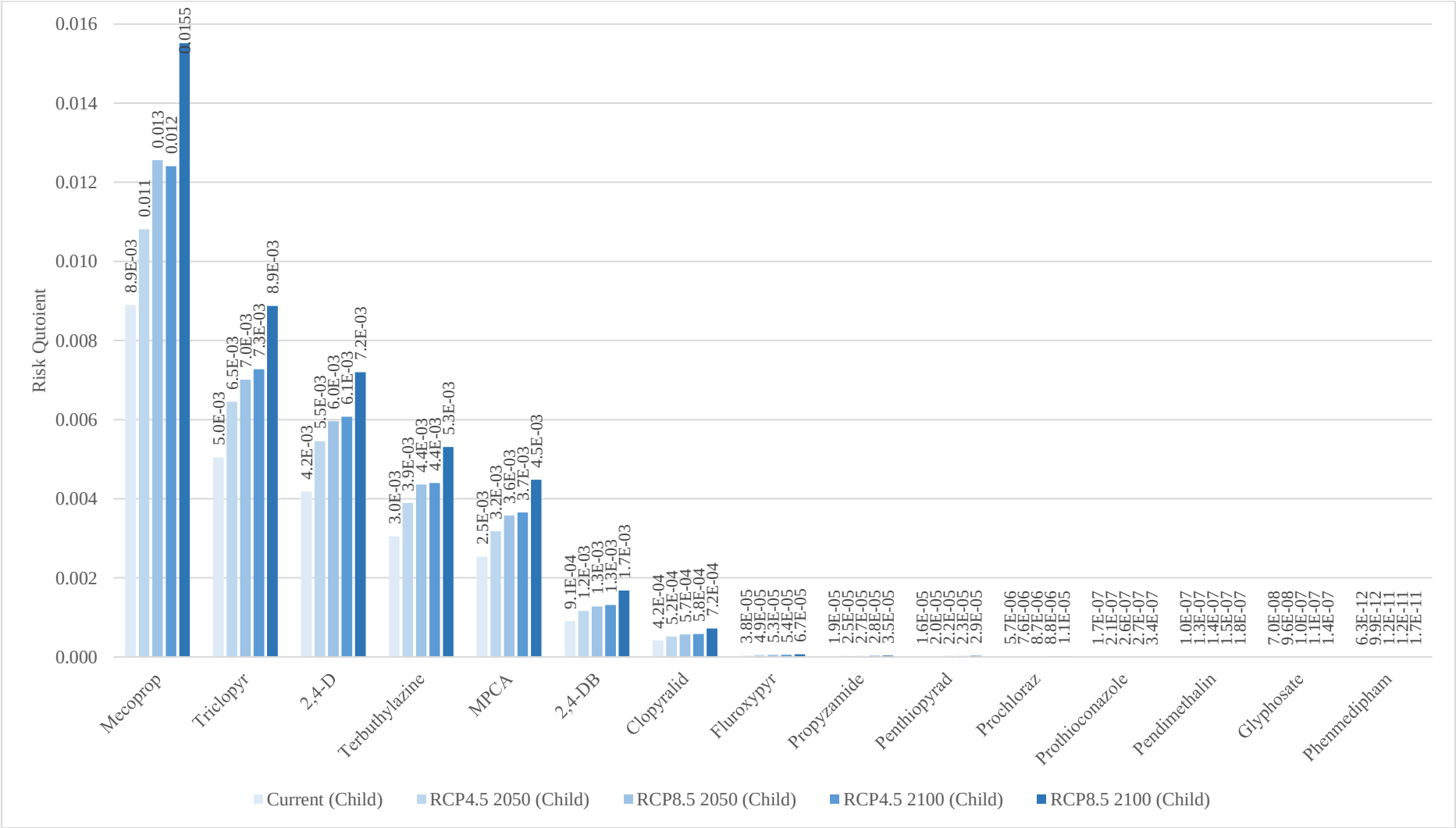


Figure C7: 99th percentile risk quotient for children in Dunleer (NE) for modelled scenarios

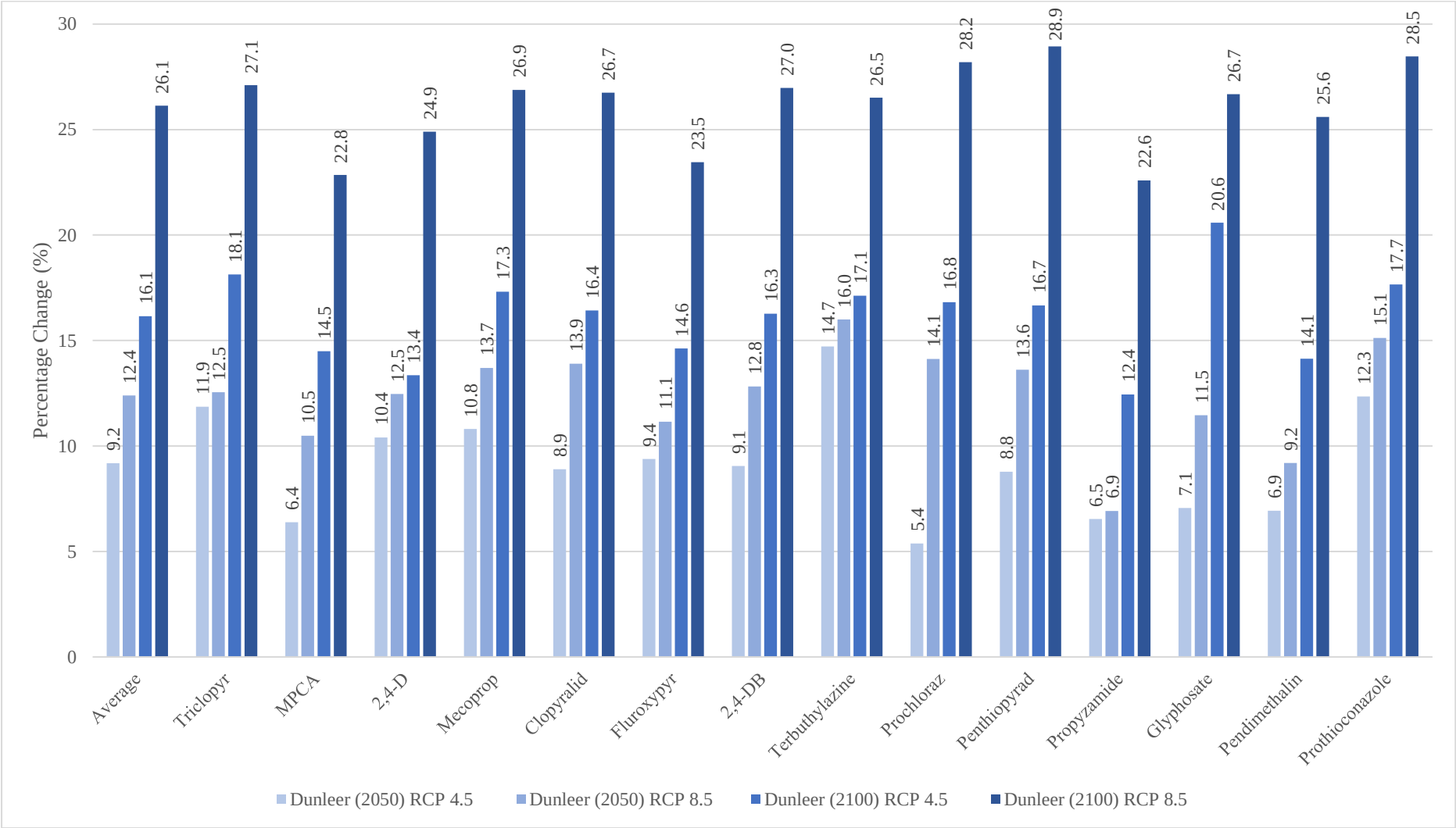


Figure C8: Percentage increase to 95th percentile predicted environmental concentrations in Dunleer (NE) for future climate scenarios relative to current condition

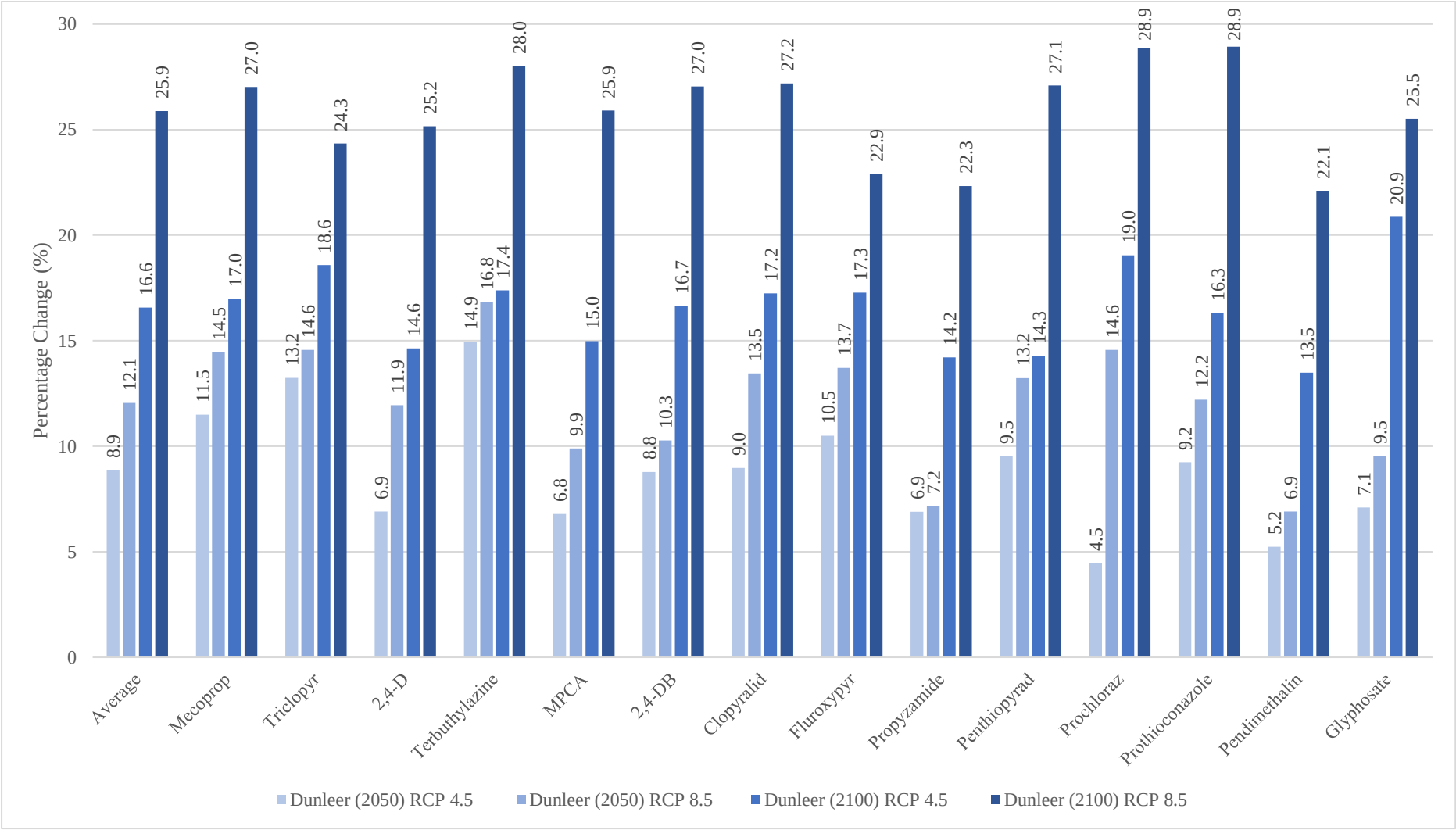


Figure C9: Percentage increase to 99th percentile risk quotient (child) for future climate scenarios relative to current condition in Dunleer (NE)

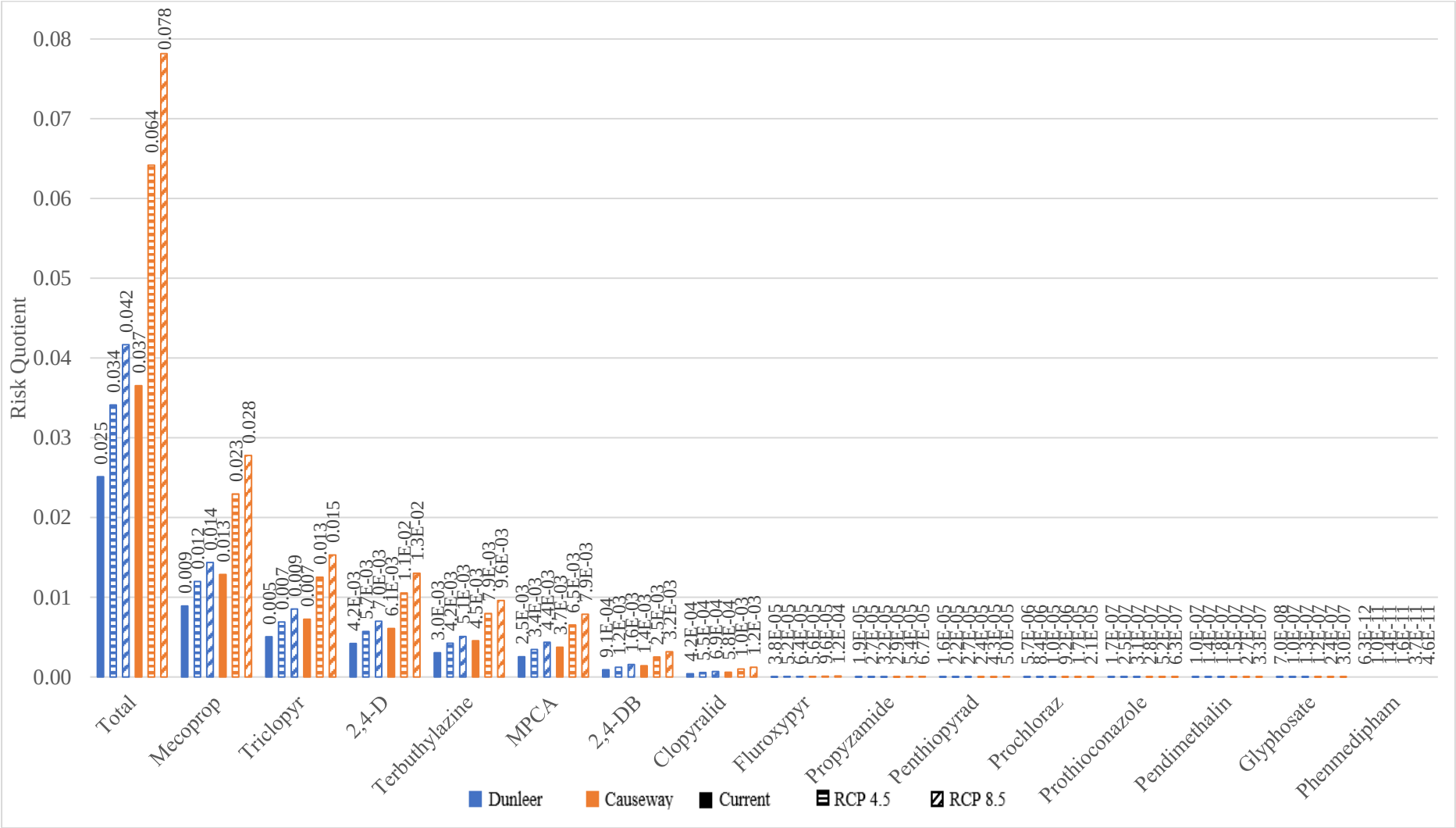


Figure C10: 99th percentile risk quotient (child) Dunleer (NE) vs Causeway (SW) for 2100 condition