



OLLSCOIL NA GAILLIMHE
UNIVERSITY OF GALWAY

PESTICIDE MANAGEMENT FOR BETTER WATER QUALITY

John McGinley

Civil Engineering
College of Science and Engineering
University of Galway

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Philosophy

Research Supervisors:

Prof Mark G. Healy, College of Science and Engineering, University of Galway

Dr Alma Siggins, College of Science and Engineering, University of Galway

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DECLARATION

I declare that this dissertation entitled “Pesticide management for better water quality” is the result of my own work, except where explicitly stated otherwise, for which references are made. This thesis has not been submitted, in whole or in part, in support for another degree to any University or Institution.

John McGinley

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ABSTRACT

The growth of the global population has forced the intensification of agricultural practices in order to achieve increased crop yields and production rates. This has been accomplished by elevated pesticide usage. While this intensified pesticide application has been beneficial in preventing diseases in agricultural crops, it has also amplified the contact of these compounds with air, soil and aquatic environments. This has resulted in an increased risk of human health issues, including neurological, respiratory and carcinogenic effects. Several physical, chemical, and biological treatment approaches have been employed to remove pesticides from aqueous solutions. One of the most extensively used remediation methods of pesticides is adsorption onto low-cost agricultural and industrial materials, which is simple and cost-effective. However, further investigations on readily available low-cost adsorbents are required. Therefore, the aims of this thesis were to (1) review the prevalence of pesticides, including legacy pesticides, in European waterways (2) develop a tool to help farmers assess the potential risk of pesticide transmission to waterways (3) assess low-cost agricultural and industrial materials as herbicide adsorbents for the removal of commonly used herbicides in Ireland, and (4) evaluate their potential in field-scale studies.

This study found that legacy pesticides are still being detected in European surface water and groundwater at concentrations exceeding the maximum allowable concentration of 100 ng.l⁻¹. Current remediation methods employed at drinking water facilities do not completely remove pesticides. There is still a need for remediation of existing contamination arising from legacy pesticides and ongoing pesticide use. New and emerging remediation methods for legacy pesticides include metal organic frameworks, nanoparticles, and membrane technologies.

One of the many problems facing the farming community is being able to assess the potential risk of loss of pesticides to waterways. The screening tool, developed in this study, allows farmers and end-users to estimate the potential risk of applying various pesticides to different soil textures.

A remediation technology was developed beginning with batch adsorption studies and progressing to trials for *in situ* treatment of herbicides in streams. The batch adsorption studies showed that granulated activated carbon (GAC) was the best medium for the removal of five commonly used herbicides in Irish agriculture, with >95% removal. The adsorption kinetic studies showed that the majority of the adsorption was completed within 18 h, while the adsorption isotherm process followed the Freundlich model, verifying multilayer adsorption. The *in situ* remediation trials involved both filter bag and filter pipe interventions at two agricultural catchment areas and an urban recreational setting. These trials showed that the filter pipes reduced the herbicide concentrations more efficiently than the filter bags, with a 48% reduction in detections observed for the filter pipes compared to 13% for the filter bags.

The main findings of this thesis are that (1) legacy pesticides, including some which have been removed from the market for over 20 years, are still being detected throughout Europe at levels exceeding the maximum allowable concentration of 100 ng.l⁻¹, (2) the remediation system, tested at both batch and field scale, is the first such system that has been demonstrated to be capable of removal of a range of herbicides from an environmental setting. This research, while supporting the European “Farm to Fork” strategy, highlights not only the issues of legacy pesticides and their remediation, but also demonstrates that small *in situ* remediation systems are feasible approaches to the problem of pesticide contamination of waterways.

Table of Contents

ACKNOWLEDGEMENTS	iii
ABSTRACT	v
Table of Contents	vii
List of Figures	xii
List of Tables	xiv
Abbreviations	xvi
Chapter 1 – Introduction	1
1.1 Overview	1
1.2 Knowledge gaps and project aims	4
1.3 Thesis structure and objectives	6
1.4 Contribution to existing knowledge	8
1.4.1 Peer-reviewed publications (published)	8
1.4.2 Oral presentations	8
References	10
Chapter 2 – Impact of historical legacy pesticides on achieving legislative goals in Europe	13
Abstract	14
2.1 Introduction	15
2.2 Methodology	18
2.3 Pesticide usage and pathways of loss	20
2.3.1 Usage of pesticides in the EU-27	20
2.3.2 Pathways of pesticide loss	24
2.4 Legacy issues	26
2.5 Mitigation options	28
2.5.1 Metal-Organic Frameworks	29
2.5.2 Nanoparticles	34
2.5.3 Membrane removal of pesticides	37
2.5.4 Semiconductors	38
2.5.5 Vegetated buffers	38
2.6 Management implications across Europe	40

2.7 Conclusions	42
Acknowledgements	42
References	44

Chapter 3 – An Assessment of potential pesticide transmission, considering the combined impact of soil texture and pesticide properties: A meta-analysis55

Abstract	56
3.1 Introduction	57
3.2 Materials and Methods	59
3.2.1 <i>Literature review methodology, pesticide selection and grouping</i>	59
3.2.1.1 <i>Herbicide group</i>	60
3.2.1.2 <i>Fungicide group</i>	60
3.2.1.3 <i>Insecticide group</i>	63
3.2.2 <i>Adsorption modelling</i>	63
3.2.3 <i>Pesticide transport potential ranking</i>	64
3.3 Results and Discussion	65
3.3.1 <i>Variances in adsorption as a function of soil texture</i>	65
3.4 Conclusions	68
Acknowledgements	69
References	70

Chapter 4 – Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon74

Abstract	75
4.1 Introduction	76
4.2 Materials and Methods	77
4.2.1 <i>Chemicals and materials used</i>	77
4.2.2 <i>Batch adsorption assays</i>	79
4.2.2.1 <i>Adsorption kinetics</i>	79
4.2.2.2 <i>Adsorption Isotherms</i>	80
4.2.3 <i>Effect of pH on adsorption</i>	80
4.2.4 <i>Herbicide analysis</i>	81
4.2.5 <i>GAC characterisation</i>	81
4.3 Results and Discussion	82

4.3.1 <i>Media analysis</i>	82
4.3.2 <i>Adsorbent screening</i>	84
4.3.3 <i>GAC characterisation</i>	85
4.3.4 <i>Adsorption kinetics</i>	87
4.3.5 <i>Adsorption Isotherms</i>	89
4.3.6 <i>Effect of pH</i>	90
4.4 Conclusions	92
Acknowledgements	92
References	93
Chapter 5 – Monitoring of herbicides in natural waters of two Agricultural Catchment areas and an Urban environment	98
Abstract	99
5.1 Introduction	100
5.2 Methodology	101
5.2.1 <i>Study areas</i>	101
5.2.2 <i>Identification of monitoring locations and interventions used</i>	103
5.2.3 <i>SEM microscopy and CAC characterisation</i>	104
5.2.4 <i>Herbicide sampling and analysis</i>	105
5.2.5 <i>Statistical analysis</i>	106
5.3 Results and Discussion	106
5.3.1 <i>Outlet monitoring</i>	106
5.3.2 <i>Media characterisation</i>	111
5.3.3 <i>Herbicide removal by filter bag configuration</i>	112
5.3.4 <i>Herbicide removal by filter pipe configuration</i>	115
5.3.5 <i>Comparison of the filter bag and filter pipe configurations</i>	117
5.4. Conclusions	118
Acknowledgements	119
References	120
Chapter 6 – Conclusions and Recommendations	125
6.1 Overview	125
6.2 Conclusions	127
6.3 Recommendations	128

Appendix A – Supplementary Information to Chapter 2	130
Table A.1 <i>Herbicide usage (t) per country from 2011 to 2020</i>	131
Table A.2 <i>Fungicide usage (t) per country from 2011 to 2020</i>	132
Table A.3 <i>Insecticide usage (t) per country from 2011 to 2020</i>	133
Table A.4 <i>Pesticide usage (kg) per hectare (Ha) per country from 2011 to 2020</i>	134
Table A.5 <i>Reported legacy pesticides in Europe between 2011 and 2020</i>	148
Table A.6 <i>Mitigation systems for removal of pesticides</i>	157
References	159
Appendix B – Supplementary Information to Chapter 3	164
Table B.1 <i>Solubility ranking</i>	165
Table B.2 <i>Soil half-life ranking</i>	166
Table B.3 <i>Adsorption capacity ranking</i>	166
Table B.4 <i>Median pesticide adsorption values (mg.g⁻¹) by soil texture</i>	167
Table B.5 <i>Risk ranking of pesticide solubility, half-life (DT₅₀), permeability and adsorption values</i>	168
References	169
Appendix C – Supplementary Information to Chapter 4	171
Figure C.1 <i>SEM images of GAC at a resolution of 100 μm (left) and 5 μm (right)</i>	172
Table C.1 <i>Kinetic Isotherm equations</i>	173
Table C.2 <i>Kinetic model parameters of herbicides on GAC</i>	174
Table C.3 <i>Adsorption Isotherm equations</i>	175
Table C.4 <i>Parameters of adsorption isotherms for herbicides onto GAC</i>	176
Appendix D – Supplementary Information to Chapter 5	177
Figure D.1 <i>Comparison of herbicide removal capacity of GAC and CAC against the herbicides MCPA, Mecoprop-P, 2,4-D, Triclopyr and Fluroxypyr</i>	178
Figure D.2 <i>SEM images of GAC (a and b) and CAC (c and d) at a resolution of 100 μm (left) and 10 μm (right). EDX spectra of e) GAC and f) CAC</i>	179
Table D.1 <i>Pests controlled and optimal spraying conditions for herbicides</i>	180
Table D.2a <i>Minimum, maximum and mean concentrations and frequency of detection of the studied pesticides before the bag interventions, between the bag</i>	

<i>interventions and before the pipe intervention, and after the pipe intervention in Corduff</i>	181
Table D.2b <i>Minimum, maximum and mean concentrations and frequency of detection of the studied pesticides before the bag interventions, between the bag interventions and before the pipe intervention, and after the pipe intervention in Dunleer</i>	182
Table D.2c <i>Minimum, maximum and mean concentrations and frequency of detection of the studied pesticides before the bag interventions, between the bag interventions and before the pipe intervention, and after the pipe intervention in Urban</i>	183
Appendix E	185

List of Tables

Table 2.1. Summary of pesticide adsorption over metal-organic frameworks	30
Table 2.2. Summary of pesticide adsorption over nanoparticle materials	36
Table 3.1. Applications, target pests, and physico-chemical properties of selected pesticides	61
Table 3.2. Pesticide transmission risk rankings	66
Table 4.1 LOD and LOQ values for the chosen herbicides	81
Table 4.2 Chemical and physical characterisation of the chosen media	83
Table 5.1 Minimum, maximum and mean concentrations and frequency of detection of the studied herbicides at the outlet points in the sampling areas	107
Table 5.2 Physico-chemical properties of detected herbicides	109
Table A.1 Herbicide usage (t) per country from 2011 to 2020	131
Table A.2 Fungicide usage (t) per country from 2011 to 2020	132
Table A.3 Insecticide usage (t) per country from 2011 to 2020	133
Table A.4 Pesticide usage (kg) per hectare (Ha) per country from 2011 to 2020 ...	134
Table A.5 Reported legacy pesticides in Europe between 2011 and 2020	148
Table A.6 Mitigation systems for removal of pesticides	157
Table B.1 Solubility ranking	165
Table B.2 Soil half-life ranking	166
Table B.3 Adsorption capacity ranking	166
Table B.4 Median pesticide adsorption values (mg g^{-1}) by soil texture.....	167
Table B.5 Risk ranking of pesticide solubility, half-life (DT_{50}), permeability and adsorption values	168
Table C.1 Kinetic Isotherm equations	173
Table C.2 Kinetic model parameters of herbicides on GAC	174
Table C.3 Adsorption Isotherm Equations	175
Table C.4 Parameters of adsorption isotherms for herbicides onto GAC	176
Table D.1 Pests controlled and optimal spraying conditions for herbicides	180
Table D.2a Minimum, maximum and mean concentrations and frequency of detection of the studied pesticides before the bag interventions, between the bag interventions and before the pipe intervention, and after the pipe intervention in Corduff	181

Table D.2b Minimum, maximum and mean concentrations and frequency of detection of the studied pesticides before the bag interventions, between the bag interventions and before the pipe intervention, and after the pipe intervention in Dunleer182

Table D.2c Minimum, maximum and mean concentrations and frequency of detection of the studied pesticides before the bag interventions, between the bag interventions and before the pipe intervention, and after the pipe intervention in Urban183

List of Figures

Figure 1.1. Flowchart of thesis structure including study objectives	7
Figure 2.1. Methodology flowchart	20
Figure 2.2. Pesticide usage, given as classes of pesticides, in the study area, for the years 2011 - 2020 (Eurostat – Pesticide sales, 2022)	21
Figure 2.3. Tonnes of pesticide used per hectare agricultural land across EU for the years 2011-2020 (Data sources: Eurostat - Pesticide Sales, 2022; Eurostat - Land use, 2022). Herbicides are shown in red, fungicides in blue and insecticides in black	23
Figure 2.4. Pesticide transfer routes to surface and ground water (Lunardi et al., 2022; Reproduced with permission)	24
Figure 2.5. Timeline of reported exceedances of some selected prohibited pesticides. Herbicides are denoted by circles, fungicides by triangles and insecticides by diamonds (Citations are in Table A.5)	27
Figure 4.1. Chemical structures of chosen herbicides	78
Figure 4.2. Herbicide removal by twelve raw or processed waste materials at an adsorbent concentration of 5 g.l ⁻¹ and herbicide concentrations of 100 mg.l ⁻¹ , following equilibration for 72 h at 10 °C (± 0.5 °C) and shaking at 160 rpm. Error bars represent standard error (stdev/√n, where n is the number of replicates, three in this case)	84
Figure 4.3. FTIR spectra of GAC after being stirred in either water or one of the herbicide solutions for 72 h	86
Figure 4.4. Herbicide adsorption kinetics on GAC	87
Figure 4.5. Herbicide removal over a range of media concentrations, expressed as % herbicide removal. The adsorption study was carried out at a herbicide concentration of 100 mg.l ⁻¹ and an equilibrium time of 72 h. Medium = GAC in all cases	89
Figure 4.6. Freundlich adsorption isotherm of MCPA, Mecoprop-P, 2,4-D, Triclopyr and Fluroxypyr on GAC. Modelled data are shown as a colour coded line	90
Figure 4.7. Effect of pH on MCPA adsorption by GAC. MCPA = 100 ppm solution in ultrapure water, no pH adjustment; MCPA 24 h = MCPA solution after shaking with GAC (5 g.l ⁻¹) for 24 h, no pH adjustment; MCPA pH 9 = MCPA solution after shaking with GAC (5 g.l ⁻¹) for 24 h, pH 9; MCPA pH 7 = MCPA solution after shaking with GAC (5 g.l ⁻¹) for 24 h, pH 7; MCPA pH 5 = MCPA solution after shaking with GAC (5 g.l ⁻¹) for 24 h, pH 5	91

Figure 5.1 Map of Ireland showing location of the three sampling sites with blue stars. The outlet points at the two agricultural catchments are denoted with red stars, while the locations of the interventions in Year 2 are marked with black crosses	102
Figure 5.2 a) Schematic of different configurations of the intervention positioned in the stream. The blue arrow indicates direction of water flow. Filter bags are upstream from the filter pipe. Sampling points, colour-coded (see Section 2.4), are also indicated on the diagram. b) Image showing filter bags and filter pipe in position at Corduff stream	104
Figure 5.3 Exceedances of herbicides at outlet points in Corduff, Dunleer and Urban sampling areas for Year 1 (2021) and Year 2 (2022) of the study	110
Figure 5.4 Herbicide detections for the filter bag interventions across all sampling areas	113
Figure 5.5 Herbicide detections for the filter pipe interventions across all sampling areas	116
Figure C.1. SEM images of GAC at a resolution of 100 μm (left) and 5 μm (right)	172
Figure D.1 Comparison of herbicide removal capacity of GAC and CAC against the herbicides MCPA, Mecoprop-P, 2,4-D, Triclopyr and Fluroxypyr	178
Figure D.2 SEM images of GAC (a and b) and CAC (c and d) at a resolution of 100 μm (left) and 10 μm (right). EDX spectra of e) GAC and f) CAC	179

Abbreviations

2,4-D	2,4-Dichlorophenoxyacetic acid
3D	Three-dimensional
Å	Angstrom
ATR	Attenuated total reflectance
BWO	Bismuth tungstate
CAC	Coconut-based activated carbon
CaCl ₂	Calcium chloride
Cl _o	Clopyralid
cm ⁻¹	Wavenumber
CO ₂	Carbon dioxide
DAFM	Department of Agriculture, Food and the Marine
DDT	Dichlorodiphenyltrichloroethane
DT ₅₀	Pesticide half-life
EEA	European Environment Agency
EPA	Environmental Protection Agency
EU	European Union
FAO	Food and Agriculture Organisation of the United Nations
Flu	Fluroxypyr
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granulated activated carbon
GDP	Gross domestic product
GIS	Geographic information system
GUS	Groundwater Ubiquity Score
ha	Hectare
HP-BC	Herbal pomace biochar
HSE	Health Service Executive
IPM	Integrated pest management
ISCRAES	International Symposium on Climate-Resilient Agri- Environmental Systems
KG	Knowledge gap
K _{oc}	Organic carbon-water partition coefficient
K _{ow}	Octanol-water partition coefficient

kt	Kilotonne
LOD	Limit of detection
LOQ	Limit of quantification
M	Molar
MAC	Maximum allowable concentration
MCPA	4-Chloro-2-methylphenoxyacetic acid
MOF	Metal organic framework
MW	Molecular weight
MWTPS	Mains water treatment plant sludge
ng	Nanogram
nm	Nanometre
NP	Nanoparticle
NPC	Nanoporous carbon
P _{ow}	Octanol-water partition coefficient
PPDB	Pesticide properties database
PPP	Plant protection product
PRZM	Pesticide root zone model
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
rpm	Revolutions per minute
S-BC	Spruce biochar
SAP	Super-absorbent polymer
SEE	Standard error of estimates
SEM	Scanning electron microscope
stdev	Standard deviation
SUD	Sustainable use of pesticides
S _w	Water solubility
t	Tonne
TiO ₂	Titanium dioxide
Tri	Triclopyr
USEPA	United States Environmental Protection Agency
VBS	Vegetated buffer strip
WHO	World Health Organisation
WMS	Web mapping service

A person who has never made a mistake has never tried anything new.

Albert Einstein

The measure of intelligence is the ability to change.

Albert Einstein

Dedicated to Anne and Thomas.

Der er altid muligheder

Chapter 1 – Introduction

1.1 Overview

Pesticides are substances that are intended to prevent, destroy, repel, or mitigate any pest (USEPA, 2023). With a rapidly increasing human population, rising food demand and limited available agricultural land, extensive and inefficient use of pesticides continues to escalate, leading to increased concern about their potential impacts on both human health and the environment (Chow et al., 2020; Mojiri et al., 2020; Harmon O’Driscoll et al., 2022). Pesticides used in agriculture are categorised into families of chemicals according to the pest they control, including herbicides, fungicides, insecticides, bactericides, molluscicides. The agriculture industry in Ireland used 2.9 kt of pesticides in 2020, of which 1.83 kt were herbicides, defined as a category of pesticides used to control undesired plants, or weeds (Eurostat – Pesticide sales, 2023).

Less than 10% of pesticides applied in agricultural practices reach their target organism (Schulz, 2004; Ali et al., 2019). As a result, they can migrate to both surface and ground water resources by various pathways, including surface run-off, leaching, spray-drift and direct losses (Ravier et al., 2005; Cosgrove et al., 2019; Halbach et al., 2021; Cosgrove et al., 2022). Mobility in soil represents the potential for a pesticide to leave its application site and enter water sources, which increases the likelihood of pesticide exposure to drinking water consumers. Two of the main factors influencing the transport of pesticides are physico-chemical properties of soil (Boivin et al., 2005), and adsorption and desorption to and from soil particles (Paszko and Jankowska, 2018). The concentration of pesticides in both soil and soil solution is determined by the adsorption of pesticides on the soil surface and how pesticides are either transported or degraded (Gondar et al., 2013). Surface run-off is the predominant pathway to freshwater contamination, mainly through heavy rainfall events, which causes environmental degradation in aquatic systems (Harrison et al., 2019; Kraemer et al., 2022).

The persistence of pesticide residues in soil has been categorised using pesticide half-life (DT_{50}), which is defined as the time it takes for a certain amount of a pesticide to

be reduced by 50% of the amount at application (Lewis et al., 2016). On this basis, pesticides are grouped into four categories: non-persistent (soil $DT_{50} < 30$ days), moderately persistent (soil DT_{50} 30-100 days), persistent (soil DT_{50} 100-365 days), and very persistent (soil $DT_{50} > 365$ days; Silva et al., 2019). The latter two categories of pesticides can remain in the environment for several decades after their use has been banned, giving rise to “legacy” pesticides. The detection of legacy pesticides in water samples has been mainly attributed to desorption processes from soils or sediments, including handling, dredging, or disposal of the contaminated soil/sediment (Postigo et al., 2021; Pizzini et al., 2021; Mishra et al., 2022).

In the European Union (EU), Council Directive 98/83/EC (EU, 1998) established the framework to protect human health from adverse effects of any contamination of water intended for human consumption. This Directive set the maximum allowable concentration (MAC) of pesticides, either individually or in total, as 100 $ng.l^{-1}$ or 500 $ng.l^{-1}$, respectively. However, these values are frequently exceeded (Postigo et al., 2021; EPA, 2022), due to the effects of both legacy and recently applied pesticides.

Numerical models have become an essential support to monitoring programmes to provide information regarding the likelihood of pesticide exposure (Lammoglia et al., 2018), and to reduce pesticide exceedances. Software has been developed for surface run-off models (PRZM, Suárez, 2005) and leaching models (MACRO, Stenemo and Jarvis, 2010). However, the comprehensive assessment of pesticide transport requires expertise to use complex equations and modelling systems, making the models very data-hungry. Therefore, their application outside of defined modelling scenarios can be challenging. A simple transmission risk ranking using soil texture-specific adsorption isotherm data for several groups of pesticides, their solubility in water, soil half-life and soil permeability, is currently unavailable to the agricultural land management sector. Such a simple decision making support tool would allow the agricultural sector to assess, either by soil texture or pesticide type, the risk of potential loss of pesticides to receptors, such as streams or drains.

Ongoing pesticide exceedances are problematic as conventional water treatment methods are ineffective in the complete removal of pesticides, particularly weakly adsorbable and highly polar pesticides (Larasti et al., 2021; Intisar et al., 2022; Taylor

et al., 2022). Some water treatment facilities incorporate powdered or granulated activated carbon (GAC) filters to remove pesticides (EPA & HSE, 2019; de Souza et al., 2020). GAC is an excellent adsorbent for pesticides, due to its large surface area (300–2500 m².g⁻¹) and highly microporous structure (Chen et al., 2020). However, use of GAC filters in drinking water treatment facilities is either not common practice in many countries or the weakly adsorbable and highly polar pesticides shorten the functional lifetime of the GAC filter, leading to expensive regeneration of the filter (Taylor et al., 2020). Several physical, chemical, and biological treatment approaches have been employed to remove pesticides from aqueous solutions (Mojiri et al., 2020).

Many studies relating to the application of different adsorbents for pesticide elimination have been published over the last few decades (Maggi et al., 2020; Mojiri et al., 2020; Lunardi et al., 2022). The main advantages of adsorption methods are simplicity and flexibility of design, ease of operation, and insensitivity to toxic contaminants (Mojiri et al., 2020). The use of agricultural waste materials, either raw or pyrolysed, or industrial waste materials, is potentially a viable method of pesticide mitigation (Jatoi et al., 2021; Jing et al., 2021). The use of such low-cost waste materials as adsorption media for pesticides could be environmentally beneficial, as opposed to the cost of the disposal of such materials. Many pyrolysed materials, including both biochars and activated carbons, have been used as adsorbents for pesticides (Jatoi et al., 2021; Taylor et al., 2022). However, there is a dearth of field/pilot studies using adsorbent media for pesticide removal. Instead, research work has mainly comprised adsorption studies of pesticides using source water, environmentally-relevant aqueous solutions, or spiked samples (Kodali et al., 2021; Singh et al., 2021; Sanz-Santos et al., 2022). Such field/pilot studies may be informative in providing information of the configuration of potential intervention devices and their implementation in waterways.

As herbicides account for the biggest proportion of pesticide usage, not only in Ireland but worldwide (Mojiri et al., 2020), their removal from aqueous environments is, therefore, an important environmental objective. Therefore, this thesis will focus on the removal of herbicides.

1.2 Knowledge gaps and project aims

Further research is needed to identify methods of herbicide remediation from application sources, where current best management practices are proving either inefficient or ineffective, rather than in a drinking water treatment facility. Such an alternative approach may involve treatment in the field. The primary goal of this study was to address this need. The knowledge gaps addressed by this research are outlined below:

1. The EU intends to make food systems healthy, sustainable and environmentally friendly through its current Farm to Fork strategy. The use of pesticides in agriculture contributes to pollution of soil, water and air. In order to reduce the risks to the environment, a reduction in the use of chemical pesticides by 50 % by the year 2030 is proposed. This target may be compromised by the prevalence and persistence of legacy pesticides arising from historical pesticide application to land, as the current strategy overlooks the challenges of these legacy pesticides and their remediation. There is a consequent need for improved EU strategies which target legacy pesticides in order to meet future policy requirements.
2. Mathematical models are widely used to predict the fate and transport of pesticides in the environment, and modelling presents an appealing alternative to environmental monitoring, which is both costly and time-consuming. However, pesticide transport models used for pesticide registration in the EU are highly complex and can take hours to run for a single pesticide. Instead, a quick and easily applied screening tool, using soil texture and physiochemical pesticide properties including water solubility, soil half-life and soil permeability, could be designed as a decision-making support tool for agricultural land management, which would allow the agricultural sector to assess, either by soil texture or pesticide type, the potential risk of loss of pesticides to receptors.
3. Many media have been used as adsorbents for pesticides. One such medium is biochar, a carbon-rich, porous material, which has been used for the removal

of pollutants, including pesticides, from aqueous environments. However, its potentially adverse effects on soil biota have raised concerns regarding the long-term safety of its application (Brtnicky et al., 2021). The limitations of GAC, a coal-based activated carbon, and biochar, for the long term remediation of pesticides from waterways, highlight the need for a further investigation of potential low-cost media sources that can give comparable results. An alternative option is the use of agricultural waste materials.

4. In recent years, activated carbons, derived from renewable, readily available agricultural materials have been reported in batch adsorption studies, which use source water, environmentally-relevant aqueous solutions, or spiked samples. However, there is a dearth of field/pilot studies for the removal of pesticides. Field studies using filters containing adsorbent media are needed to investigate their potential as an early treatment intervention in the removal of herbicides.

To address these knowledge gaps (KGs), the aims of this study were to:

1. Review the prevalence of legacy pesticides in waterways and to assess emerging remediation techniques for the removal of legacy pesticides [addressing KG 1].
2. Develop a simple decision-making support tool to assess the potential risk of loss of pesticides to receptors, based on soil texture and pesticide properties including water solubility, soil half-life and soil permeability [addressing KG 2].
3. Assess the potential of several raw and pyrolysed low-cost industrial and agricultural materials as pesticide adsorbents for the removal of several commonly used herbicides in Ireland [addressing KG 3].
4. Assess in-field potential of the medium which showed greatest promise in batch adsorption tests by using the medium in filter bags in selected agricultural catchments [addressing KG 4].

1.3 Thesis structure and objectives

A flowchart of the structure of this study is given in Fig. 1.1. Chapter 2 reviews the current knowledge regarding pesticide use in Europe, as well as pathways of pesticide movement to waterways. In this chapter, the issues of legacy pesticides, including exceedances, are examined, as well as existing and emerging methods of pesticide remediation, particularly of legacy pesticides. In Chapter 3, a risk ranking of transmission of pesticides through soil to waterways, taking into account physiochemical properties of the pesticides (soil half-life and water solubility), soil permeability, and the relationship between adsorption of pesticides and soil texture, is presented. Chapter 4 reports the kinetics and adsorption isotherms of five herbicides (MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr) from aqueous solutions onto a range of raw and pyrolysed waste materials. Chapter 5 describes a field-scale study investigating how filters, containing adsorbent media, placed in fields, were used to manage herbicide exceedances close to the source, thereby reducing the impact on the environment. Finally, Chapter 6 addresses the overall conclusions of these chapters, with recommendations for future research.

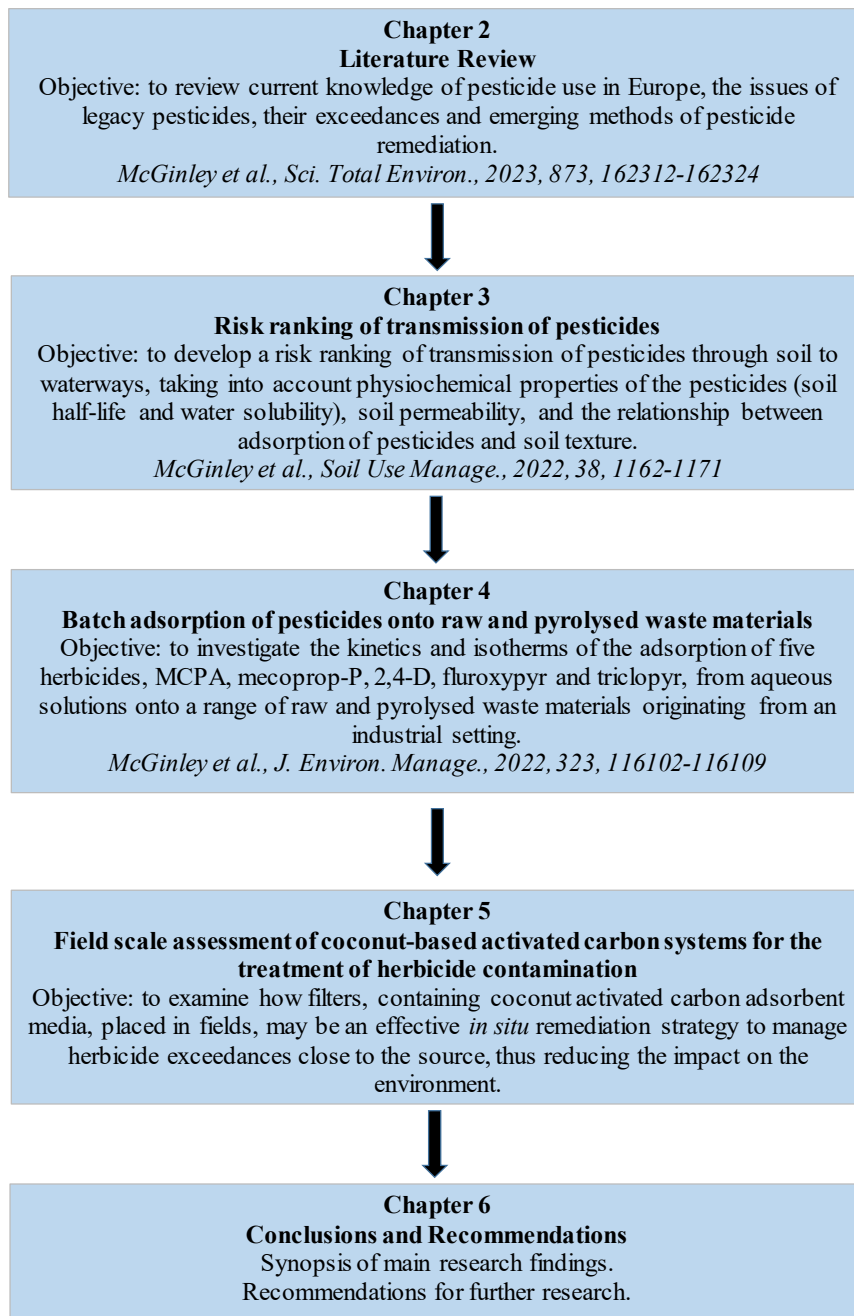


Figure 1.1 Flowchart of thesis structure including study objectives.

1.4 Contribution to existing knowledge

1.4.1 Peer-reviewed publications (published)

To date, three peer review papers have been published from this work, based on Chapters 2, 3, and 4, respectively.

McGinley, J., Healy, M. G., Ryan, P. C., Harmon O’Driscoll, J., Mellander, P.-E., Morrison, L., Siggins, A., 2023. Impact of historical legacy pesticides on achieving legislative goals in Europe. *Science of the Total Environment*, 873, 162312-162324. <http://dx.doi.org/10.1016/j.scitotenv.2023.162312>

McGinley, J., Harmon O’Driscoll, J., Healy, M. G., Ryan, P., Mellander, P.-E., Morrison, L., Callery, O., Siggins, A., 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. DOI: 10.1111/sum.12794

McGinley, J., Healy, M. G., Ryan, P. C., Mellander, P.-E., Morrison, L., Harmon O’Driscoll, J., Siggins, A., 2022. Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon. *Journal of Environmental Management*, 323, 116102-116109. <https://doi.org/10.1016/j.jenvman.2022.116102>

McGinley, J., Healy, M. G., Scannell, S., Ryan, P. C., Harmon O’Driscoll, J., Mellander, P.-E., Morrison, L., Siggins, A., 2023. Field scale assessment of coconut-based activated carbon systems for the treatment of herbicide contamination. *Chemosphere*. Under review.

The first page of each of the published journal papers is presented in Appendix E.

1.4.2 Oral presentations

EPA/DAFM Steering Committee meetings:

- Online, April 2020

- Online, October 2020
- Online, April 2021
- Online, September 2021
- Online, April 2022
- Online, September 2022

McGinley, J., Healy, M. G., Harmon O’Driscoll, J., Ryan, P. C., Mellander, P.-E., Morrison, L., Siggins, A., Batch adsorption of herbicides from aqueous solution by granulated activated carbon. Centre for One Health Annual Conference, Galway, Ireland, November 4, 2021.

McGinley, J., Healy, M. G., Harmon O’Driscoll, J., Ryan, P. C., Mellander, P.-E., Morrison, L., Siggins, A., An assessment of potential pesticide transmission, considering the impact of soil texture and pesticide properties. International Symposium on Climate-Resilient Agri-Environmental Systems (ISCRAES), Dublin, Ireland, August 30, 2022.

McGinley, J., Healy, M. G., Harmon O’Driscoll, J., Ryan, P. C., Mellander, P.-E., Morrison, L., Siggins, A., The use of rapid, small-scale column tests to determine the efficiency of two activated carbon media in the removal of herbicides from water. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America (Tri-societies) annual meeting, Baltimore, USA, November 4, 2022.

McGinley, J., Healy, M. G., Scannell, S., Ryan, P. C., Harmon O’Driscoll, J., Mellander, P.-E., Morrison, L., Siggins, A., Field scale assessment of coconut-based activated carbon systems for the treatment of herbicide contamination. College of Science and Engineering, Inaugural Research and Innovation Day, University of Galway, May 4, 2023.

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Chapter 2 – Impact of historical legacy pesticides on achieving legislative goals in Europe

This chapter reviews the prevalence of pesticides, especially legacy pesticides, in European waterways, with unapproved pesticides being detected in European surface and ground waters at levels exceeding the legal limits. The remediation of these legacy pesticides was also investigated. The current EU food production strategy aims to reduce the overall use of chemical pesticides by 50 % by 2030. The omission of legacy pesticides from this strategy may result in that target not being achieved.

The contents of this chapter have been published in Science of the Total Environment (McGinley et al., 2023. Impact of historical legacy pesticides on achieving legislative goals in Europe, 873, 162312-162324).

Science of the Total Environment 873 (2023) 162312



Review

Impact of historical legacy pesticides on achieving legislative goals in Europe

J. McGinley^{a,b}, M.G. Healy^{a,b}, P.C. Ryan^{c,d}, Harmon O'Driscoll^c, P.-E. Mellander^e, L. Morrison^{b,f}, A. Siggins^{b,g,*}



John McGinley collected, reviewed, analysed, and extracted relevant information from the scientific papers, and is the primary author of this article. Prof Mark G. Healy contributed to the conceptualisation and the writing of the paper. Dr Alma Siggins contributed to the conceptualisation and the writing of the paper. Dr P. C. Ryan contributed to the review and writing. J. Harmon O'Driscoll contributed to the review and writing. Dr P.-E. Mellander contributed to the review and writing. Dr L. Morrison contributed to the review and writing. Supplementary information for this paper is included in Appendix A.

Impact of historical legacy pesticides on achieving legislative goals in Europe

J. McGinley^{1,2}, M. G. Healy^{1,2}, P. C. Ryan^{3,4}, J. Harmon O'Driscoll³, P.-E. Mellander⁵, L. Morrison^{2,6}, A. Siggins^{2,7*}.

¹ Civil Engineering, University of Galway, Ireland.

² Ryan Institute, University of Galway, Ireland.

³ Discipline of Civil, Structural and Environmental Engineering, School of Engineering, University College Cork, Ireland.

⁴ Environmental Research Institute, University College Cork, Cork, Ireland

⁵ Agricultural Catchments Programme, Teagasc Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland.

⁶ Earth and Ocean Sciences, Earth and Life Sciences, School of Natural Sciences, University of Galway, Ireland.

⁷ School of Biological and Chemical Sciences, University of Galway, Ireland.

* Corresponding author: alma.siggins@universityofgalway.ie

Abstract

Pesticides are widely used in agriculture to optimise food production. However, the movement of pesticides into water bodies negatively impacts aquatic environments. The European Union (EU) aims to make food systems fair, healthy and environmentally friendly through its current Farm to Fork strategy. As part of this strategy, the EU plans to reduce the overall use and risk of chemical pesticides by 50% by 2030. The attainment of this target may be compromised by the prevalence of legacy pesticides arising from historical applications to land, which can persist in the environment for several decades. The current EU Farm to Fork policy overlooks the potential challenges of legacy pesticides and requirements for their remediation. In this review, the current knowledge regarding pesticide use in Europe, as well as pathways of pesticide movement to waterways, are investigated. The issues of legacy pesticides, including exceedances, are examined, and existing and emerging methods of pesticide remediation, particularly of legacy pesticides, are discussed. The fact that some legacy pesticides can be detected in water samples, more than twenty-five years

after they were prohibited, highlights the need for improved EU strategies and policies aimed at targeting legacy pesticides in order to meet future targets.

Keywords:

Pesticides; European policy; detection; mitigation methods.

2.1 Introduction

Pesticides are defined as substances that are used to suppress, eradicate or prevent organisms which are considered harmful to crops or nuisance, including biocidal products and plant protection products (EU, 2021a). Pesticide use is not only associated with the mass production of foodstuffs to cater for the global demand, but also their unintended release from both agricultural and urban sectors into non-target ecosystems (Schreiner et al., 2016; Chow et al., 2020; Mojiri et al., 2020). Once released into the environment, pesticides can move through soil or surface water to streams and groundwater, where they can have unintended ecological effects such as accumulation in aquatic organisms and loss of ecosystem biodiversity (Beketov et al., 2013; Stehle and Schulz, 2015; Arisekar et al., 2019). Pesticides also may have carcinogenic, mutagenic, neurotoxic and/or teratogenic effects on human health (Pereira et al., 2015; Harmon O’Driscoll et al., 2022).

Pesticide residues are widespread in soils where crops have been planted and grown (Li and Niu, 2021; Shahid and Khan, 2022; Yang et al., 2022a). The persistence of pesticide residues in soil has been categorised using pesticide half-life (DT_{50}), which is defined as the time required for the chemical concentration under defined conditions to decline to 50% of the amount at application (Lewis et al., 2016). Non-persistent pesticides have a $DT_{50} < 30$ days, moderately persistent have a DT_{50} of 30-100 days, persistent have a DT_{50} of 100-365 days, and very persistent have a $DT_{50} > 365$ days (Silva et al., 2019). “Persistent” and “very persistent” pesticides can remain in the environment for several decades after their use has been prohibited, giving rise to so-called “legacy” pesticides.

The detection of legacy pesticides in water samples has been mainly attributed to their desorption from soils or sediments, where they may have accumulated during previous

pesticide applications (Postigo et al., 2021; Pizzini et al., 2021). Legacy pesticides in the environment arise from a four-step process: (1) application of pesticides to the land, (2) run-off to streams and rivers, (3) partition to sediments, and (4) desorption/resuspension from sediments. Depending on their properties (e.g. polarity, octanol-water partition coefficient), pesticides can be adsorbed onto soil or sediment particles, with hydrophobic pesticides being particularly affected (Khanzada et al., 2020). High pollutant levels in sediments can give rise to further pollution of the waterway due to the possible resuspension of the pollutants in the water during handling, dredging, or disposal of the contaminated sediment (Pizzini et al., 2021; Mishra et al., 2022). Ivanova et al. (2021) demonstrated that the intensive usage of dichlorodiphenyltrichloroethanes (DDT-related pesticides) in the past was observed in river sediments taken from all rivers in Moldova. They suggested that the contamination was from agricultural deposition that had undergone degradation under either aerobic or anaerobic conditions. In a similar study, Qu et al. (2018) found high concentrations ($0.6 - 99.6 \text{ ng.g}^{-1}$) of organochlorine pesticides in marine sediments from the Gulfs of Naples and Salerno, which were attributed to historical applications. Pesticide residues can bioaccumulate in soils, soil microorganisms, aquatic microorganisms, air and food chains (Silva et al., 2019; Li, 2022). Urseler et al. (2022) reported on the detection of atrazine in groundwater and bovine milk samples in Argentina. They recorded atrazine concentrations of $1.40 \text{ }\mu\text{g.l}^{-1}$ in groundwater and $20.97 \text{ }\mu\text{g.l}^{-1}$ in the milk samples. The latter value is over the limit value for human consumption of $20 \text{ }\mu\text{g.l}^{-1}$ established by the USEPA (USEPA, 2018). They also concluded that the detection of atrazine in the milk samples indicated that the quality of milk was affected by the groundwater that the cattle consumed. While studies have focused on the relationship between sediment adsorption/desorption and legacy pesticides, there is a deficiency of articles contemplating potential soil legacy issues regarding the role of soil adsorption during the process of pesticide movement to waterways, despite the ongoing Farm to Fork strategy (EU, 2020).

Many international organisations have established regulations regarding pesticides and their permissible detectable concentration limits in the environment (WHO, 2017; USEPA, 2019; EU, 2021b, Australian Government, 2022). Within the European Union (EU), the Regulation on Plant Protection Products (Regulation (EC) No.

1107/2009) on placement of pesticides on the market ensures a high level of protection of both human and animal health and the environment (EU, 2009a). Council Directive 98/83/EC (EU, 1998) on the quality of water intended for human consumption sets the maximum allowable concentration for pesticides, either individually or total, as $0.1 \mu\text{g}\cdot\text{l}^{-1}$ or $0.5 \mu\text{g}\cdot\text{l}^{-1}$, respectively. At EU level, the monitoring of pesticide residues in soil is not required, in contrast to the monitoring of pesticides in water, which is regulated by the EU Water Framework Directive (EU, 1998).

Sustainable food production in the EU aims to make food systems fair, healthy and environmentally friendly (EU, 2020). As part of this Farm to Fork strategy, the EU plans to reduce the overall use and risk of chemical pesticides by 50% by 2030. The EU also plans to revise the Sustainable Use of Pesticides Directive (Directive 2009/128/EC), as well as promoting greater use of safe alternative methods of protecting harvests from pests and diseases (EU, 2009b). This will be achieved by making the best use of nature-based, technological and digital solutions to deliver better climatic and environmental results, and reduce and optimise the use of pesticides (EU, 2020). One such solution is the common European agricultural data space which will enhance the competitive sustainability of EU agriculture through the analysis of production, land use, environmental and other data. This will allow a precise and tailored application of production methods at farm level (EU, 2020). The EU's current sustainable food production policy leaves the issues of legacy pesticides unaddressed (EU, 2020). Furthermore, any policy regarding future use of pesticides needs to be linked with remediation of existing problems, including legacy pesticides.

Several physical and chemical treatment approaches, including adsorption, membrane filtration and advanced oxidation processes, as well as biological approaches, such as bioremediation, activated sludge processes and phytoremediation, have been employed to remove pesticides from aqueous solutions (Mojiri et al., 2020). Each method provides its own benefits and drawbacks in terms of both technical and economic aspects (Saleh et al., 2020). Chemical adsorption is more economical, more efficient and faster than biological approaches (Uddin, 2017). While the ease of operation and the flexibility of the design are the main advantages of an adsorption method, the main disadvantage is the requirement for a regeneration process (Mojiri

et al., 2020). It is therefore important for the future quality of both water and soil that more efficient and effective mitigation methods for the removal of pesticides are developed. One of the most extensively used remediation methods of pesticides is adsorption onto low-cost materials (Mojiri et al., 2020). This is simple and cost-effective. However, the issues of incomplete removal of pesticides and the generation of toxic side products are the main disadvantages of this method (Mojiri et al., 2020; Shahid et al., 2021).

In the context of the above discussion of legacy pesticides and their remediation being beyond the scope of the Farm to Fork strategy, this review will address these knowledge gaps in order to better facilitate achievement of the 2030 targets. To do this, the current knowledge regarding pesticide use in Europe, as well as pathways of loss of pesticides, will be examined. The specific issue of legacy pesticides, including exceedance and persistence in the environment, will be examined in detail. Finally, existing and emerging methods of pesticide mitigation, particularly of legacy pesticides, will be discussed.

2.2 Methodology

The methodology followed during this review is outlined in Fig. 2.1. The main steps that were followed were, first, a literature search on legacy pesticides, their mitigation and current regulations; second, refining of papers obtained, and finally, extraction of relevant information from those papers and websites, where appropriate. A detailed literature search was undertaken by searching key words including: pesticide, soil, surface water, groundwater, adsorption, legislation, legacy, and mitigation. The search was limited to peer-reviewed papers published, in English, between 2011 and 2020. A geographical limitation of the twenty-seven countries of the EU was employed for the search. The twenty-seven countries of the EU will be referred to as the “EU-27” throughout this article. Search engines used included databases such as Scopus, as well as publisher-specific search engines including ScienceDirect, the American Chemical Society, and the Royal Society of Chemistry. References from several papers found in these searches were also examined for relevant information. Research papers were selected based on the relevance to the review. A total of 628 articles and a small number of book chapters and reports were reviewed.

Pesticides can be categorised not only by type of use, but also by target organism, the origin of their active substances, or their hazard category. The EU and the Pesticide Properties Database (PPDB) classify pesticides into the categories of herbicide, fungicide, insecticide, and others, while the PPDB also includes physico-chemical, human health and ecotoxicological data (Lewis et al., 2016; EU, 2021c). The classification of pesticide used herein is based on pesticidal activity, that is, fungicide, herbicide, insecticide, etc., not on hazard.

The information on pesticide usage required for this review is not readily available. The Eurostat pesticide sales website contains information on pesticide sales across the EU-27, for each individual country, covering the years 2011-2020 (Eurostat - Pesticide Sales, 2022). This information is divided into six pesticide categories (fungicides, herbicides, insecticides, molluscicides, plant growth regulators and other protection products), which are further subdivided in various groupings based on class of compounds to give 157 pages of data. The appropriate herbicide, fungicide and insecticide data for each EU member state were mined from the online data and correlated for use. Land use data were also downloaded from the Eurostat website (Eurostat - Land Use, 2022) and the relevant arable land use data for each EU member state were extracted for use. The kilogram of pesticide used per hectare of land data was calculated for each EU member state by dividing the appropriate herbicide, fungicide and insecticide data by the relevant land use data.

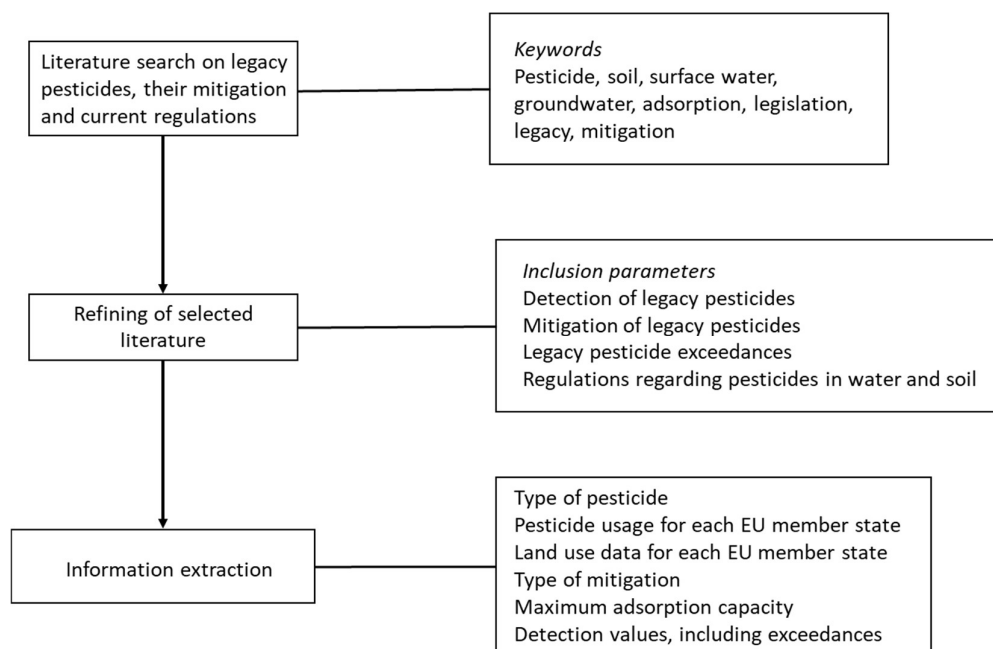


Figure 2.1 Methodology flowchart.

2.3 Pesticide usage and pathways of loss

2.3.1 Usage of pesticides in the EU-27

The sale of pesticides used within the EU-27 over the ten-year period (2011 - 2020) has fluctuated from 356 kt in 2011 to 350 kt in 2020, with the highest sales of 368 kt recorded in 2018 (Fig. 2.2). The largest year-on-year increase was between 2019 and 2020, when the sales of pesticides increased by 21 kt, while the biggest year-on-year decrease of 33 kt was between 2018 and 2019. In 2019, the weather was the most significant influence on the pesticide market with dry conditions and drought across major areas of Europe, leading to reduced disease pressure and lower demand for both herbicides and fungicides (IHS Markit, 2020). The top five pesticide consumers across the EU-27 were Spain, France, Italy, Germany and Poland, with average annual sales over the ten-year period of 74, 68, 58, 46, and 24 kt, respectively. In contrast, the five countries with the lowest average annual pesticides sales were Malta, Luxembourg, Estonia, Slovenia, and Cyprus with 108, 150, 621, 1046, and 1139 t, respectively. Despite the introduction of the regulations, Regulation No 1107/2009 on Plant Protection Products, Regulation No 396/2005 on Maximum Residue Levels in Food, Directive 2009/128/EC on Sustainable Use of Pesticides, and Regulation No 528/2012 on Biocidal Products (EU 2005; EU 2009a; EU 2009b; EU, 2012), no decline in

overall pesticide use has been observed over the past ten years. One reason for this could be the rapid replacement of unapproved pesticides with alternatives by manufacturers.

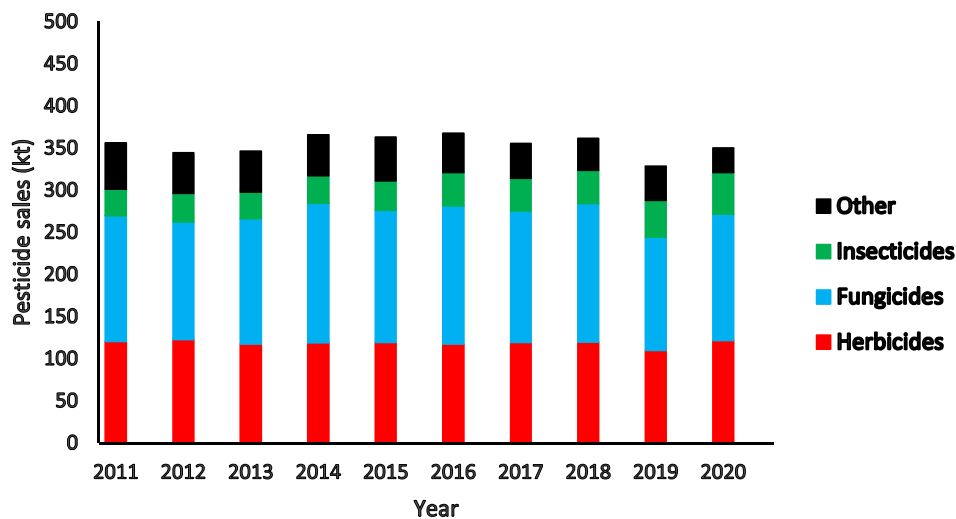


Figure 2.2 Pesticide usage, given as classes of pesticides, in the study area, for the years 2011 - 2020 (Eurostat – Pesticide sales, 2022).

Fungicides and herbicides were the dominant pesticides used in the EU-27 from 2011 - 2020, as per Fig. 2.2, accounting for 40 - 44% and 30 - 36% respectively, of total pesticide sales. A smaller proportion (9 - 16%) of pesticides used were insecticides, with the remainder represented by a mixture of plant growth regulators, anti-sprouting agents, and molluscicides. The use of herbicides and fungicides increased from 2011 to 2019, at which point usage decreased by up to 17% for fungicides. Two possible causes for this decrease were: (1) the increasing strict regulatory environment (IHS Markit, 2020), and (2) weather conditions. The use of insecticides has increased over the ten-year period, with increases ranging from 35 kt in 2011 to 64 kt in 2020. This increase can be accounted for by such factors as economic growth, the emergence of new pests and diseases, as well as increased insecticide resistance (Sparks et al., 2020).

The variation in pesticide usage per hectare ($\text{kg}\cdot\text{ha}^{-1}$) of agricultural land was considerable between countries within the EU-27, from Ireland with $0.6 \text{ kg}\cdot\text{ha}^{-1}$ up to $> 11 \text{ kg}\cdot\text{ha}^{-1}$ for Malta (Fig. 2.3, Table A.1). Most countries reported fluctuating usage

over the ten-year period (2011 - 2020). Comparing the amount used per ha in 2011 to that used in 2020, eleven countries, Belgium, Czechia, Denmark, Ireland, Lithuania, Luxembourg, Netherlands, Portugal, Romania, Slovenia, and Sweden, reported decreasing usage of pesticides per hectare (Fig. 2.3 and Tables A.2 - 4). Sixteen countries in 2020 applied less than 2 kg.ha⁻¹, compared to eighteen countries in 2014 (EU, 2017). However, as reported by López-Ballesteros et al. (2022), the available pesticide usage data across the EU-27 in terms of area of application is sparse, with only Spanish and Irish databases including values of both basic and treated/sprayed areas. Focussing on the weight of pesticide applied per unit area can be problematic. While the quantity of pesticide applied can be related to its toxicity, the toxicity of pesticides differs from one pesticide to the next. As a result of these differences, the environmental pollution risk might not be proportional to the quantity of pesticide applied (López-Ballesteros et al., 2022). Jess et al. (2018) reported that, while there was a 34% reduction in the area of arable crops grown in Northern Ireland since 1992, there was an increase of 37% in the area treated by pesticides, which was attributed to intensification of agriculture.

Although sixteen countries in the EU-27 applied less than 2 kg.ha⁻¹ of pesticides, the overall amount of pesticides being applied across the EU-27 continues to rise. The recent EU strategy on sustainable food production, implemented in 2020, proposes to cut the overall pesticide use in the EU-27 by 50% by 2030, as well as reducing nutrient losses (especially nitrogen and phosphorus) by 50% (EU, 2020). One possible way of achieving this would be to transition from a grassland-dominated system to a more arable crop-based system. Whilst this could achieve the required reduction in nutrient loss, it could also lead to an increase in pesticide usage, particularly herbicides, required for arable and vegetable crops.

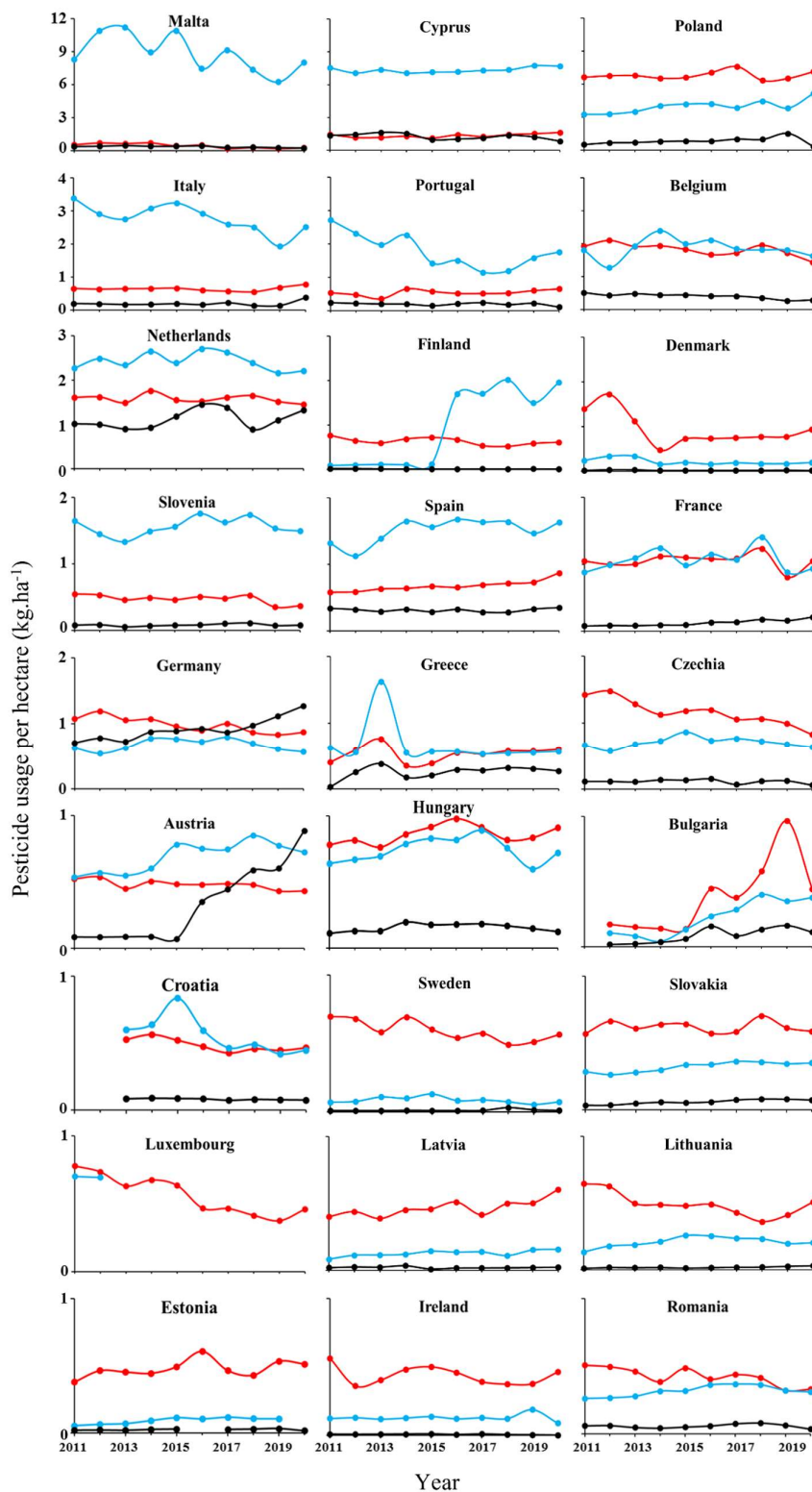


Figure 2.3 Tonnes of pesticide used per hectare agricultural land across EU for the years 2011-2020 (Data sources: Eurostat - Pesticide Sales, 2022; Eurostat - Land use, 2022). Herbicides are shown in red, fungicides in blue and insecticides in black.

2.3.2 Pathways of pesticide loss

A significant percentage of pesticides applied in agricultural practices never reach their target organism (Ali et al., 2019), with Schulz (2004) estimating that 10% of applied pesticides reach non-target areas. As a result, and due to the widespread use of pesticides in agricultural and urban areas, they can migrate to various surface water resources by several pathways, including surface run-off (Chen et al., 2019; Cosgrove et al., 2022), leaching (Cosgrove et al., 2019), spray-drift (Ravier et al., 2005), groundwater inflow (Gzyl et al., 2014) and sub-surface drainage systems (Halbach et al., 2021) (Fig. 2.4). Surface run-off is the predominant pathway, mainly through heavy rainfall events and snowmelt, particularly in saturated fields, or fields with hilly slopes or fields with shallow level of water table (Jing et al., 2021). The input of pesticides to surface water is particularly high during the main application period of spring and summer, and also increases during rainfall events (Szöcs et al., 2017).

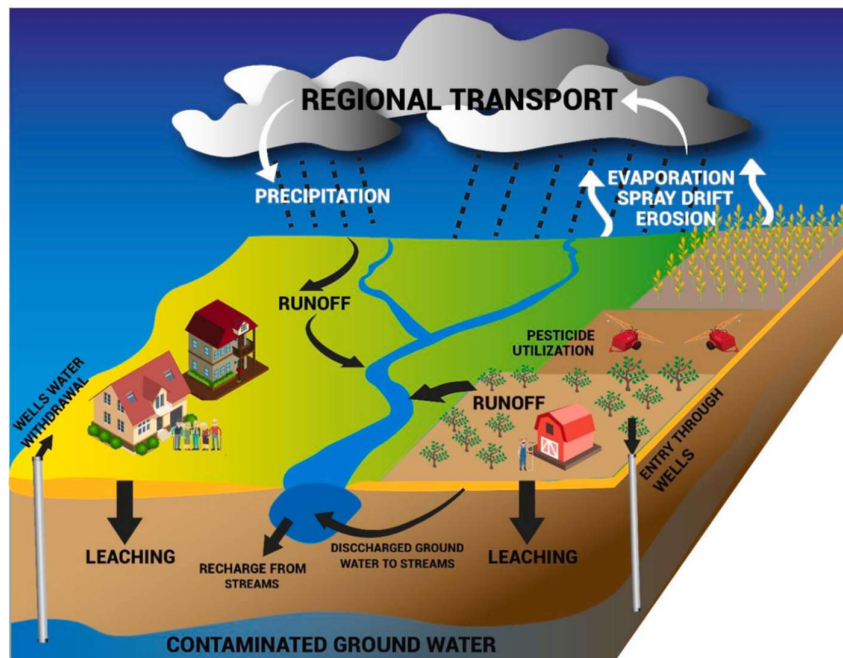


Figure 2.4 Pesticide transfer routes to surface and ground water (Lunardi et al., 2022; Reproduced with permission).

The main factors influencing the transport of pesticides to receptors are adsorption and desorption to and from soil particles (Paszko and Jankowska, 2018), DT_{50} (Fantke et

al., 2014), and physico-chemical properties of soil (Boivin et al., 2005). Adsorption is predominantly influenced by the properties and chemical composition of the soil, which is a complex mixture of inorganic materials and organic matter (Leovac et al., 2015), and the physico-chemical properties of the pesticide (Kodešová et al., 2011). The adsorption of pesticides on the soil surface determines how pesticides are either transported or degraded, which will, ultimately, determine the concentration of pesticides in both soil and soil solution (Gondar et al., 2013; McGinley et al., 2022). The relationship between the organic content of the soil and pesticide adsorption has been well examined in the literature (Rojas et al., 2013; Wei et al., 2015; Wu et al., 2018). Many soil characteristics have been investigated with regard to pesticide adsorption, including pH (Kodešová et al., 2011; Gondar et al., 2013), organic content (Boivin et al., 2005; Conde-Cid et al., 2019), pore size (Siek and Paszko, 2019), cation exchange capacity (Kodešová et al., 2011), and soil texture (McGinley et al., 2022). McGinley et al. (2022) showed that there is a high potential pesticide transmission risk from soils containing either <20% clay or > 45% sand.

Mixtures of pesticides are commonly detected in agricultural soils (Schaeffer and Wijntjes, 2022). Silva et al. (2019) analysed 76 target pesticides in 311 agricultural topsoils across the EU and observed that almost 60% of the soils contained mixtures of two or more residues in various combinations. There are several reasons for this, including pesticides being applied as tank mixtures, repeated pesticide applications during the season, and the binding of pesticides to the soil matrix leading to a reduction in bioavailability, which in turn may lead to significantly reduced degradation. Mixtures of two or more pesticides can form a complex substance that may express properties unique to that combination (de Souza et al., 2020). Research on the impact of such mixtures on soil biota has shown that the threshold value of a pesticide for certain organisms, as defined in the risk assessment, can be exceeded (Sybertz et al., 2020). Mixtures of pesticides can elicit synergistic effects on biota, even if compounds within the mixture are contained in concentrations below the individual level effects (Sybertz et al., 2020). The annual repetition of pesticide spraying can result in high exposure of soil organisms to pesticides for long periods of time, since some pesticides can remain in the soil for long periods of time depending on their specific degradation or DT₅₀, as discussed in detail in the next sub-section (Sybertz et al., 2020).

2.4 Legacy issues

Soil microorganisms play an essential role in soil dynamics and nutrient cycling, and have been used as soil quality indicators (Ashworth et al., 2017). They are responsible for regulating gas exchange, inducing microaggregation and altering the biochemical soil environment (White and Rice, 2009). The implementation of a no-tillage process increases a soil's total organic carbon and decreases its pH, thereby affecting the potential adsorption and long-term leaching of pesticides (López-Piñeiro et al., 2019). While a soil's microbial activity may increase under reduced tillage conditions, this does not necessarily imply faster degradation of pesticides (Jørgensen and Spliid, 2016). Increased crop rotations may increase the functions performed by soil microbial communities, which would benefit plant growth. However, because of the increase in crop rotation, extensive pesticide applications may adversely affect the soil richness and microbial diversity. Groundwater makes up the largest reservoir of freshwater in the world (EU, 2008). Approximately 75% of EU residents rely on groundwater for their drinking water supply (EU, 2008). Agricultural practices can deliver high quantities of pesticides into aquifers, which can make groundwater unsuitable for domestic use (Hakoun et al., 2017; McManus et al., 2017; Aguiar Jr. et al., 2017).

Many toxic pesticides have been banned by the EU, although some can persist in the environment for decades (Ccanccapa-Cartagena et al., 2019). In 2022, 452 active substances were approved for use as plant protection products (PPP) in the EU-27, while 937 had been prohibited (EU Pesticides Database, 2022). Of the active substances that were on the market before 1993, 70% have since been withdrawn (EU, 2017). McKnight et al. (2015) found that several banned pesticides, such as dinitro-*ortho*-cresol (prohibited in 1998) and simazine (prohibited in 2004), were found in either streams, sediments or groundwater in Denmark between 2010 and 2012, either at or above the EU maximum allowed concentration for pesticides of $0.1 \mu\text{g.l}^{-1}$. The number of reported detections of unapproved pesticides that were detected in water sources across Europe for the time period 2011-2020 are shown in Table A.5, with several pesticides being detected on numerous occasions in the same year. Fig. 2.5 shows the top 12 herbicides, fungicides and insecticides, from Table A.5, that were

detected across the EU-27 after they were not approved by the EU, with several being detected many years after being unapproved for use.

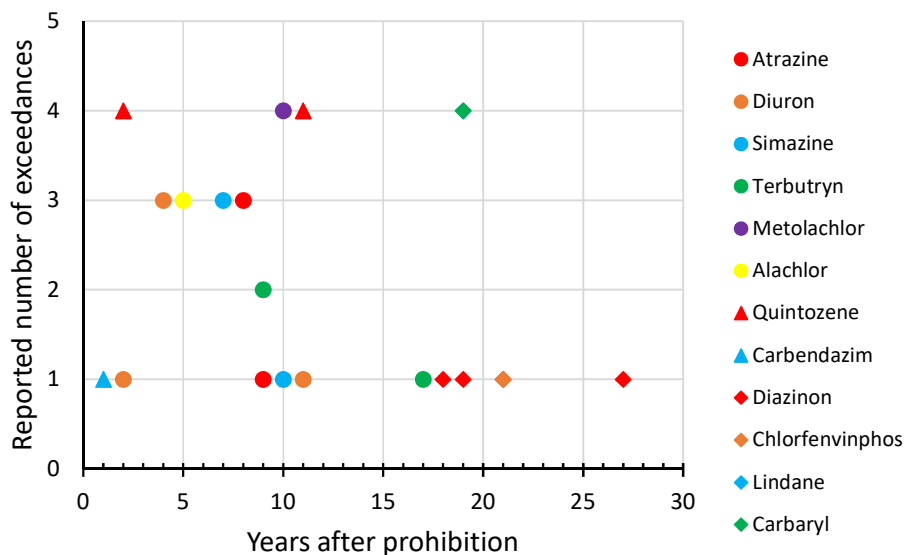


Figure 2.5 Timeline of reported exceedances of some selected prohibited pesticides. Herbicides are denoted by circles, fungicides by triangles and insecticides by diamonds (Citations are in Table A.5).

The legislation that defines the maximum allowable concentration of pesticides in drinking water in the EU has been described as the most stringent in the world (Knauer, 2016; Climent et al., 2019). Because of this stringency, many unapproved pesticides continue to be detected in Europe at levels exceeding legal limits in both surface and ground water (Table A.4). In total, 233 pesticide detections have been observed in EU waterways after they were prohibited for use in the EU, including some that were banned in the last century, although not all were above the maximum permissible concentration (Table A.4). This includes 121 herbicide detections from 29 different herbicides, 27 fungicide detections from 15 different fungicides, and 85 insecticide detections from 27 different insecticides. Soil half-life expresses the potential for degradation of a pesticide in soil (Melin et al., 2020). Given the short DT_{50} of some of these pesticides, they should no longer be detected in surface waters during the time period of 2011 and 2020. Papadakis et al. (2018) suggested that the detection of prometryn, several years after it has been “not approved”, was due to the ongoing, illegal use of the herbicide, groundwater inflows into streams, or long-range

transport and atmospheric deposition. A further possible scenario that could explain their presence is that the pesticides have been bound to soil particles and had only been disturbed prior to the sampling period during which they were detected (Postigo et al., 2021).

The most commonly detected unapproved herbicides in surface waters, for the period 2011 - 2020, were atrazine (17), diuron (13), simazine (12), terbutryn (11), metolachlor (9) and alachlor (9) (Table A.4). Atrazine is strongly hydrophobic, meaning it has a low solubility in water (de Souza et al., 2020). Furthermore, it breaks down slowly in water, having negligible breakdown in neutral or slightly basic solution, with an aqueous DT₅₀ of more than 2 years, which categorises it as “very persistent”. In slightly acidic solutions, the aqueous DT₅₀ decreases to approximately 84 days (de Souza et al., 2020). According to Fig. 2.5, atrazine was detected multiple times up to nine years after approval was removed, which is well beyond the DT₅₀ value of two years. This highlights how persistent pesticides can be in the soil.

The most commonly detected unapproved fungicides in surface waters, for the period 2011 - 2020, were hexachlorobenzene (6), quintozone (5), and carbendazim (2) (Table A.4). Twelve different fungicides were detected for the period 2011 - 2020. The range of concentrations found for hexachlorobenzene (0.029 - 0.048 µg.l⁻¹) were all below the maximum allowed concentration. Twenty seven different unapproved insecticides were detected in surface waters over the ten year period 2011 - 2020 (Table A.4). The most commonly detected insecticides were diazinon (12), chlorfenvinphos (8), lindane (7) and carbaryl (5) (Table A.4). From Fig. 2.5, diazinon was detected 27 years after approval was removed. The fact that the DT₅₀ value for diazinon is 18 days (Lewis et al., 2016) indicates how long these pesticides can remain in the environment. If the pesticide is adsorbed by either soil or sediment, then the DT₅₀ tail of the pesticide can obviously be extended indefinitely.

2.5 Mitigation options

Conventional methods to remove pollutants, including pesticides, from the environment include adsorption, sedimentation, advanced oxidation processes and

membrane technologies (Mojiri et al., 2020; Jatoi et al., 2021; Shahid et al., 2021). Although these methods are commonly used, they can involve high operating costs, can generate toxic side products and do not completely remove the pollutants (Mon et al., 2018). The development of a more efficient and safer removal systems is necessary. A complete survey of mitigation systems is beyond this review. A list of these systems, along with relevant references, is given in Table A.6. Some new, or emerging, systems are now discussed.

2.5.1 *Metal-Organic Frameworks*

With the development of nanotechnology, Metal Organic Frameworks (MOFs) have emerged as powerful functional materials for the remediation of contaminated water (Mon et al., 2018; Mondol and Jung, 2021; Wagner et al., 2021; Lunardi et al., 2022). MOFs are arrays of inorganic nodes, either single ions or clusters of ions, connected by organic linkers. The resulting 3D network has a well-built pore structure, and structure tunability, which provides high selectivity for pesticide adsorption. Furthermore, these materials can have a high surface area, typically 3000 - 4000 m² g⁻¹ (Lunardi et al., 2022).

MOFs can be divided into four groups: (1) pristine MOFs, (2) functionalisation of MOFs, (3) MOF-based composites and (4) MOF-derived materials. Pristine MOFs are composed of the inorganic-organic hybrid porous materials without any functionalisation. In the functionalisation of MOFs group, functional groups are incorporated into the MOFs *via* traditional synthesis conditions using organic linkers identical to the pristine ligand but with attached functional groups, thereby increasing the number of adsorption sites and selectivity (Lunardi et al., 2022). In MOF-based composites, the MOF has been integrated with other functional materials, such as graphene oxide, to increase their adsorption capacity (Lunardi et al., 2022). MOF-derived materials, which are highly porous nano- or mesoporous-materials, are obtained by pyrolysing MOFs under a protective atmosphere, to give a material with improved diffusivity (Lunardi et al., 2022). Table 2.1 shows some of the recent published research in this area on the adsorption of unapproved pesticides.

Table 2.1. Summary of pesticide adsorption over metal-organic frameworks.

MOF Type	Adsorbent	Pesticide	BET Surface area (m ² .g ⁻¹)	Total pore volume (cm ³ .g ⁻¹)	Max. capacity (mg.g ⁻¹)	Reference
<i>Pristine</i>	UiO-67 (Zr)	Atrazine	2345	1.249	11.9	Akpinar and Yazaydin, 2018
	NU-1000 (Zr)	Atrazine	2210	n.d.	36	Akpinar et al., 2019
	CaFu	Imidacloprid	2308	0.11567	467.2	Singh et al., 2021
	MIL-53 (Al)	Dimethoate	866	n.d.	154.8	Abdelhameed et al., 2021a
	Al-TCPP	Chlorantraniliprole	1359	0.8	371.9	Xiao et al., 2021
	UiO-66 (Zr)	Ciprofloxacin	730.6	0.046	111.7	Bayazit and Sahin, 2020.
		Naproxen	730.6	0.046	43.9	
		NU-1000 (Zr) Zr-LMOF	Fenamiphos Parathion-methyl	1980 1453.2	n.d. n.d.	212.3 n.d.
<i>Modified</i>	MIL-101-C1 (Cr)	Diuron	951.3	0.554	148.97	Yang et al., 2019
		Alachlor	951.3	0.554	122.72	
		Tebuthiuron	951.3	0.554	79.47	
		Gramoxone	951.3	0.554	49.05	
	MIL-101-C2 (Cr)	Diuron	502.6	0.302	135.87	
		Alachlor	502.6	0.302	107.67	
		Tebuthiuron	502.6	0.302	73.35	
		Gramoxone	502.6	0.302	45.41	
	MIL-101-C3 (Cr)	Diuron	490.6	0.282	141.42	
		Alachlor	490.6	0.282	104.02	
		Tebuthiuron	490.6	0.282	69.71	
		Gramoxone	490.6	0.282	50.18	
	MIL-101-C4 (Cr)	Diuron	492.4	0.285	161.25	
		Alachlor	492.4	0.285	105.15	
		Tebuthiuron	492.4	0.285	81.73	
		Gramoxone	492.4	0.285	64.11	
	MIL-101-C5 (Cr)	Diuron	543.2	0.319	186	
Alachlor		543.2	0.319	149.79		

MOF Type	Adsorbent	Pesticide	BET Surface area (m ² .g ⁻¹)	Total pore volume (cm ³ .g ⁻¹)	Max. capacity (mg.g ⁻¹)	Reference
		Tebuthiuron	543.2	0.319	94.57	
		Gramoxone	543.2	0.319	57.99	
	MIL-53-NH ₂ (Al)	Dimethoate	1060	n.d.	266.9	Abdelhameed et al., 2021a
	Al-(BDC) _{0.5} (BDC-NH ₂) _{0.5}	Dimethoate	1260	n.d.	513.4	
<i>Composites</i>	Al-MOF@cotton	Diazinon	-	n.d.	367.62	Abdelhameed and Emam, 2022
		Chlorpyrifos	-	n.d.	296.77	
	Fe-MOF@cotton	Diazinon	-	n.d.	402.02	
		Chlorpyrifos	-	n.d.	340.33	
	Ti-MOF@cotton	Diazinon	-	n.d.	459.73	
		Chlorpyrifos	-	n.d.	372.01	
	Zr-MOF@cotton	Diazinon	-	n.d.	464.69	
		Chlorpyrifos	-	n.d.	389.69	
	ZIF8@MPCA	Chipton	-	0.029	160.9	Liang et al., 2021
		Alachlor	-	0.029	196.2	
	UiO66-NH ₂ @MPCA	Chipton	6.42	0.035	246.8	
		Alachlor	8.87	0.035	232.8	
	Cu-BTC@cellulose acetate	Dimethoate	965.8	n.d.	321.9	Abdelhameed et al., 2021b
	M-ZIF-8@ZIF-67	Fipronil	219	0.07	n.d.	Li et al., 2020
	BSA/PCN-222 (Fe)	Methyl parathion	1015	n.d.	370.4	Sheikli et al., 2021
		Diazinon	1015	n.d.	400	
	ZIF-8/GO (Zn)	Chlorpyrifos	720.6	0.80	54.3	Nikou et al., 2021
		Diazinon	720.6	0.80	47.2	
	Fe ₃ O ₄ @C@UiO-66 (Zr)	Triticonazole	552	0.18	148.81	Wang et al., 2022
		Epoxiconazole	552	0.18	150.15	
		Prothioconazole	552	0.18	188.32	
		Imazaquin	552	0.18	173.31	
		Metalaxyl	552	0.18	135.14	
		Myclobutanil	552	0.18	145.99	

MOF Type	Adsorbent	Pesticide	BET Surface area (m ² .g ⁻¹)	Total pore volume (cm ³ .g ⁻¹)	Max. capacity (mg.g ⁻¹)	Reference
		Hexaconazole	552	0.18	169.49	
		Diniconazole	552	0.18	141.84	
	Fe ₃ O ₄ /MIL-101 (Fe)	Fenitrothion	957.48	0.78	209.71	Samadi-Maybodi and Nikou, 2021
<i>Derived</i>	NiO/Co@C	Chlorothalonil	n.d.	n.d.	110.6	Zhao et al., 2022
		Tebuconazole	n.d.	n.d.	43.69	
		Chlorpyrifos	n.d.	n.d.	113.3	
		Butralin	n.d.	n.d.	47.57	
		Deltamethrin	n.d.	n.d.	50.0	
		Pyridaben	n.d.	n.d.	78.8	
	CDM-74 (Zn)	DEET	1395	1.75	340	Bhadra et al., 2020

Akpinar and Yazaydin (2018) studied the performance of three pristine MOFs (ZIF-8, UiO-66 and UiO-67) for the adsorption of the unapproved herbicide atrazine. Because of their larger pore apertures and large pore size, UiO-67 adsorbed significantly more atrazine than either of the other MOFs. In a further study, Akpinar et al. (2019) showed that the MOF NU-1000 had a maximum adsorption capacity of 36 mg.g^{-1} for atrazine, which was three times larger than that of UiO-67. This increase was due to the increased pore size of NU-1000, which facilitates easier diffusion of the herbicide.

The functionalisation of pristine MOFs is an effective way of enhancing adsorption performances. Yang et al. (2019) modified Cr-MIL-101 with substituted furan and thiophene groups and used them in the detection of four unapproved herbicides, alachlor, diuron, gramoxone (paraquat) and tebuthiuron. They observed that all the functionalised MOFs showed efficient adsorption capacities towards the herbicides, which were preferable to that of the pristine MOF. The adsorption of the unapproved insecticide dimethoate onto amine-modified MOFs was investigated by Abdelhameed et al. (2021a). Different amino ratios were synthesised using aluminium as the metal centre and two different ligands, BDC and BDC-NH₂. Their results showed that a 1:1 ratio of ligands gave an Al-(BDC)_{0.5}(BDC-NH₂)_{0.5} MOF which had the highest surface area and the highest adsorption capacity for dimethoate. The 1:1 MOF had a maximum adsorption capacity of 513.4 mg.g^{-1} , which was higher than the pristine MOF Al-BDC (154.8 mg.g^{-1}) or the amino MOF Al-BDC-NH₂ (266.9 mg.g^{-1}).

MOF-based composites, which are MOFs coupled with other functional materials, have been shown to improve adsorption performance compared to individual substances (Lunardi et al., 2022). Abdelhameed and Emam (2022) synthesised MOF@cotton hybrids by inclusion of MOFs (based on Al, Fe, Ti and Zr) within cotton fibres. These were used in the adsorption of the unapproved pesticides, diazinon and chlorpyrifos. Maximum adsorption capacities were in the range $296.8 - 464.7 \text{ mg.g}^{-1}$, with Zr-MOF@cotton exhibiting the highest adsorption capacity for both pesticides. Nikou et al. (2021) prepared a MOF composite ZIF-8/GO, based on graphene oxide, which was also used as an adsorbent for diazinon and chlorpyrifos. The maximum adsorption capacity for both diazinon and chlorpyrifos, in this case, was found to be

54.3 mg.g⁻¹ and 47.2 mg.g⁻¹ respectively, which are significantly lower than the values observed by Abdelhameed and Emam (2022) for their composite cotton material. Abdelhameed et al. (2021b) synthesised a porous MOF composite based on cellulose acetate (Cu-BTC@CA). The surface area of the porous CA membrane was significantly increased by incorporation of Cu-BTC within the membrane from 347.2 m².g⁻¹ to 965.8 m².g⁻¹, while the maximum adsorption capacity for dimethoate increased from 207.8 mg.g⁻¹ to 321.9 mg.g⁻¹ on using the MOF composite rather than the CA membrane itself. Liang et al. (2021) constructed two MOF composites using multi-walled carbon nanotubes as the template to give two MOF-modified aerogel, ZIF8@MPCA and UiO66-NH₂@MPCA. The UiO66-NH₂@MPCA was better at the adsorption of the herbicides, chipton and alachlor, with maximum adsorption capacity values of 246.8 m².g⁻¹ and 232.8 m².g⁻¹, respectively. The authors ascribed the improved adsorption performance to be due to the large pore at the micron level of MPCA which enabled the fast adsorption of the herbicides.

MOF-derived nanoporous carbon (NPC) and carbon hybrid materials have received much attention recently for pollutant removal, because of their high surface area, versatile porous structure and ease of production (Yu et al., 2021). Zhao et al. (2022) synthesised a hollow MOF-derived NiO/Co@C magnetic nanocomposite using cobalt ions as inducers without the conventional preparation of Fe₃O₄. This nanocomposite was successfully used for the adsorption removal of six organic nitrogen pesticides from waste water. In a comparison with commercial materials (activated carbon, single walled carbon nanotube and multi-walled carbon nanotube), the extraction efficiency of the MOF-nanocomposite was significantly higher than those of the commercial materials, particularly for the pesticide chlorothalonil.

Although MOFs show promise in pesticide remediation from water, their competitiveness, in terms of cost, selectivity and reusability against other adsorbents, has to be taken into consideration.

2.5.2 Nanoparticles

Nanotechnology emerged as the scientific innovation of the twenty-first century (Jadoun et al., 2021). The use of nanoparticles for the removal of pesticides from water

have been reviewed in many articles (Ighalo et al., 2021; Nguyen et al., 2022; Shan et al., 2022; Kajitvichyanukul et al., 2022; Mehta et al., 2022; Intisar et al., 2022). Nanoparticles (NPs) are characterised by a large surface area, typically up to 2500 $\text{m}^2\cdot\text{g}^{-1}$, which gives them an adsorption rate considerably higher than that of conventional adsorbents. They are more active and faster in the removal and eradication of both inorganic contaminants and organic pollutants, such as pesticides. They have been used to either adsorb or degrade pesticides. Table 2.2 shows the most recently published material on the adsorption and degradation of prohibited pesticides by NPs.

While adsorption is a scalable and cost-effective method of eliminating pesticides, it has a major disadvantage of creating secondary waste as a result of the adsorption of the pesticides. Photocatalytic degradation is a more ecologically friendly technique, as the degradation process results in the transformation of the pesticides into less hazardous intermediates, which then degrade further to produce H_2O and CO_2 (Qumar et al., 2022). The photodegradation process is governed by the adsorption capability of the organic contaminants of the photocatalyst surface. However, to achieve a high photodegradation rate, the pesticide adsorption must also be effective. A further disadvantage of the degradation process is that degradation efficiency was found to be negligible in the absence of the photocatalyst, indicating that light intensity is an important factor influencing the efficiency process of the photocatalytic degradation of pesticides (Veerakumar et al., 2021; Adabavazeh et al., 2021).

Table 2.2. Summary of pesticide adsorption over nanoparticle materials.

NP type	Adsorbent	Pesticide	BET Surface area (m ² .g ⁻¹)	Total pore volume (cm ³ .g ⁻¹)	Max. capacity (mg.g ⁻¹)	Photocatalytic efficiency (%)	Reference
<i>Adsorption</i>	Biochar-alginate	Chlorpyrifos	131.09	0.165	6.25	-	Jacob et al., 2022
	Fe ₃ O ₄ @SiO ₂ @SBA- 3-SO ₃ H MMNP	Paraquat	67.15	0.141	14.7	-	Kouchakinejad et al., 2022
	AG-g-PAO/CuFe ₂ O ₄	Chlorpyrifos	1.03	-	769.2	-	Hassanzadeh-Afruzi et al., 2022
	Alum nWTR	Thiamethoxam	129	0.051	50.0	-	El-Kammah et al., 2022
	rGO@ZnO	Chlorpyrifos	79.51	0.065	-	-	Gulati et al., 2020
<i>Degradation</i>	Co-Fe ₃ O ₄ @UiO-66	Fenitrothion	202	0.385	23.6	96.6	Zheng et al., 2022
	Co ₃ O ₄ /MCM-41	Methyl parathion	623	0.53	175.2	100	Salam et al., 2020
		Ag@ZnONSt	Methyl parathion	39.72	0.398	-	100
	Pd@ZnONSt	Trifluralin	39.72	0.398	-	-	-
		Methyl parathion	32.34	0.375	-	100	-
		Trifluralin	32.34	0.375	-	-	-
	PANI/ZnO-CoMoO ₄	Imidacloprid	142.6	-	-	97.4	Adabavazeh et al., 2021
	FGD-20	Simazine	75.8	-	-	97	Boruah et al., 2021

2.5.3 Membrane removal of pesticides

Membrane processes, such as nanofiltration, reverse osmosis and forward osmosis are very efficient in the removal of microcontaminants, such as pesticides, from water sources (Fujioka et al., 2020; Khanzada et al., 2020). Vitola et al. (2021) developed a phosphotriesterase-loaded membrane which was capable of degrading the pesticide paraoxon-ethyl in vegetative water (defined as water provided by a mill producing extra virgin olive oil) containing biomolecules similar in size and structure to the pesticide. The stability of the phosphotriesterase-loaded membrane was four times higher in vegetative waters than the free enzyme. The immobilised enzyme also showed activity towards the pesticide degradation in vegetative water after four months, whereas the free enzyme showed activity for three weeks only.

Yang et al. (2022b) developed an NH₂-MIL-125 (Ti)-based filter paper membrane, which was used to remove organophosphorus pesticides, including fenitrothion, from aqueous solutions. The combination of the Ti-based MOF with the filter paper created a low-cost membrane which resulted in the rapid separation of samples and the removal of organophosphorus pesticides. When compared with the MOF itself, the filter paper membrane demonstrated the same removal efficiency of organophosphorus pesticides.

Khairkar et al. (2020) fabricated hydrophobic membranes for pesticide removal using polyamide-polydimethylsiloxane chemistries. These reverse osmosis membranes exhibited increased pesticide adsorption from the feed waters compared to commercial reverse osmosis membranes (95% removal of imidacloprid compared to 89% for the commercial membrane). The procedure for the synthesis of the membranes is cost effective and easy to incorporate into membrane manufacturing processes.

Lopes et al (2020) evaluated the potential of a membrane bioreactor to treat effluents from a fruit processing factory for the removal of pesticides. The removal efficiency of atrazine by the reactor was only partial (45%), which highlighted the requirement of other treatment technologies to get complete removal of the pesticide. When combining the membrane reactor with a post-treatment of activated carbon, the

removal efficiency increased to >99.9%, indicating that the membrane reactor in combination with an activated carbon post-treatment system was very successful.

Mohammed and Jaber (2022) synthesised a Pickering emulsion liquid membrane, using Fe_3O_4 nanoparticles and oleic acid, for the extraction of Abamectin from aqueous solutions. Extraction percentages of 99% were obtained in 10 minutes, with minimal breakage percentage. The membrane could be recycled for three cycles with no loss of extraction capability. Krishnan et al. (2022) modified a polyvinylidene fluoride (PVDF) membrane with either an amine or a bismuth tungstate (BWO) modified MOF for the reduction and photodegradation of pirimicarb. The BWO-modified MOF membrane showed the best removal of the pesticide (84%) and also the best photocatalytic degradation of the pesticide (86%).

2.5.4 *Semiconductors*

Semiconductor-assisted photocatalysis, based on the use of TiO_2 , is a well-studied, advanced oxidation process for the degradation of pollutants, including pesticides (Luna-Sanguino et al, 2020; Shafiee et al., 2022). Some of the advantages of this semiconductor are its cheap price, stability and chemical and biological inertness. Zeshan et al. (2022) discuss the basic mechanism of TiO_2 -based photocatalysis, types of reactors used for photocatalysis, and conditions for pesticide demineralisation into non-hazardous compounds, such as CO_2 and H_2O . They demonstrated that advancements in the characteristics of TiO_2 -based photocatalysts by doping or composites enhanced the efficiency of mineralisation. They also showed that TiO_2 -based photocatalysts mineralised the pesticides more efficiently in natural sunlight, thereby promoting their potential use in pilot-scale experiments.

2.5.5 *Vegetated buffers*

Vegetated buffer strips (VBS) can protect streams and other wetland habitats, as well as improving water quality (Lovell and Sullivan, 2006). A vegetated buffer strip is defined as an area of land located between land used for agriculture and land not in agricultural production (e.g., forest, stream, river, pond). A VBS can decrease the

amount of pesticide transported to surface water from fields during rainfall (Wang et al., 2018).

Villamizar et al. (2020) reported a study of mitigation approaches to compare the efficacy of propyzamide removal in a 900-ha headwater catchment. They observed that increasing the VBS to 20-m-width would be the most effective mitigation intervention. Prosser et al. (2020) reviewed the efficacy of VBS to reduce pesticide transport into surface waters from agricultural fields, and found that it varied widely, ranging from 10 to 100%. They also observed that the majority of studies investigating the ability of VBS to limit pesticide transport had studied herbicides (89%). Whilst the study of the transport of fungicides and insecticides is limited, the authors believed that the buffers would be as effective at mitigating the transport of fungicides and insecticides as they were at limiting the transport of herbicides (Prosser et al., 2020). Lorenz et al. (2022) showed that the presence of VBS contributed to a reduction in pesticide risk compared to when no VBS were present. Furthermore, they demonstrated, through the use of modelling, that the risk to freshwaters was reduced by 29%, if a 5-m buffer strip was used, and 47%, if a 10-m buffer strip was used. Andrade et al. (2021) demonstrated that the pesticide concentration found in run-off water depended on the pesticide solubility, the slope of the streams and the percentage of woody riparian vegetation cover, and that all of these factors should be taken into account when designing mitigation measures for the run-off of pesticides. Butkovskiy et al. (2021) evaluated the use of novel bed mixtures, consisting of pumice, vermiculite and water super-absorbent polymer (SAP), for the retention of ionic and water soluble pesticides in unplanted and planted pot experiments. They observed that mixtures of all three materials resulted in high retention of both hydrophobic and hydrophilic pesticides, but with lower leaching potential compared to systems without SAP. They suggested that mixtures of such materials would provide treatment options in VBS.

Le Cor et al (2021) demonstrated the buffering effect of a pond, as a VBS. Upstream of the pond, ecotoxicological standards were exceeded with pesticide concentrations of up to $23.9 \mu\text{g.l}^{-1}$, while downstream of the pond, the concentration of the pesticides reduced by 90% with few exceedances and a maximum concentration of $0.5 \mu\text{g.l}^{-1}$, reflecting significant water quality improvement. Chaumet et al. (2022) also demonstrated the buffering effect of a pond, which reduced between 29 and 56% of

the targeted pesticide molecules (metolachlor, boscalid, epoxiconazole, tebuconazole, aclonifen, and pendimethalin). They argued that riparian wetlands should be among the beneficial suggestions for agricultural land management, which could be further enhanced by promoting vegetation as an alternative route to pesticide retention or degradation.

2.6 Management implications across Europe

Following the introduction of the EU Directive on Sustainable Use of Pesticides (SUD) in 2009 (EU, 2009b), many papers have been published regarding measures for reducing pesticide use. A recent review focussed on the effectiveness of public policy instruments in reducing pesticide use by farmers in Europe (Lee et al., 2019). Bans, zoning, monitoring and penalties were placed in the regulatory domain, while those of the certification, training, and advisory services were in the informative domain. While the review determined that no specific instrument was guaranteed to reduce pesticide use, they suggested that measures were frequently identified as ineffective if based on the sole use of regulatory-based instruments, namely bans and prescriptions (maximum doses or pesticide levels). On the other hand, prescriptions and subsidies, prescriptions and advisory services, or prescriptions, taxes, training, monitoring and advisory services, were seen as most beneficial to pesticide reduction.

In a separate review of pesticide monitoring to assess surface water quality, Chow et al. (2020) attributed a reduction in pesticide use as the main factor linked to reductions in aquatic pesticide concentration. The reduction in pesticide use included bans and use restrictions. While the restriction or banning of a pesticide is a powerful mitigation measure, directly affecting the quantity of pesticide available for transport to surface waters, the benefits can be obscured if a banned pesticide is simply replaced by another pesticide. Furthermore, the effectiveness of a pesticide use regulation depends on the quantity of pesticide that a farmer uses, which is influenced by both the weather conditions and pest pressure.

As previously mentioned, the latest Farm to Fork strategy (EU, 2020) aims to cut chemical pesticide use across the EU-27 by 50% in 2030. To achieve this, the Commission intends to “revise the Sustainable Use of Pesticides Directive (EU,

2009b), enhance provisions on integrated pest management (IPM) and promote greater use of safe alternative ways of protecting harvests from pests and diseases” (EU, 2020). The IPM will be one of the main tools in reducing the use and dependence on chemical pesticides. One approach, that is intended to achieve this goal, is the placing of pesticides containing biologically-active substances on the market. In a recent EU factsheet, it was noted that, although member states had made progress implementing the SUD, fewer than one in three states had completed the review of their National Action Plan within the five-year legal deadline (EU, 2021a).

The target of reducing chemical pesticide use by 50% by 2030 has come under attack from pesticide and agribusiness lobbyists, who claim that the target is overly ambitious and unrealistic for EU farmers to achieve (Save bees and farmers, 2020). The pesticide industry also called for an impact assessment to be made that would look at possible negative effects of the legislation on EU agriculture. The call for an impact assessment has been supported by a large number of EU member states. In response, the EU Commission has said that not enough was being done to reduce the level of pesticide usage across the EU by member states, resulting in the proposed strategy (Save bees and farmers, 2020).

Farm Europe is a multicultural think tank that aims to stimulate thinking on rural economies and which focuses on all EU policy areas that impact on rural business (FarmEurope, 2021). They develop their own analyses and innovative solutions and have recently reported that the impact of the Farm to Fork strategy (EU, 2020) on the agricultural sector across Europe will cause revenues of farmers to plummet by up to € 5,000 on average per holding (FarmEurope, 2021). They also believe that the EU net trade position will worsen, and that there will be an increase in producer prices that would cost consumer prices to rise across the EU (FarmEurope, 2021). They believe that, as a result of this strategy, agricultural sectors will face massive restructuring, with the abandonment of the least productive lands and a huge reduction in the number of farm holdings (FarmEurope, 2021). A report from the Economic Research Service of the United States Department of Agriculture reported that, if the Farm to Fork Strategy was implemented by the EU, the impacts would include a decline in agricultural production by up to 12%, an increase in food costs, and a significant reduction in the EU’s gross domestic product (GDP: ERS USDA, 2020).

There has been considerable media coverage regarding the 50% chemical pesticide reduction by the year 2030. However, the positive messaging, as proposed by the EU Commission, has largely been lost. This would suggest that the informative instrument, discussed by Lee et al. (2019), has not worked properly and now it appears as if the EU Commission is trying to force this strategy through by means of regulation instruments.

2.7 Conclusions

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

Amongst several emerging mitigation methods for the removal of pesticides from water, MOFs are among the most promising, due to their well-defined pore structure and high surface areas. One disadvantage that all adsorbent materials have is the removal of the pesticides from the adsorbents, and the interactions of the cleaning materials with the pesticides requires further exploration. The most cost-effective method is the use of VBS to protect streams and other wetland habitats as well as improving water quality. Buffer strips of at least 5 m width are appropriate to substantially reduce the risk to freshwaters posed by pesticide use. Further research is required to investigate the applicability and cost-effectiveness of potential remediation processes of pesticides on larger scales.

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Chapter 3 – An Assessment of potential pesticide transmission, considering the combined impact of soil texture and pesticide properties: A meta-analysis

This chapter presents a screening tool based on soil texture-specific adsorption isotherm data and the pesticide properties of water solubility, soil half-life and soil permeability. The screening tool allows the farmer to see if the pesticide of choice for the required job was environmentally friendly or if, through its use, there was a potential threat to the environment.









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RESEARCH ARTICLE

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An assessment of potential pesticide transmission, considering the combined impact of soil texture and pesticide properties: A meta-analysis

John McGinley¹  | Jenny Harmon O'Driscoll²  | Mark G. Healy¹  |
Paraic C. Ryan²  | Per Eric Mellander³  | Liam Morrison⁴  | Oisín Callery⁴  |
Alma Siggins^{1,3} 

John McGinley collected, reviewed, analysed, and extracted relevant information from the scientific papers, and is the primary author of this article. Prof Mark G. Healy contributed to the conceptualisation and the writing of the paper. Dr Alma Siggins contributed to the conceptualisation and the writing of the paper. Jenny Harmon O'Driscoll contributed through the development of risk ranking tables. Dr P. C. Ryan contributed to the review and writing. Dr P.-E. Mellander contributed to the review and writing. Dr L. Morrison contributed to the review and writing. Dr O. Callery contributed to the review and writing. Supplementary information for this paper is included in Appendix B.

**An assessment of potential pesticide transmission, considering the combined
impact of soil texture and pesticide properties: A meta-analysis**

J. McGinley¹, J. Harmon O'Driscoll², M. G. Healy¹, P. Ryan², P.-E. Mellander³, L. Morrison⁴, O. Callery⁴, A. Siggins^{1,3,*}.

¹ Civil Engineering and Ryan Institute, National University of Ireland Galway, Galway, Ireland.

² Civil and Environmental Engineering, University College Cork, Cork, Ireland.

³ Teagasc Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland.

⁴ Earth and Ocean Sciences, School of Natural Sciences and Ryan Institute, National University of Ireland Galway, Galway, Ireland.

* Corresponding author.

Abstract

Pesticides are widely employed as a cost-effective means of reducing the impacts of undesirable plants and animals. The aim of this paper is to develop a risk ranking of transmission of key pesticides through soil to waterways, taking into account physico-chemical properties of the pesticides (soil half-life, and water solubility), soil permeability, and the relationship between adsorption of pesticides and soil texture. This may be used as a screening tool for land managers, as it allows assessment of the potential transmission risks associated with the use of specified pesticides across a spectrum of soil textures. The twenty eight pesticides examined were differentiated into three groups: herbicides, fungicides and insecticides. The highest risk of pesticide transmission through soils to waterways is associated with soils containing <20% clay or >45% sand. In a small number of cases, the resulting transmission risk is not influenced by soil texture alone. For example, for Phenmedipham, the transmission risk is higher for clay soils than for silt loam. The data generated in this paper may also be used in the identification of critical source areas, which have a high likelihood of pesticide transmission to waterways. Furthermore, they have the potential to be applied to GIS mapping, where the potential transmission risk values of the pesticides can be layered directly onto various soil textures.

Keywords: Adsorption; Freundlich isotherm; half-life; pesticides; soil texture.

3.1 Introduction

A pesticide is any substance, plant protection product or biocide, that is used to repel, control or kill organisms that are considered to be pests (DAFM, 2017). The umbrella term “pesticides” includes herbicides, fungicides, insecticides, molluscicides, bactericides and rodenticides (Mojiri et al., 2020). In Europe, total annual pesticide sales during the period 2011 to 2016 rose from 386,400 to 439,400 tonnes of active ingredients, with France, Spain, Italy and Germany collectively accounting for 80% of the European market (Peña, 2020). In line with increases in global population, the use of pesticides in agriculture has increased to improve crop yields and production rates (Gavrilescu, 2005; Morillo and Villaverde, 2017). While this intensified pesticide application has been beneficial in preventing hazardous diseases in agricultural crops (Maggi et al., 2020), it has also amplified the contact of these compounds with soil (Morillo and Villaverde, 2017), air (Raheison et al., 2019) and aquatic environments (Burri et al., 2019), and increased the risk of subsequent human exposure. This has resulted in human health issues, such as neurological, respiratory and carcinogenic effects (Van Maele-Fabry et al., 2017; Ye et al., 2017; Pouchieu et al., 2018). In 2007, globally, there was an estimated 258,000 deaths from pesticide self-poisoning (WHO, 2016).

It has been suggested that, under “worst case” scenarios, such as improper handling and unfavourable weather condition, as little as 1% of applied pesticides may reach their target organism, with the remainder entering soil and water environments (Ali et al., 2019), *via* direct losses, runoff, spray drift, or leaching (Álvarez-Martín et al., 2017; Cosgrove et al., 2019; Haddad et al., 2019; Mojiri et al., 2020), resulting in contamination of surface water or groundwater (Rojas et al., 2014). The European Environment Agency (EEA) reported that, of the 73,510 natural water bodies with known chemical and ecological status in the European Union (EU), 25,108 failed to achieve good chemical status (EEA, 2018), due to hydromorphological pressures, diffuse water pollution from agricultural practices, waste water treatment plants and sewage systems, as well as high inflow of nutrients and chemical contaminants including pesticides leading to accelerated loss of biodiversity (EEA, 2016).

Mathematical models are now widely used to predict the fate and transport of pesticides in the environment (Hartz et al., 2017; Bach et al., 2017; Rumschlag et al., 2019; D'Andrea et al., 2020). Modelling presents an appealing alternative to environmental monitoring, which is costly and time-consuming. Modelling is fast, cost effective and can predict how soil and climate conditions may affect, for example, the environmental fate of pesticides (Bach et al., 2017; McGrath et al., 2019). The main factors influencing the transport of pesticides to receptors are soil half-life (DT_{50} ; Fantke et al., 2014), adsorption and desorption to and from soil particles (Paszko and Jankowska, 2018), and physico-chemical properties of soil (Boivin et al., 2005). The adsorption of pesticides on the soil surface determines how pesticides are either transported or degraded, which ultimately determines the concentration of pesticides in both soil and soil solution (Gondar et al., 2013). Adsorption is predominantly influenced by the properties and chemical composition of the soil, which is a complex mixture of inorganic materials and organic matter (Leovac et al., 2015), and the physico-chemical properties of the pesticide (Kodešová et al., 2011). The relationship between the organic content of the soil and pesticide adsorption has been well examined in the literature (Rojas et al., 2013; Wei et al., 2015; Wu et al., 2018). However, the organic content of soil changes with time (Smith, 2004), meaning that it may not be a reliable metric for determining areas of high risk of pesticide loss in agricultural land management. The organic content of soil is also difficult to map, as it depends on soil and crop management practices. Conversely, the texture of the soil will remain more or less constant over time (Brouwer et al., 1985). A database of existing studies quantifying the relationship between adsorption of pesticides and the texture of the soil, using adsorption isotherm coefficients as a metric, could be a valuable tool in screening and in decision management protocols for the safe use of pesticides on certain soil textures. Although many soil factors have been investigated with regard to pesticide adsorption, including pH (Kodešová et al., 2011; Gondar et al., 2013), organic content (Boivin et al., 2005; Conde-Cid et al., 2019), pore size (Siek and Paszko, 2019), and cation exchange capacity (Kodešová et al., 2011), to date no study has conducted a meta-analysis of the literature that investigates the relationship between pesticide adsorption and soil texture.

Pesticide transport models used for national pesticide registration and licensing in the European Union, such as the FOCUS group's PRZM modelling approach, are highly complex models which take hours to run for a single pesticide (European Soil Data Centre 2022a,b). Complex and data-hungry pesticide transport modelling software, as is used for pesticide licensing and registration in the EU, is not realistic or suitable for use by small-scale pesticide users or localised pesticide management projects. Instead a quick and easily applied screening tool, such as that which is outlined in this paper, is proposed as a more practical tool for pesticide users in this case.

Therefore, the aim of this paper is to conduct a meta-analysis of literature that has assessed pesticide adsorption and soil texture data, and integrate this with pesticide properties such as soil half-life and solubility, in order to determine if a relationship exists that could guide future modelling and decision-making protocols regarding the safe use of pesticides. This information may be used in the identification of critical source areas, which would have a high likelihood of pesticide transmission to groundwater, or as an application in GIS mapping where the potential groundwater transmission risk values of the pesticides can be layered directly onto the various soil textures.

3.2 Materials and Methods

3.2.1 Literature review methodology, pesticide selection and grouping

A detailed literature search was undertaken by searching key words including: pesticide, soil, adsorption, sorption, adsorption isotherm, and soil texture triangle. The search was limited to peer-reviewed papers published, in English, since 2000 that included data on adsorption isotherm parameters and soil texture. Several reports were found in languages other than English (see, for example, Regitano et al., 2002; Rocha et al., 2013) but, as these did not meet the criteria outlined above, they were not included. No geographical limitations were employed. Search engines used included databases such as Scopus, as well as publisher-specific search engines including ScienceDirect, the American Chemical Society, and the Royal Society of Chemistry. References from several papers found in these searches were also examined for relevant information. Research papers were selected based on the relevance to the

review, with a target on the most commonly used pesticides in articles. A total of 1212 articles and a small number of book chapters and reports were reviewed.

Following this, the pesticides were ranked according to the number of studies in which they were investigated and they also had to be currently approved for use by the EU. This resulted in a short-list of 54 publications, reporting on the 28 most commonly studied pesticides, which are still available for use and are not banned in the EU or elsewhere. These 28 pesticides were grouped into herbicides, fungicides and insecticides, with no molluscicides, bactericides or rodenticides present in that group.

3.2.1.1 *Herbicide group*

Herbicides are chemical agents which are used to kill or inhibit unwanted plants or weeds (Thiour-Mauprivex et al., 2019; Oliveira et al., 2020). They can act as contact herbicides, which kill only the plant parts contacted by the chemical agent, or as systemic herbicides, which are absorbed through the roots or leaves of the plant and then moved to a different location within the plant. Furthermore, herbicide activity can be selective or non-selective. Selective herbicides kill unwanted plants without critical damage to the preferred plants. On the other hand, non-selective herbicides kill or injure all plants present. This study assessed seventeen different herbicides, employed to protect a range of crops, by targeting different weed species (Table 3.1).

3.2.1.2 *Fungicide group*

Fungicides can work preventatively or curatively, by either preventing the fungus from infecting the plant, or by partially or entirely treating an existing fungal infestation (Tleuova et al., 2020; Zhang et al., 2020). Like herbicides, they can act as contact fungicides, preventing the fungus from entering the plant, or as systemic fungicides, which are internalised by the plant and are then moved to a different site within the plant. This study assessed the transmission risk of eight different fungicides (Table 3.1).

Table 3.1. Applications, target pests, and physico-chemical properties of selected pesticides.^a

	Pesticide	Crop/Site	Target Pest	MW	Sw	Log Kow	DT ₅₀ lab
Herbicide	2,4-D	Cereals, grass, amenity use	Broad-leaved weeds	221.04	24300	-0.82	4.4
	Bensulfuron-methyl	Cereals	Weeds, sedges	410.4	67	0.79	77
	Bentazone	Cereals, vegetables	Annual weeds	240.3	7112	-0.46	20
	Chlorotoluron	Cereals, vegetables, fruit	Broad-leaved weeds, grasses	212.68	74	2.5	45
	Dimethenamid-P	Vegetables, vineyards	Broad-leaved weeds, grasses	275.8	1499	1.89	12.1
	Ethofumesate	Beet, vegetables	Broad-leaved weeds, grasses	286.34	50	2.7	21.6
	Glyphosate	Agriculture, horticulture, amenity use	Broad-leaved weeds, grasses	169.1	10500	-3.2	15
	Isoxaflutole	Crops	Broad-leaved weeds, grasses	359.32	6.2	2.34	0.9
	Lenacil	Beet, vegetables, fruit	Broad-leaved weeds, grasses	234.29	2.9	1.69	49.7
	MCPA	Cereals, grass	Broad-leaved weeds, rushes	200.62	29390	-0.81	24
	Mecoprop-P	Cereals, grass, amenity use	Broad-leaved weeds	214.65	250000	-0.19	5.24
	Metamitron	Beet crops	Broad-leaved weeds, grasses	202.21	1770	0.85	19
	Metribuzin	Cereals, vegetables	Broad-leaved weeds, grasses	214.29	10700	1.75	7.03
	Metsulfuron-methyl	Cereals, land removed from production	Broad-leaved weeds	381.36	2790	-1.87	23.2
	Pendimethalin	Cereals, vegetables, vineyards	Broad-leaved weeds, grasses	281.31	0.33	5.4	182.3
Phenmedipham	Beet, vegetables	Broad-leaved weeds	300.31	1.8	2.7	12	
Terbuthylazine	Cereals, vegetables, non-crop sites	Broad-leaved weeds, grasses, slime-forming algae	229.71	6.6	3.4	72	
Fungicide	Azoxystrobin	Cereals, vegetables	Broad-spectrum	403.4	6.7	2.5	84.5
	Metalaxyl	Many agricultural crops	Air- and soil-borne <i>Peronosporales</i>	279.33	8400	1.75	7.1
	Metalaxyl-M	Potatoes, vegetables	Air- and soil-borne pathogens	279.33	26000	1.71	6.5
	Myclobutanil	Perennial and annual crops, fruit, vines	Ascomycetes, Fungi and Basidiomycetes	288.78	132	2.89	365
	Penconazole	Vines, fruit, vegetables	Fungal pathogens	284.18	73	3.72	117.2
	Pyrimethanil	Fruit, vegetables, nuts	Fungal pathogens	199.28	110	2.84	50.9
	Tebuconazole	Cereals, vegetables, vines	Foliar diseases	307.82	36	3.7	365
	Thiabendazole	Cereals, fruit, vegetables	Post-harvest fungicide	201.25	30	2.39	1000
Insecticide	Abamectin	Fruit, vegetables	Selective acaricide, nematicide and insecticide	866.6	0.02	4.4	25.3
	α -Cypermethrin	Cereals, vegetables, beet, fruit, grassland	Broad spectrum	416.3	0.009	5.55	22.1
	Deltamethrin	Cereals, fruit, vegetables, public and industrial buildings	Wide range of sucking and chewing pests	505.2	0.0002	4.6	28.2

^a: Pesticide properties database online (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>). MW, Molecular weight (g mol^{-1}); S_w , water solubility (20°C , mg l^{-1}); K_{ow} , Octanol-water partition coefficient at pH 7, 20°C ; DT_{50} lab, 50% dissipation time under laboratory conditions (days).

3.2.1.3 *Insecticide group*

Chemical insecticides are employed to control harmful insects, as a result of either killing the insect or preventing it from doing destructive damage to plants. During the 1950s, the majority of insecticides operated from four different chemical groups (DDT and analogues, Organophosphates, Carbamates and Cyclodienes) using three modes of action (Sparks et al., 2019). These modes of action were inhibition of the acetylcholinesterase, modulation of the voltage-gated sodium channel and blockage of the *gamma*-aminobutyric acid-gated chloride channel (Sparks et al., 2019). By 2019, this number had increased to 25 different modes of action based on 55 different chemical classes (Swale, 2019). The current study assessed the transmission risk of three insecticides (Table 3.1). The number of insecticide studies included in our meta-analysis is low due to the small number of studies that fulfilled our criteria of (i) including an approved insecticide and (ii) reporting soil texture data.

3.2.2 *Adsorption modelling*

The manuscripts that fulfilled the selection criteria of this study (Supporting Information Excel file) modelled their experimental data using the Freundlich adsorption isotherm, with some also reporting the parameters of the Langmuir adsorption isotherm. The main assumption of the Langmuir adsorption isotherm model is monolayer adsorption, so all potential adsorption sites are treated equivalently (Langmuir, 1918). The Freundlich adsorption model can better describe adsorption on a heterogeneous surface (Freundlich, 1907) and is commonly used to describe pesticide adsorption in soil (Hiller et al., 2012; Papadopoulou et al., 2016; Wang et al., 2020), implying that monolayer adsorption is not representative of pesticide adsorption in soil. To facilitate comparative analysis within this paper, only the Freundlich model was used for determination of the adsorption isotherm coefficients. The Freundlich isotherm model is:

$$q_e = K_F C_e^{1/n} \quad (1)$$

where q_e is the amount of adsorbate adsorbed at the equilibrium ($\text{mg}\cdot\text{g}^{-1}$) and C_e is the concentration of the adsorbate at the equilibrium ($\text{mg}\cdot\text{L}^{-1}$); K_F is the Freundlich sorption capacity coefficient ($\text{mg}\cdot\text{g}^{-1}(\text{mg}\cdot\text{L}^{-1})^{-1/n}$) and the exponent n is the Freundlich exponent (dimensionless) (Lima et al., 2015). The adsorption of pesticides on soils

can be described using the linear form of the Freundlich equation (Papazlatani et al., 2019):

$$\log q_e = \log K_F + 1/n * \log C_e \quad (2)$$

The Freundlich sorption capacity coefficient K_F ($\text{mg.g}^{-1}(\text{mg.L}^{-1})^{-1/n}$) represents the pesticide affinity for soil, with a high K_F value indicating a stronger adsorption for the pesticide and also suggesting a lower mobility of the pesticide in the soil (Wang et al., 2020).

3.2.3 Pesticide transport potential ranking

The movement of pesticides from the target crop through the soil and to the water receptor is a function of soil permeability (m.s^{-1}), the adsorption capacity of each soil texture for the investigated pesticide (g.m^{-3}), soil half-life of the pesticide (DT_{50} , days) and the pesticide solubility in water (S_w ; mg.L^{-1}). In order to establish a soil texture-specific transport potential risk ranking for each of the pesticide groups examined in this study, a ranking system incorporating each of these parameters was developed with the highest value indicative of the greatest risk of transmission to receiving waters. The permeability of soils is well documented and was ranked according to soil texture (USDA, 2001). Soil adsorption values were generated from the median value for each pesticide/soil texture association reported in the literature (Supplementary Information, Excel file and Table B.1). The water solubility and soil half-life values were obtained from the Pesticide Properties DataBase (Tables B.S2 and B.S3, respectively; Lewis et al., 2016). Using this rubric, each parameter was independently ranked from one to twelve, where twelve was considered to be the highest risk for pesticide mobility through soil to surface and groundwater bodies, i.e. high permeability soils, low pesticide adsorption capacity, high soil half-life and high water solubility. In this study, high permeability soils were considered to be most at risk for surface and groundwater pollution. If surface water processes were only considered, low permeability soils, which would have large surface runoff potential relative to surface flow, would be considered to be most at risk. Finally, these independent risk values were combined (with equal weighting) to give a final risk ranking for each pesticide across all soil textures, but also for all of the pesticides within an individual soil texture classification.

3.3 Results and Discussion

3.3.1 *Variances in adsorption as a function of soil texture*

Table 3.2 shows the potential pesticide transmission risks as a function of water solubility, soil half-life, adsorption by soil of the pesticide and also soil texture. The potential transmission risk can be quantified either on the basis of soil texture or pesticide type, with the highest score in each case being the most transmissible.

It is unfortunate that there are not complete adsorption isotherm data studies across the soil texture triangle for each of the selected herbicides, fungicides and insecticides. These data would facilitate a better understanding of the potential pesticide transmission risk across all soil textures. Given the current findings, it is impossible to assess the potential transmission risk of pesticides in silt or sandy clay, as no data are available for silt and only limited data are available for silty clay textures.

The highest potential transmission risk ranking for each individual pesticide across all herbicides, fungicides and insecticides shows that the soil textures resulting in highest transmission risks are sandy loam and sand, with nineteen of the highest rankings being in one of these two soil textures (Table 3.2). These two soil textures have low clay content (<20%), implying that a high clay content is important in the retention of pesticides within the soil, as previously reported (Vitoratos et al., 2016; Ren et al., 2018; García-Delgado et al., 2020). This is in agreement with Komárek et al. (2010), who highlighted that the possible factors influencing pesticide adsorption were physico-chemical properties of the pesticides and soil properties, such as particle size, soil organic matter and clay content. Komárek et al. (2010) also states that generalising the behaviour of fungicides in soil is difficult to predict, given the different sorption, mobility and toxicity properties each will have, which is inferred from their different chemical structures.

Table 3.2. Pesticide transmission risk rankings^a

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

^a: Total transmission risk ranking = Risk rankings for Permeability + Adsorbency + Solubility + Half-life (Table B.5). The higher the score, the higher the risk for transmission through soil to waterways. The colour of the ranking value indicates the likelihood of potential transmission risk, with red being most likely and green being least likely.

ElGouzi et al. (2012) showed, in their work on adsorption of phenylurea pesticides by Mediterranean soils, that soils with relatively high clay content were better at pesticide retention. García-Delgado et al., (2020) suggest that the addition of organic amendments to soils, such as spent mushroom substrate, compost, manure or sewage sludge, is an effective method of immobilising pesticides in the soil as a result of increasing the organic content of the soil. Furthermore, both of these soil textures have a high sand content (>45%), which would suggest that soil textures having a high sand content are also susceptible to high potential transmission risk of pesticides.

The potential risk ranking values (Table 3.2) for the herbicide group range from 36 (for Chlorotoluron in sand) to 13 (for Isoxaflutole in silty clay). The majority of high values (>30), shown in red and orange, reside in the left hand side of Table 3.2. The soil textures in this group of sand, loamy sand, sandy loam, sandy clay loam, loam and sandy clay all have a sand content of $\geq 50\%$, except for the loam texture where the sand content is 25%. This would imply that there is a high risk of herbicide transmission if the soil contains a high sand content. Although limited adsorption data are available in the literature for the three herbicides with the highest solubility (Mecoprop-P, MCPA and 2,4-D), the trends observed for other pesticides indicate that it is likely that these herbicides would pose a high transmission risk in either sand or loamy sand textured soils.

There are two different ways that the data in Table 3.2 can be interpreted. The data can be viewed from the point of view of the pesticide. Considering the herbicide chlorotoluron, for example, the potential risk ranking varies from 36 in sand to 17 in clay. Therefore, the soil textures most likely to transmit chlorotoluron may be identified. Alternatively, the data may be examined considering only soil texture. Within sandy loam soils, for example, MCPA, Mecoprop-P, Bentazone, Metamitron and Metribuzin are some of the highest risk herbicides, with ranking values of 35, 34, 34, 35 and 34, respectively (Table 3.2). As Pendimethalin, also used for the removal of broad-leaved weeds from cereals (Table 3.1), has a much lower transmission ranking value in sandy loam soils (24, Table 3.2), it might be more appropriate for selection when applying to this soil texture. In a similar manner, the choice of Terbutylazine (14, Table 3.2) would be appropriate, when considering removing

broad-leaved weeds and grasses from cereal and vegetable crops in clay soil, than any of the other herbicides in this study (16-27, Table 3.2).

In the case of the selected fungicides, the majority of high values (>30) reside in the left hand side of Table 3.2. Indeed, Metalaxyl-M has equally high potential transmission risk rankings across the range of soil textures. Furthermore, transmission risks are available for most fungicides for sandy loam soils (Table 3.2). As the transmission risk of Azoxystrobin was deemed to be the lowest of the eight fungicides (Table 3.2), then the selection of Azoxystrobin for application on sandy loam soils could be proposed as a management tool to minimise the risk of fungicide transmission through soil to waterways. Specifically, Tebuconazole (27, Table 3.2) could be a suitable alternative to Metalaxyl or Metalaxyl-M (38 and 30, Table 3.2) for the control of air-borne pathogens of vegetables grown in sandy loam soil (Table 3.1).

Of the three insecticides, Deltamethrin has the higher transmission risk rankings across all textures (Table 3.2). The transmission risk for Abamectin was much greater in sandy soils (21, Table 3.2) than in clay soils (9, Table 3.2), again demonstrating the potential for applying the proposed transmission risk ranking scheme to pesticide selection and management. Consideration of the reported transmission risk ranking, based on soil texture, crop and target pest, will contribute to decision making practices for safer pesticide use.

3.4 Conclusions

Using soil texture-specific adsorption isotherm data for several groups of pesticides, their solubility in water, soil half-life and soil permeability, a transmission risk ranking was developed in this study. This is designed as a decision making support tool for agricultural land management, as it allows the agricultural sector to assess, either by soil texture or pesticide type, the risk of loss of pesticides to receptors. Whilst this is a simple decision making support tool, rather than the more complicated and complex PRZM modelling approach (European Soil Data Centre 2022b), it offers a manageable choice for the end user. It is also useful for modelling the loss of pesticides to water and for identification of critical source areas for better land management. The risk ranking index demonstrated specific examples of support for decision making, such

as that pendimethalin is a lower transmission risk option than MCPA, Mecoprop-P, Bentazone, Metamitron and Metribuzin in the removal of broad-leaved weeds from cereal crops. It has also illustrated that the fungicide, Azoxystrobin, is a lower transmission risk alternative to either Metalaxyl or Metalaxyl-M in sandy loam soil.

The risk ranking index indicated that there is a high risk of transmission of pesticides from soils containing <20% clay. Furthermore, the data suggest that, if the soil content contains more than 45% sand, then there is a much higher risk of potential pesticide transmission. There are several reports in the literature discussing the movement of pesticides through soil. However, the aim of this paper was to develop a tool that the farmer could easily access to see if the pesticide of choice for the required job was environmentally friendly or if there was a potential threat to the environment through its use. Further analysis should be undertaken to examine potential transmission risk rankings of pesticides not selected in this review, across all soil textures.

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Chapter 4 – Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon

This chapter presents the assessment of the potential of several raw and pyrolysed low-cost industrial and agricultural materials as pesticide adsorbents for the removal of commonly used herbicides in Ireland. GAC removed all the herbicides with >95 % efficiency, while the raw materials demonstrated little capacity for herbicide adsorption.

The contents of this chapter have been published in the Journal of Environmental Management (McGinley et al., 2022. Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon, 323, 116102-116109).



Research article

Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon



J. McGinley^a, M.G. Healy^a, P.C. Ryan^{b,c}, P.-E. Mellander^d, L. Morrison^e,
J. Harmon O'Driscoll^b, A. Siggins^{a,d,*}

John McGinley developed the experiment design, retrieved and analysed all samples derived from it, and is the primary author of this article. Prof Mark G. Healy contributed to the conceptualisation and the writing of the paper. Dr Alma Siggins contributed to the conceptualisation and the writing of the paper. Dr P. C. Ryan contributed to the review and writing. J. Harmon O'Driscoll contributed to the review and writing. Dr P.-E. Mellander contributed to the review and writing. Dr L. Morrison contributed to the review and writing. Supplementary information for this paper is included in Appendix C.

Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon

J. McGinley¹, M. G. Healy¹, P. C. Ryan^{2,3}, P.-E. Mellander⁴, L. Morrison⁵, J. Harmon O'Driscoll², A. Siggins^{1,4,*}.

¹ Civil Engineering and Ryan Institute, National University of Ireland Galway, Galway, Ireland.

² Discipline of Civil, Structural and Environmental Engineering, School of Engineering, University College Cork, Ireland.

³ Environmental Research Institute, University College Cork, Cork, Ireland

⁴ Teagasc Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland.

⁵ Earth and Ocean Sciences, School of Natural Sciences and Ryan Institute, National University of Ireland Galway, Galway, Ireland.

* Corresponding author.

Abstract

This study reports the kinetics and isotherms of the adsorption of five herbicides, MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr, from aqueous solutions onto a range of raw and pyrolysed waste materials originating from an industrial setting. The raw waste materials investigated demonstrated little capability for any herbicide adsorption. Granulated activated carbon (GAC) was capable of the best removal of the herbicides, with >95% removal observed. A first order kinetic model fitted the data best for GAC adsorption of 2,4-D, while a pseudo-first order model fitted the data best for GAC adsorption of fluroxypyr and triclopyr, indicating that adsorption was *via* physisorption. A pseudo-second order kinetic model fitted the GAC adsorption of MCPA and mecoprop-P, which is indicative of chemisorption. The adsorption of the herbicides in all cases was best described by the Freundlich model, indicating that adsorption occurred onto heterogeneous surfaces.

Keywords: Herbicides; UV-vis spectroscopy; adsorption; kinetics; isotherm.

4.1 Introduction

A global population increase has necessitated an intensification of agricultural practices in order to achieve improved crop yields and production rates (Morillo and Villaverde, 2017). This has been accomplished, in part, by increased pesticide usage (Gavrilescu, 2005; Morillo and Villaverde, 2017; Khalid et al., 2020). Total annual pesticide sales in Europe during the period 2011 to 2016 rose by approximately 14% from 386,400 to 439,400 tonnes of active ingredients (Peña, 2020). In the United States, the use of the broad spectrum herbicide glyphosate has risen by approximately 197 times from 635 tonnes in 1974 to 125,000 tonnes in 2014 (Zhang et al., 2019). While increased pesticide application has been beneficial in preventing hazardous diseases in crops, improving yields, and maintaining the economic viability of agriculture (Maggi et al., 2020), it has also increased the risk of subsequent human exposure, resulting in human health issues, such as neurological, respiratory and carcinogenic effects (Van Maele-Fabry et al., 2017; Ye et al., 2017; Pouchieu et al., 2018). It has also intensified the contact of these compounds with aquatic environments (Burri et al., 2019; Liu et al., 2019; Sahin and Karpuzcu, 2020). Moriji et al. (2020) reported on pesticide concentrations in various aquatic environments across the world and found that pesticide levels ranged from 7 ng.l⁻¹ to 121,222 ng.l⁻¹, often well above the maximum allowable concentration of pesticides in drinking water (100 ng.l⁻¹; Council of the European Union, 1998). As herbicides account for the biggest proportion of pesticide usage (Moriji et al., 2020), their removal from aqueous environments is, therefore, an important scientific and environmental objective, according to the Food and Agriculture Organization of the United Nations (FAO, 2021).

Many media have been used as adsorbents for herbicides (Bayat et al., 2018; Papazlatani et al., 2019; Amoah-Antwi et al., 2020). Granulated activated carbon (GAC) is often used as an adsorbent for pesticides in Water Treatment Plants (EPA/HSE, 2019), due to its large surface area (300-2500 m².g⁻¹) and highly microporous structure (Jusoh et al., 2011). Typical adsorption capacities for the herbicides MCPA and 2,4-D on GAC range from 174.2 mg.g⁻¹ to 181.8 mg.g⁻¹, respectively (Ocampo-Pérez et al., 2012; Salman and Hameed, 2010). Biochar, a carbon-rich, porous material, has been used as a soil amendment because of its ability

to adsorb pesticides from soils (Khalid et al., 2020), as well as for removal of pollutants from aqueous environments (Zhang et al., 2020; Kamali et al., 2021; Rana et al., 2021). However, its potentially adverse effects on soil biota, physico-chemical changes in soil and even the presence of toxic substances in the biochar itself, have raised concerns regarding the long-term safety of its application (Brtnicky et al., 2021; Xiang et al., 2021). An alternative option is the use of agricultural and industrial waste materials (Ahmad and Danish, 2018; Jing et al., 2021). Industrial activities generate waste products from both consumption and production; however, the utilisation of these by-products is seldom examined in the literature (Grace et al., 2015). One drawback with the usage of industrial by-products for pesticide removal from aquatic environments is the possibility of introducing potentially toxic metals into those environments (Grace et al., 2016). A recent review by Tran et al. (2017) highlights errors and inconsistencies in publications on adsorption studies of contaminants from aqueous solution, including the inaccurate use of technical terms, mistakes relating to the study of adsorption kinetics and isotherms, as well as issues with adsorption mechanisms.

The aim of this study was to examine the adsorption of five of the most commonly used herbicides in Ireland (DAFM, 2017), namely MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr (see Fig. 4.1), from aqueous solutions onto a range of raw materials originating from an industrial setting and pyrolysed materials. These five herbicides belong to the same class of herbicides, namely phenoxy acid herbicides, and are readily analysed by available methods.

4.2 Materials and Methods

4.2.1 Chemicals and materials used

The chemicals used were of analytical grade and solutions were prepared using Milli-Q ultrapure water [18.3 mΩ Milli-Q Element systemTM, Merck Millipore, UK]. The herbicides and chemicals were purchased from Sigma-Aldrich and used without further purification, specifically: MCPA (4-chloro-2-methylphenoxyacetic acid, $C_9H_9ClO_3$, 200.62 g.mol⁻¹), mecoprop-P (*R*-2-(4-chloro-2-methylphenoxy)propionic acid, $C_{10}H_{11}ClO_3$, 214.65 g.mol⁻¹), 2,4-D (2,4-dichlorophenoxyacetic acid,

$C_8H_6Cl_2O_3$, 221.04 $g \cdot mol^{-1}$), fluroxypyr (4-amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid, $C_7H_5Cl_2FN_2O_3$, 255.03 $g \cdot mol^{-1}$), and triclopyr (3,5,6-trichloro-2-pyridyloxyacetic acid, $C_7H_4Cl_3NO_3$, 256.47 $g \cdot mol^{-1}$). Solutions were prepared at a concentration of 100 $mg \cdot l^{-1}$ for each herbicide in 0.01 M $CaCl_2$ in Milli-Q ultrapure water and were shaken for a minimum of 24 h.

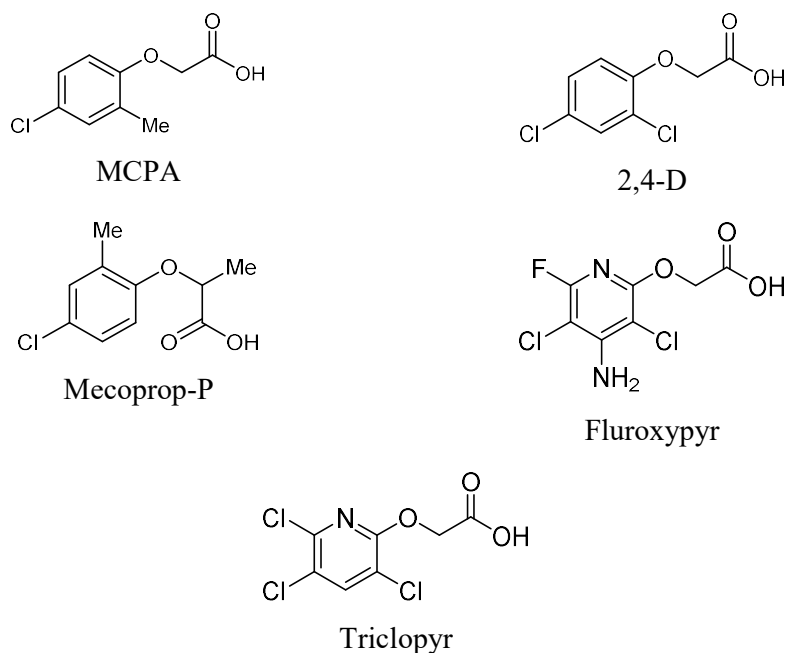


Figure 4.1 Chemical structures of chosen herbicides

Twelve different materials, identified as potential adsorbents, were selected based on criteria such as low cost, bulk availability and potential for local sourcing. These were GAC, peat fibre, bottom ash, fly ash, blast slag, Phoslock[®], zeolite, water treatment plant alum sludge (modified to adjust the physical characteristics to facilitate hydraulic conductivity without affecting the chemical characteristics of the alum sludge), two spruce biochars (S-BC1 and S-BC2), and two herbal pomace biochars (HP-BC1 and HP-BC2). The production processes and characterisation of all four biochars have been previously described (Siggins et al., 2020). Phoslock[®] is the commercial name for a bentonite clay which reacts with phosphate and locks up phosphorus safely (Zamparas et al., 2015). All adsorbents were dried at 105 °C for 24 h, then crushed or cut to a particle size of 1–2 mm, and stored in airtight containers at room temperature.

4.2.2 Batch adsorption assays

An initial 72 h batch test adsorption assay was used to assess the abilities of each of the twelve materials to adsorb the selected herbicides. The results of these tests were used to identify the best performing adsorbents for further investigation. All batch tests were set up in 40 ml amber glass vials, with 40 ml of equilibration solution (100 mg.l⁻¹) and an adsorbent dose of 5 g.l⁻¹. Vials were sealed with a PTFE-lined cap and equilibrated for up to 72 h at 10 °C on a mechanical reciprocal shaker at 160 rpm. Control vials containing no adsorbent were included to precisely calculate adsorption by each material and account for loss of herbicides by other means. Once equilibration was reached, samples were filtered through a PTFE syringe filter (0.45 µm) and analysed immediately.

4.2.2.1 Adsorption kinetics

The two highest performing adsorbents from the 72 h batch study were assessed for the rate at which they adsorb herbicides, using a kinetic study. Replicate vials for each material were sampled at times of 0, 1, 2, 3, 4, 6, 16, 18, 20 and 24 h. The values for time point zero were determined by adding a herbicide solution to the adsorbent in vials, and to an adsorbent-free control vial, followed by immediate filtration and analysis. The data were fitted to the linear version of first and second order (Ahmad et al., 2013), pseudo-first (Lagergren, 1898) and pseudo-second order (Ho and McKay, 1999), Elovich (Roginsky and Zeldovich, 1934) and intraparticle diffusion (McKay and Poots, 1980) kinetic equations to see which kinetic equations modelled the kinetic data the best (Table C.1). The goodness of fit of all models was assessed by calculating the coefficient of determination (r^2 ; Eq. 1) and the non-linear models were also assessed by calculation of the chi-squared value (χ^2 ; Eq. 2). High r^2 and low χ^2 values are indicative that the data are a good fit to the model.

$$r^2 = 1 - \frac{\sum (q_{exp} - q_{calc})^2}{\sum (q_{exp} - q_{exp.mean})^2} \quad (1)$$

$$\chi^2 = \sum \frac{(q_{exp} - q_{calc})^2}{q_{calc}} \quad (2)$$

where: q_{exp} is the experimental sorption capacity (mg.g^{-1}), q_{calc} is the modelled sorption capacity (mg.g^{-1}), and $q_{exp,mean}$ is the mean of the experimental sorption capacities.

The standard error of estimates (SEE; Eq. 3) values was used to investigate the goodness of fit for the kinetic models. A high r^2 and low SEE are indicative that the data are a good fit to the model.

$$SEE = \sqrt{\frac{(\sum q_{exp} - \sum q_{calc})^2}{(n - 2)}} \quad (3)$$

where: q_{exp} is the experimental sorption capacity (mg.g^{-1}), q_{calc} is the modelled sorption capacity (mg.g^{-1}), and $q_{exp,mean}$ is the mean of the experimental sorption capacities.

4.2.2.2 Adsorption Isotherms

Once an optimum time was identified from the kinetics experiments, an adsorption isotherm test was conducted for the media. The adsorption capability of the selected media were assessed across an adsorbent range of 0.25-5 g.l^{-1} , using a herbicide solution at a herbicide concentration of 100 mg.l^{-1} for 72 h. Experimental data were modelled by linear and non-linear Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906), Koble-Corrigan (Koble and Corrigan, 1952), Temkin (Vijayaraghavan et al., 2006) and Dubinin-Radushkevich (Vijayaraghavan et al., 2006) adsorption isotherms, using MS Excel's Solver plugin to determine the best fitting parameters by maximising for r^2 for the non-linear models.

4.2.3 Effect of pH on adsorption

The impact of pH on the adsorption capabilities of the two best performing media was investigated. The herbicide solutions were prepared as described in Section 2.1. Each solution was then divided into three portions, each buffered with NaOH to a pH of either 5, 7, or 9. The pH range for all unbuffered herbicide solutions was 3-4. Batch assays were conducted over 24 h using 40 ml amber glass vials, with 40 ml of appropriate buffered solution (100 mg.l^{-1}) and an adsorbent dose of 5 g.l^{-1} .

4.2.4 Herbicide analysis

Herbicide concentrations in the filtered samples, for all herbicides, were directly quantified. Methods for the determination of pesticide adsorption are limited by the high cost of the mass spectrometry equipment required for their analyses, coupled with the time-consuming pre-treatment techniques (Huang et al., 2009; Wang et al., 2019). UV-Vis spectrometry, as an analytical technique for the detection of pesticides in solution, has been widely used for more than twenty years (Bekbölet et al., 1999; Spaltro et al., 2018; Rizzi et al., 2020) despite the poor sensitivity of the technique when compared to the low level detection (ng.l^{-1}) as provided by modern mass spectrometry techniques. All samples were analysed using a Varian CARY 50 UV-Vis-NIR spectrophotometer (Varian Inc., now Agilent Technologies Inc., Santa Clara, CA, USA). Quantification was measured at the appropriate wavelength for each herbicide: 571 nm (glyphosate), 278 nm (MCPA), 280 nm (mecoprop-P), 283 nm (2,4-D), 263 nm (fluroxypyr) and 295 nm (triclopyr) (Lewis et al., 2016). UV-Vis readings were compared to standard curves in a range of 10-100 mg.l^{-1} for quantification of each herbicide.

The LOD (mg.l^{-1}) and LOQ (mg.l^{-1}) for each herbicide using UV-Vis spectroscopy were calculated and are shown in Table 4.1.

Table 4.1 LOD and LOQ values for the chosen herbicides.

	LOD (mg.l^{-1})	LOQ (mg.l^{-1})
MCPA	0.76	2.55
Mecoprop-P	6.03	18.27
2,4-D	3.82	12.73
Glyphosate	4.51	15.03
Triclopyr	1.25	4.17
Fluroxypyr	3.00	9.98

4.2.5 GAC characterisation

A Hitachi S4700 Scanning Electron Microscope (SEM) equipped with a Bruker X-Flash EDX detector was used to image the sample of GAC and to determine its

elemental composition. Fourier Transform Infrared Spectroscopy (FTIR) spectra analysis was carried out to identify functional groups on the surface of GAC, with and without the adsorption of the herbicides, using a PerkinElmer Spectrum 400 fitted with an ATR reflectance attachment. Spectra were collected in the 4000 to 650 cm^{-1} range with a resolution of 4 cm^{-1} and twenty integrated scans on a diamond/ZnSe window.

4.3 Results and Discussion

4.3.1 Media analysis

The chemical characterisation of the media used has been previously reported (Grace et al, 2015; Siggins et al., 2020), with the exception of the modified water treatment plant sludge (Table 4.2).

Table 4.2 Chemical and physical characterisation of the chosen media.

Media	GAC ^a	Peat fibre	Bottom ash ^a	Fly ash ^a	Blast slag ^a	Phoslock	Zeolite ^a	MWTPS	S-BC1	S-BC2 ^b	HP-BC1 ^b	HP-BC2
Parameter												
Al (mg.kg ⁻¹)	49	217	n/d ^c	1223	2083	816	263	77405	821	n/d ^c	n/d ^c	n/d ^c
C (mg.kg ⁻¹)	n/d ^c	54.3	n/d ^c	n/d ^c	n/d ^c	7000	n/d ^c	13	42.9	n/d ^c	n/d ^c	n/d ^c
Ca (mg.kg ⁻¹)	n/d ^c	4133	n/d ^c	n/d ^c	n/d ^c	10100	n/d ^c	25367	55878	33000	39000	167000
Fe (mg.kg ⁻¹)	14	623	n/d ^c	189	90	331	23	3836	1375	3600	6100	11000
K (mg.kg ⁻¹)	n/d ^c	322	n/d ^c	n/d ^c	n/d ^c	2800	n/d ^c	86	53199	10000	26000	274000
Mg (mg.kg ⁻¹)	3.78	1082	2120	13.6	20.4	1400	12.8	190	11436	3300	6400	73000
P (mg.kg ⁻¹)	87	169	171	1044	4	2500	3	576	33482	2000	8900	96000
Moisture (%)	5	11.9	n/d ^c	n/d ^c	n/d ^c	9.9	n/d ^c	77	5.8	27	22.3	37.2
Org C (%)		97.8	n/d ^c	n/d ^c	n/d ^c	5.5	n/d ^c	n/d ^c	50.5	74.3	66.6	61.9
Pore diameter (Å)	61	I ^d	74	109	203	144	87	I ^d	137	390	60	60
Pore volume (cm ³ .g ⁻¹)	0.496	I ^d	0.001	0.002	0.01	0.113	0.104	I ^d	0.033	0.03	0.001	0.03
Surface area (m ² .g ⁻¹)	579	0.003	1.80	1.779	2.49	35.72	38.67	I ^d	11.46	39	216	374

^a Grace et al., 2015.^b Siggins et al., 2020.^c n/d: not detected.^d Immeasurable

4.3.2 Adsorbent screening

GAC performed the best for the adsorption of all herbicides (> 95% removal; Fig. 4.2). The raw materials had limited adsorption of any of the herbicides.

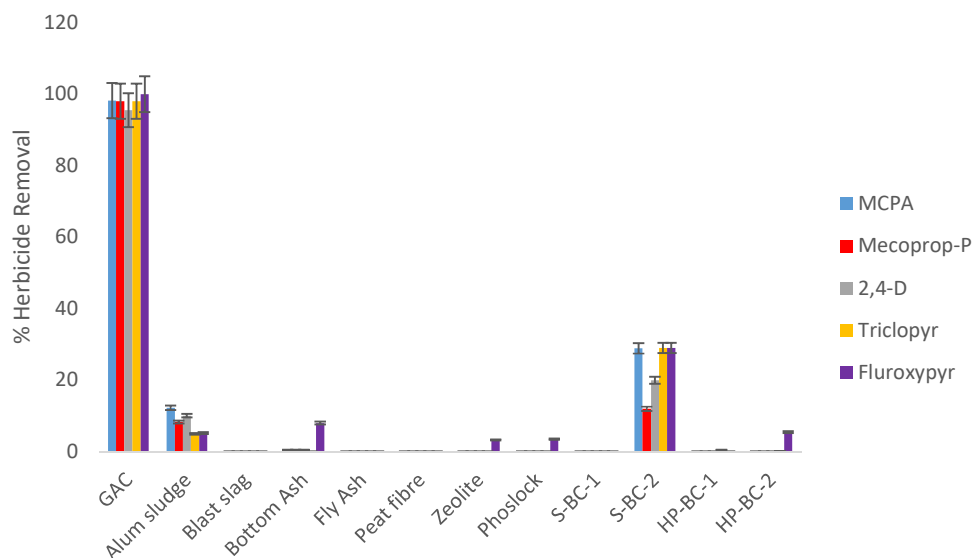


Figure 4.2 Herbicide removal by twelve raw or processed waste materials at an adsorbent concentration of 5 g.l^{-1} and herbicide concentrations of 100 mg.l^{-1} , following equilibration for 72 h at $10 \text{ }^\circ\text{C}$ ($\pm 0.5 \text{ }^\circ\text{C}$) and shaking at 160 rpm. Error bars represent standard error (stdev/\sqrt{n} , where n is the number of replicates, three in this case).

Of the four biochars investigated, S-BC-2 performed best removing MCPA, triclopyr and fluroxypyr (Fig. 4.2). The pore diameter of the four biochars varied from 60-390 Å (Siggins et al., 2020), which is sufficient to prevent size exclusion that occurs when the pore diameter is less than 1.7 times the second largest dimension of the target compounds (Kasaoka, 1987). Size exclusion occurs when dissolved molecules of various sizes flow over a material containing pores, with the smaller molecules entering the pores but the larger ones being excluded. In the case of the herbicides examined in the current study, adsorbent pore diameters of $>17 \text{ }^\circ\text{Å}$ should be sufficient to prevent size exclusion. The surface area for each of the twelve raw or processed waste materials was determined (Table 4.2) and showed that GAC had the largest surface area of all the media used in this study. The media with the second and third largest surface areas were HP-BC1 and HP-BC2 but neither of these demonstrated any

adsorption of the herbicides used. Interestingly, S-BC2 has only a surface area of $39 \text{ m}^2 \cdot \text{g}^{-1}$, yet it is the second best media at the adsorption of the herbicides, suggesting that surface area alone is not the main factor in the adsorption process. MCPA, mecoprop-P, 2,4-D, triclopyr and fluroxypyr all contain an aromatic ring, either phenyl or pyridinyl in nature. This would suggest that π - π interactions between the aromatic rings of the herbicides and the surface of GAC promote the adsorption of these five herbicides. As herbicides are more complex molecules than simple metal ions, which adsorb using electrostatic chelation interactions as the main mechanistic pathway (Ma et al., 2015), the adsorption mechanisms will also be more complex. Further to the presence or absence of an aromatic ring, the adsorption mechanism of the selected herbicides will be dependent on the electron-donating abilities of the various functional groups attached to each herbicide, as well as the ionisability of any amine groups present. For all the herbicides, there are possible interactions available involving the carboxylate groups, the various halogen and amino groups present, as well as the nitrogen atom of the pyridine ring in the cases of triclopyr and fluroxypyr. Based on the adsorption data shown in Fig. 4.2, it was decided to use, for both the kinetic and isotherm studies, GAC for the adsorption of MCPA, mecoprop-P, 2,4-D, triclopyr and fluroxypyr.

4.3.3 GAC characterisation

The surface morphology of GAC is shown in Fig. C.1. The surface of the GAC is not smooth but, instead, shows small clusters distributed over smooth platelets. No distinct pores were observed.

IR spectra were obtained of GAC samples that had been stirred in either water or the various herbicide solutions for 72 h (Fig. 4.3). The spectrum of GAC stirred in water showed a few minor shoulders at 1618 cm^{-1} , 1230 cm^{-1} , and 965 cm^{-1} , similar to that observed by Siggins et al. (2020), but with the addition of a water band at 3200 cm^{-1} , which is presumably due to surface water molecules. The spectra of GAC in all the herbicide solutions also showed the presence of this water peak. The differences between the spectra of GAC in water and of GAC in the various herbicide solutions are very subtle, as was expected (Fig. 4.3).

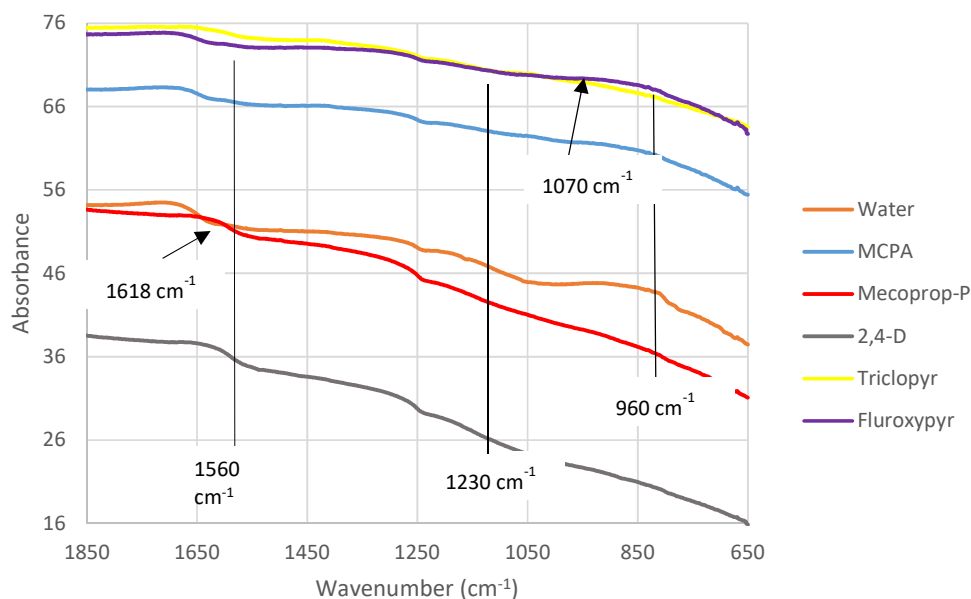


Figure 4.3 FTIR spectra of GAC after being stirred in either water or one of the herbicide solutions for 72 h.

The spectra in Fig. 4.3 suggest that the adsorption of MCPA and mecoprop-P by GAC is by the same mechanism, as the IR values for GAC from both these solutions are similar, with the peak at 1618 cm^{-1} for GAC in water moving to 1555 cm^{-1} in both MCPA and mecoprop-P. This shift in peak position would suggest that a bonding interaction between the herbicide and GAC had occurred, which would imply that the mechanism of adsorption was by chemisorption. Similarly, the data also suggest that both triclopyr and fluroxypyr are adsorbed by GAC as again there are shifts in the peak at 1618 cm^{-1} to 1550 cm^{-1} . A new shoulder at 1068 cm^{-1} in both of these spectra indicates the presence of a pyridine ring which is involved in a binding interaction with the GAC, as this peak is normally at 1078 cm^{-1} for pyridine itself (Amudha et al., 2022). As this shift in peak position is only by a small number of wavenumbers, it would suggest that this binding interaction is by physisorption and not chemisorption. The FTIR spectrum of 2,4-D also shows a shift in the peak at 1618 cm^{-1} but, otherwise, very little information can be gathered from it. This may suggest that 2,4-D adsorbs by a different mechanism to either MCPA and mecoprop-P or triclopyr and fluroxypyr.

4.3.4 Adsorption kinetics

Adsorption kinetics were undertaken for each of the herbicides with their best adsorbent: GAC for MCPA, mecoprop-P, 2,4-D, triclopyr and fluroxypyr (Fig. 4.4). Maximum adsorption was reached for all herbicides adsorbed by GAC within 18 h of contact time (Fig. 4.4). Both MCPA and mecoprop-P demonstrated a two-phase adsorption characterised by a fast initial adsorption stage followed by a slower stage, as has been previously reported in kinetic adsorption studies (Ahmad et al., 2013).

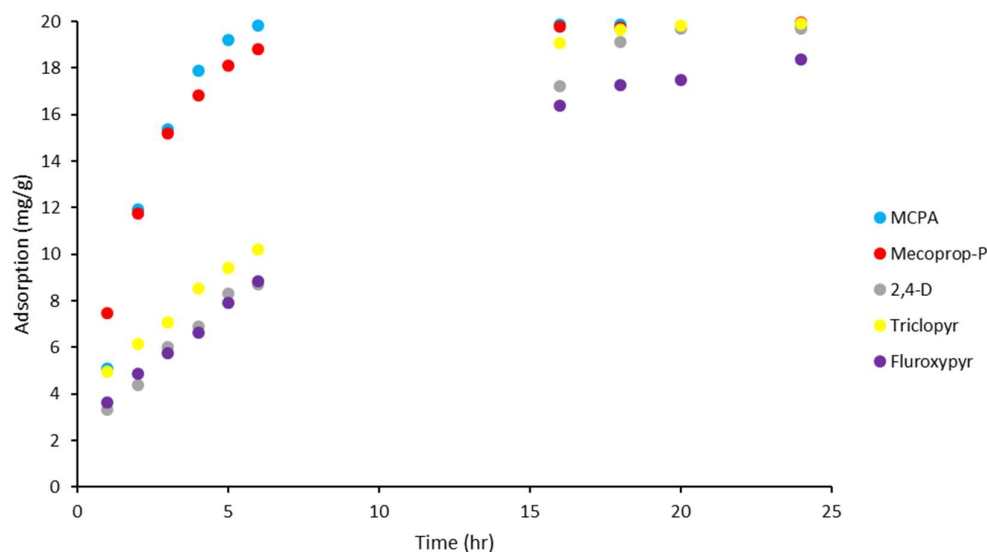


Figure 4.4 Herbicide adsorption kinetics on GAC.

The experimental kinetic data were fitted to a range of kinetic models (Table C.1), and from these, the kinetic parameters were obtained (Table C.2). Alberti et al. (2012) described adsorption as a sequential four step process: (1) transport of adsorbate to adsorbent, (2) diffusion of the adsorbate through the film layer surrounding the adsorbent, (3) intraparticle diffusion and (4) chemisorption. Fitting experimental data to kinetic models that have differing assumptions and evaluation of the fit, represented by high r^2 and low SEE values, allows the identification of the rate limiting step in the adsorption process.

These parameters indicate that the adsorption of both MCPA and mecoprop-P to GAC were pseudo-second order in nature, as a result of the high r^2 (≥ 0.995) and low SEE

(≤ 0.004) values (Tables C.S2). This indicates that chemisorption (step 4) is the rate-limiting step for these reactions and adsorption of these compounds occurs in a monolayer on the respective adsorbents' surface (Ahmad et al, 2013). This agrees with the IR spectra of GAC adsorption of both MCPA and mecoprop-P (Fig. 4.3), which suggested that both of these herbicides were adsorbed by a similar mechanism. This concurs with the kinetic results from previously reported studies for the adsorption of MCPA by activated carbon (Ocampo-Pérez et al., 2012; Pandiarajan et al., 2018). To the best of our knowledge, no kinetic adsorption studies of mecoprop-P using GAC as an adsorbent have been reported.

The adsorption of 2,4-D by GAC was best described by a first order kinetic model, as a result of the respective r^2 (0.989) and SEE (0.030) values (Table C.2), which indicates that the transport of adsorbate to the adsorbent is the rate limiting step. The IR data (Fig. 4.3) suggested that 2,4-D was adsorbed by a different mechanism to both MCPA and mecoprop-P, even though a similar shift in the shoulder at 1618 cm^{-1} was observed in all three cases. This is in contrast to the reported studies (Pandiarajan et al., 2018; Bahrami et al., 2018; Amiri et al., 2020) where pseudo-first order and pseudo-second order kinetic models were documented, which would suggest that intraparticle diffusion and chemisorption were the rate limiting steps. In the current study, 12-20 mesh GAC was used, whereas 6-16 mesh GAC, Filtersorb 300 (F300) activated carbon, orange peel activated carbon, granulated activated carbon and canola-stalk-derived activated carbon, respectively, were used in the other studies (Aksu and Kabasakal, 2004; Salman and Hameed, 2010; Pandiarajan et al., 2018), which may have resulted in different rate limiting steps for the adsorption process.

In the current study, the kinetic adsorption of triclopyr and fluroxypyr by GAC fitted best to a pseudo-first order kinetic model (Table C.2), which indicated that the rate limiting step was intraparticle diffusion (step 3). The IR spectra (Fig. 4.3) of GAC in both of these solutions showed an extra band in each spectrum at approximately 1074 and 1062 cm^{-1} , respectively. This band is due to the presence of a pyridine ring being present and involved in a bonding interaction with the GAC, as the IR band for pyridine itself is at 1078 cm^{-1} (Amudha et al., 2022). Pastrana-Martínez et al. (2010) reported on the adsorption of fluroxypyr onto different types of activated carbon and showed that a pseudo-second order kinetic model was the best fit for all types of the

activated carbon chosen, which indicated that the rate limiting step was chemisorption. Again, the pore size of the various activated carbons in both studies could be one of the important factors in determining the overall kinetic model. To the best of our knowledge, no kinetic adsorption studies of triclopyr using GAC as adsorbent have been reported.

4.3.5 Adsorption Isotherms

In order to get an insight into the adsorption capacity of the materials for herbicides, adsorption isotherm experiments were carried out (Fig. 4.5).

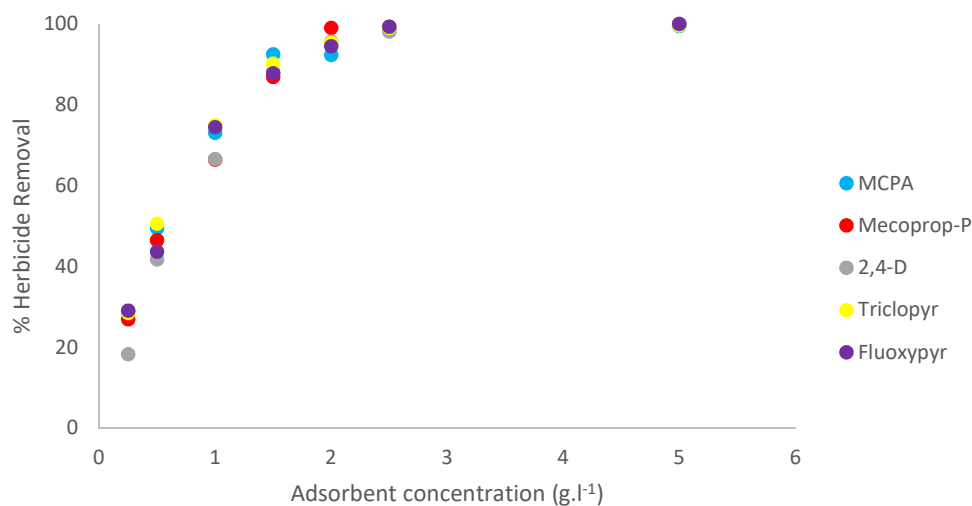


Figure 4.5 Herbicide removal over a range of media concentrations, expressed as % herbicide removal. The adsorption study was carried out at a herbicide concentration of 100 mg.l⁻¹ and an equilibrium time of 72 h. Medium = GAC in all cases.

GAC removed >99% (19.9 mg.g⁻¹) of all five target herbicides over 72 h at a concentration of 5 g.l⁻¹ (Fig. 4.3). All isotherms showed the L-type of Giles classification (Giles, 1974). For the adsorption of the various herbicides by GAC, this indicates that the aromatic rings of the herbicide molecules are adsorbed parallel to the carbon surface, as previously shown by Ocampo-Pérez (2012). They also suggested that there was no competition for active adsorption sites on the carbon surface between the contaminant molecules and water molecules.

The various models, described in the Materials and Methods section, were applied in their linearised and non-linearised forms (Table C.3), with Table C.4 showing the isotherm parameters derived from each model. In all cases, based on the obtained r^2 values, the adsorption of all herbicides were best described by the Freundlich model (Fig. 4.6), which indicates that adsorption occurred as mono- and multi-layer adsorption on a heterogeneous surface. This involves both physisorption and chemisorption, which is in agreement with the pseudo-second order kinetic model obtained for both MCPA and mecoprop-P (Lin et al., 2015; Rizzi et al., 2019; Rizzi et al., 2020). Furthermore, an adsorption strength value of n which lies between 1 and 10 indicates that adsorption is favourable, as in the case of the herbicides, MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr (Table C.4).

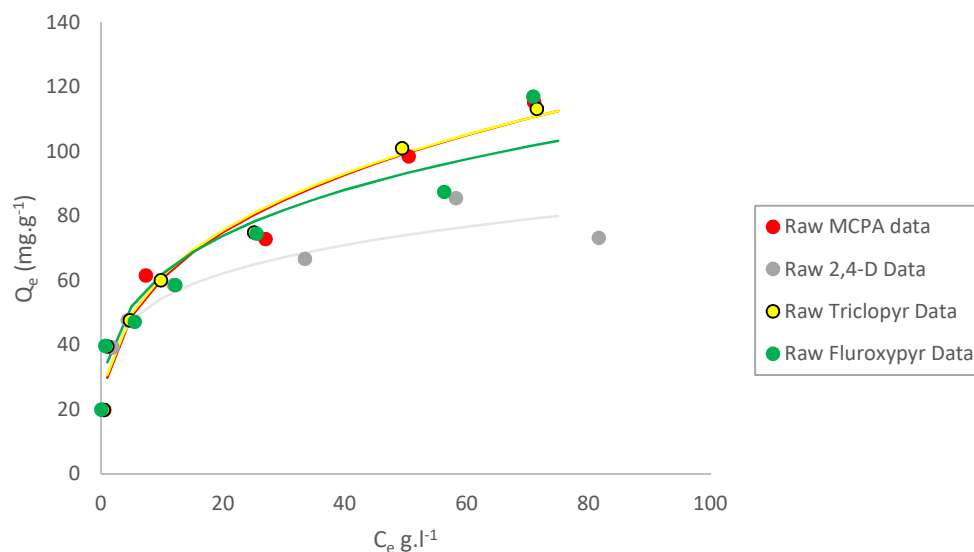


Figure 4.6 Freundlich adsorption isotherm of MCPA, Mecoprop-P, 2,4-D, Triclopyr and Fluroxypyr on GAC. Modelled data are shown as a colour coded line.

4.3.6 Effect of pH

The pH of an aqueous solution is one of the most significant parameters that influences the adsorption process, as it affects both the surface charge and the speciation of the target compound (Tan et al., 2015). No statistically significant change in the adsorption of any of the herbicides, after 24 h, was detected at any pH studied compared to the adsorption observed when pH was not adjusted, indicated in the

Figure by the caption MCPA 24 h (Fig. 4.7). The ability of corn cob biochar to adsorb 2,4-D has been reported to have decreased dramatically in response to pH, from 95% at pH 2 to 5% at pH 12 (Binh and Nguyen, 2020). However, Essandoh et al. (2017) reported the effect of pH on the adsorption of both MCPA and 2,4-D onto switch grass biochar. They observed very little reduction in % removal of either MCPA or 2,4-D over a pH range of 2 to 8, with the % removal being reduced from 90% at pH 2 to 80% at pH 8. This led them to suggest that, at naturally encountered pH values, switch grass biochar was a good adsorbent of MCPA and 2,4-D. It would appear that the influence of pH is dependent on the specific adsorbent, and that the adsorbents in our study were not affected.

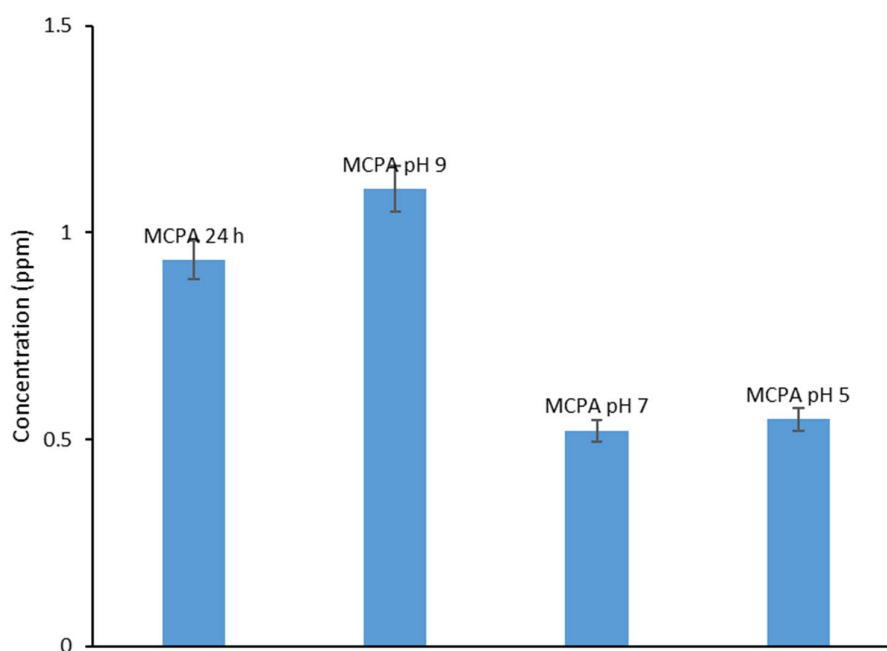


Figure 4.7 Effect of pH on MCPA adsorption by GAC. MCPA = 100 ppm solution in ultrapure water, no pH adjustment; MCPA 24 h = MCPA solution after shaking with GAC (5 g.l⁻¹) for 24 h, no pH adjustment; MCPA pH 9 = MCPA solution after shaking with GAC (5 g.l⁻¹) for 24 h, pH 9; MCPA pH 7 = MCPA solution after shaking with GAC (5 g.l⁻¹) for 24 h, pH 7; MCPA pH 5 = MCPA solution after shaking with GAC (5 g.l⁻¹) for 24 h, pH 5. Error bars show standard error where n = 3.

4.4 Conclusions

The waste materials investigated demonstrated little capability for any herbicide adsorption. GAC was the best adsorbent observed for the removal of the herbicides investigated, with >95% removal. The data, supported by adsorption kinetic models and FTIR spectra, suggest that MCPA and mecoprop-P both fitted a pseudo-second order kinetic model, indicating that chemisorption was the rate limiting step. The experimental data also suggested that fluroxypyr and triclopyr fitted a pseudo-first order kinetic model, indicating that the rate limiting step was intraparticle diffusion, while 2,4-D fitted a first order kinetic model, indicating that the transport of adsorbate to the adsorbent is the rate limiting step. The kinetic studies also indicated that the majority of the adsorption, in all cases, was completed within 18 h. The adsorption process followed the Freundlich isotherm model verifying monolayer and multilayer adsorption and in all cases the adsorption process was found to be favourable.

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Chapter 5 – Field assessment of coconut-based activated carbon systems for the treatment of herbicide contamination

This research outlined in this chapter assessed, in the field, the potential of coconut-based activated carbon (CAC) by using filter bags containing the medium in two agricultural catchments and one urban area. One configuration used filter bags containing 16 kg of sieved CAC, while the second configuration used the same filter bags, but in this case filled with 12 kg of sieved CAC, and fitted into a polyethylene pipe to fill the full diameter of the centre section of the pipe.

The contents of this chapter have been submitted to the *Chemosphere* for publication.

John McGinley developed the experiment design, installed and retrieved all Chemcatcher[®] passive sampling devices and interventions, and analysed the data derived from the field work, and is the primary author of this article. Prof Mark G. Healy contributed to the conceptualisation and the writing of the paper. Dr Alma Siggins contributed to the conceptualisation and the writing of the paper. S. Scannell installed and retrieved interventions. Dr P. C. Ryan contributed to the review and writing. J. Harmon O'Driscoll contributed to the review and writing. Dr P.-E. Mellander contributed to the review and writing. Dr L. Morrison contributed to the review and writing. Supplementary information for this paper is included in Appendix D.

Field assessment of coconut-based activated carbon systems for the treatment of herbicide contamination

J. McGinley^{1,2}, M. G. Healy^{1,2}, S. Scannell^{1,2}, P. C. Ryan^{3,4}, J. Harmon O'Driscoll³, P.-E. Mellander⁵, L. Morrison^{2,6}, A. Siggins^{2,7*}.

¹ Civil Engineering, University of Galway, Ireland.

² Ryan Institute, University of Galway, Ireland.

³ Discipline of Civil, Structural and Environmental Engineering, School of Engineering, University College Cork, Ireland.

⁴ Environmental Research Institute, University College Cork, Cork, Ireland

⁵ Agricultural Catchments Programme, Teagasc Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland.

⁶ Earth and Ocean Sciences, Earth and Life Sciences, School of Natural Sciences, University of Galway, Ireland.

⁷ School of Biological and Chemical Sciences, University of Galway, Ireland.

* Corresponding author

Abstract

Once released into the environment, herbicides can move through soil or surface water to streams and groundwater. Filters containing adsorbent media placed in fields may be an effective solution to herbicide loss in the environment. However, to date, no study has investigated the use of adsorbent materials in intervention systems at field scale, nor has any study investigated their optimal configuration. Therefore, the aim of this paper was to examine the efficacy of low cost, coconut-based activated carbon (CAC) intervention systems, placed in streams and tributaries, for herbicide removal. Two configurations of interventions were investigated in two agricultural catchments and one urban area in Ireland: (1) filter bags and (2) filter bags fitted into polyethylene pipes. Herbicide sampling was conducted using Chemcatcher[®] passive sampling devices in order to identify trends in herbicide exceedances at the sites, and to quantifiably assess, compare, and contrast the efficiency of the two intervention configurations. The CAC was capable of complete herbicide removal, when the water

flow was slow, and the interventions spanned the width and depth of the waterway. Overall, the reduction in herbicide concentrations was better for the filter pipes than for the filter bags ($p < 0.05$). This study demonstrates that CAC may be an effective *in situ* remediation strategy to manage herbicide exceedances close to the source, thereby reducing the impact on environmental and public health.

Keywords:

Herbicides, Chemcatchers[®], Monitoring, Interventions, Water quality, Remediation

5.1 Introduction

Herbicides are substances used to control undesired plants, also known as weeds (de Souza et al., 2020; Mojiri et al., 2020; Ighalo et al., 2021). However, extensive and inefficient use of herbicides has led to contamination of soils and waterways (Khalid et al., 2020; Shahid et al., 2021; Zeshan et al., 2022). Once released into the environment, herbicides can move through soil or surface water to streams and groundwater, where they can accumulate in aquatic organisms as well as causing loss of ecosystem biodiversity (Aksoy et al., 2017; Ramakrishnan et al., 2021; Wenzel et al., 2022). In the European Union (EU), Council Directive 98/83/EC (EU, 1998) on the quality of water intended for human consumption sets the maximum allowable concentration (MAC) for herbicides, either individually or in total, as 100 ng.l⁻¹ or 500 ng.l⁻¹, respectively. However, these values are frequently exceeded (Postigo et al., 2021; EPA, 2022; McGinley et al., 2023). Such exceedances are particularly problematic as conventional water treatment methods are ineffective in the removal of herbicides (Larasti et al., 2021; Intisar et al., 2022; Taylor et al., 2022). While some water treatment facilities incorporate powdered or granulated activated carbon (GAC) filters to remove herbicides (EPA & HSE, 2019; de Souza et al., 2020), this is not common practice in many countries. An alternative approach may involve treatment at the source, i.e., in the field, rather than in a treatment plant. This early intervention for removal of pollutants would positively impact both human and environmental health by reducing herbicide exposure.

Many low-cost media, based on either raw or pyrolysed waste materials coming from an agricultural or industrial origin, have been used as adsorbents for herbicides (Franco

et al., 2021; Jatoi et al., 2021; Taylor et al., 2022). An adsorbent that is often used for herbicide removal is GAC, due to its large surface area (300–2500 m².g⁻¹) and highly microporous structure (Chen et al., 2020; McGinley et al., 2022). In recent years, novel activated carbons, derived from renewable, readily available, low-cost agricultural materials, including canola stalk, orange peel, and coconut husk, have been widely researched in batch adsorption studies (Pandiarajan et al., 2018; Herath et al., 2019; Amiri et al., 2020). Kodali et al. (2021) reported that coconut-based activated carbon (CAC) was a promising adsorbent as it had an adsorption capacity of 103.9 mg.g⁻¹ for the organophosphorus pesticide monocrotophos mainly due to its relatively large surface area of 79.4 m².g⁻¹. However, there is a dearth of field/pilot studies using activated carbon, including CAC, as adsorbents for herbicides. Instead, research work has mainly comprised batch adsorption studies of herbicides using source water, environmentally-relevant aqueous solutions, or spiked samples (Carra et al., 2020; Kodali et al., 2021; Singh et al., 2021; Sanz-Santos et al., 2022). Such field/pilot studies would be informative in providing information of the configuration of potential intervention devices and their implementation in waterways.

Therefore, the aims of this study were to evaluate the extent of exceedances in two agricultural catchments and one urban catchment in Ireland, and using those data to design, install and assess the efficacy of two low cost, CAC-based *in situ* remediation systems capable of herbicide removal close to the source of contamination.

5.2 Methodology

5.2.1 Study areas

This study examined herbicide exceedances and the efficiency of remediation measures in two agricultural catchments and one urban catchment in Ireland (Fig. 5.1). The Corduff catchment (53° 57' 40'' N, 6° 45' 22''W) is located northwest of Carrickmacross in Co. Monaghan. The site is 578 ha in area, 89% of which is grassland (mainly beef production, with some dairying and sheep), and the remainder used for non-agricultural purposes. The topography of the Corduff catchment ranges from alluvial flatlands to shaped drumlins, with fairly steep slopes and intervening U-shaped valleys. Acid brown earths dominate the hill tops, with stagnic luvisols and

gleys on the hill slopes and valley bottoms, and the underlying rock is mainly sandstone. The Dunleer catchment ($53^{\circ} 50' 6''$ N, $6^{\circ} 23' 46''$ W) is situated west of Dunleer in Co. Louth. It is 948 ha in area, with 50% in grass (mainly for dairy and beef production), 33% in tillage (mainly winter wheat, but also winter barley, spring barley and potatoes), and the remainder in woodland and non-agricultural uses. The Dunleer catchment is dominated by an undulating landscape, with many slopes. The dominant soils in this catchment are typical stagnic luvisols, underlain with greywacke, mudstone and limestone geology. The urban site is a drain running through a golf course located in the north west of Ireland. The golf course is a parkland course, 5,650 m in length. Due to a privacy agreement, further details on its location are not disclosed. The water network within each of the agricultural catchments (Corduff and Dunleer) confluences and exits the catchment through a single outlet. Each site was instrumented with a weather station, from which the total daily rainfall (mm) was obtained.

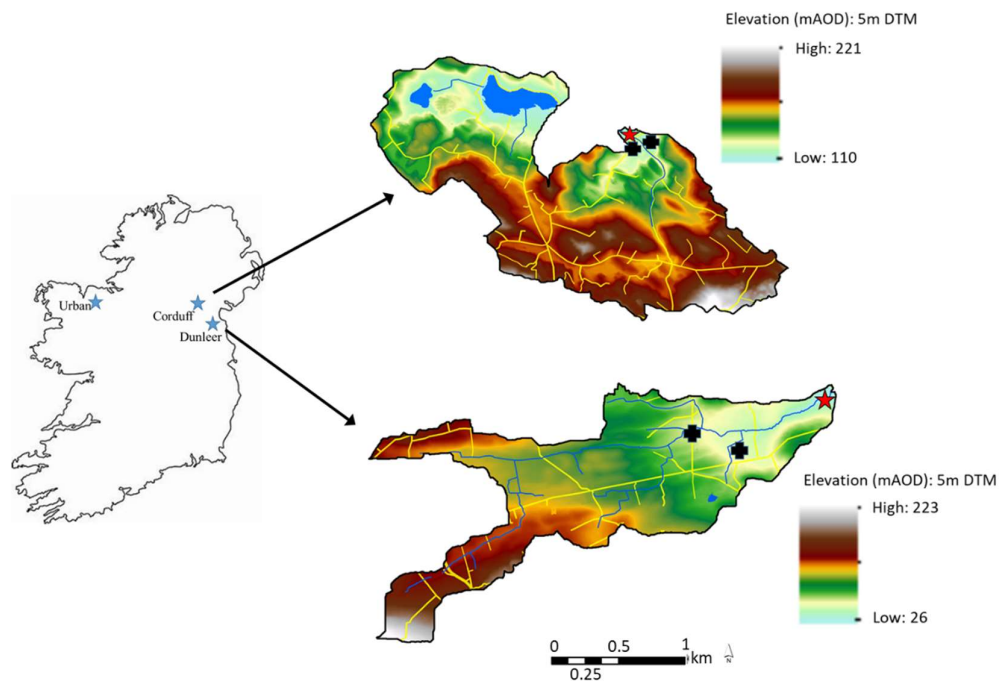


Figure 5.1 Map of Ireland showing location of the three sampling sites with blue stars. The outlet points at the two agricultural catchments are denoted with red stars, while the locations of the interventions in Year 2 are marked with black crosses.

5.2.2 Identification of monitoring locations and interventions used

High risk locations for pollution impact potential were identified at the agricultural catchment sites, based on an online Irish Environmental Protection Agency (EPA) Geographical Information System (GIS) application that contains information for flow delivery paths (WMS Layer: “PIP-P Flow Delivery Paths”) and entry points (WMS Layer: “PIP-P Flow Delivery Points”) for phosphorus (<https://gis.epa.ie/EPAMaps>). As these map layers were primarily generated based on topography and overland flow, the identified flow delivery paths and entry points were considered to be likely routes for herbicide movement from land to waterways. From these delivery paths and points, optimal locations for the placement of the interventions were selected following visual inspection and taking cognisance of physical accessibility and willingness of the farmers to grant access. Two locations were selected for Corduff and Dunleer: in both cases, these locations included a main stream and a tributary upstream (ca. 200 m and 1000 m, respectively) of the outlet. One location within the drain, ca. 10 m upstream of the outlet, was used in the Urban site.

Two configurations of interventions were investigated at each study site. Both configurations used CAC (Nova-Q, Ireland), sieved to a particle size $> 2\text{mm}$, as it had been shown to have a high adsorption affinity ($>97\%$) for acid herbicides (Fig. D.1). One configuration used filter bags (2 mm netten 400G bags, $100 \times 40\text{ cm}$; Triskell Seafood, Ireland) containing 16 kg of CAC (hereafter referred to as “filter bags”). The second configuration used the same filter bags, but in this case they were filled with 12 kg of sieved CAC, and fitted into a polyethylene pipe ($0.3\text{ m wide} \times 0.8\text{ m long}$) to fill the full diameter of the centre 0.4 m section of the pipe (hereafter referred to as “filter pipe”) (Fig. 5.2). At each intervention site, three staggered filter bags were placed perpendicular to the flow of the water, in order to maximise contact of the media with the water but not cause flooding (Fig. 5.2). Just downstream of the filter bags, the filter pipe was placed in line with the flow of the water, so an aliquot of water passed through the filter.

5.2.3 SEM microscopy and CAC characterisation

A Hitachi S4700 Scanning Electron Microscope (SEM) equipped with a Bruker X-Flash EDX detector was used to image the CAC and to determine its elemental composition. Physical and morphological analyses of the CAC, including pore volume, pore diameter and surface area, were carried out by Glantreo Ltd (Cork, Ireland).

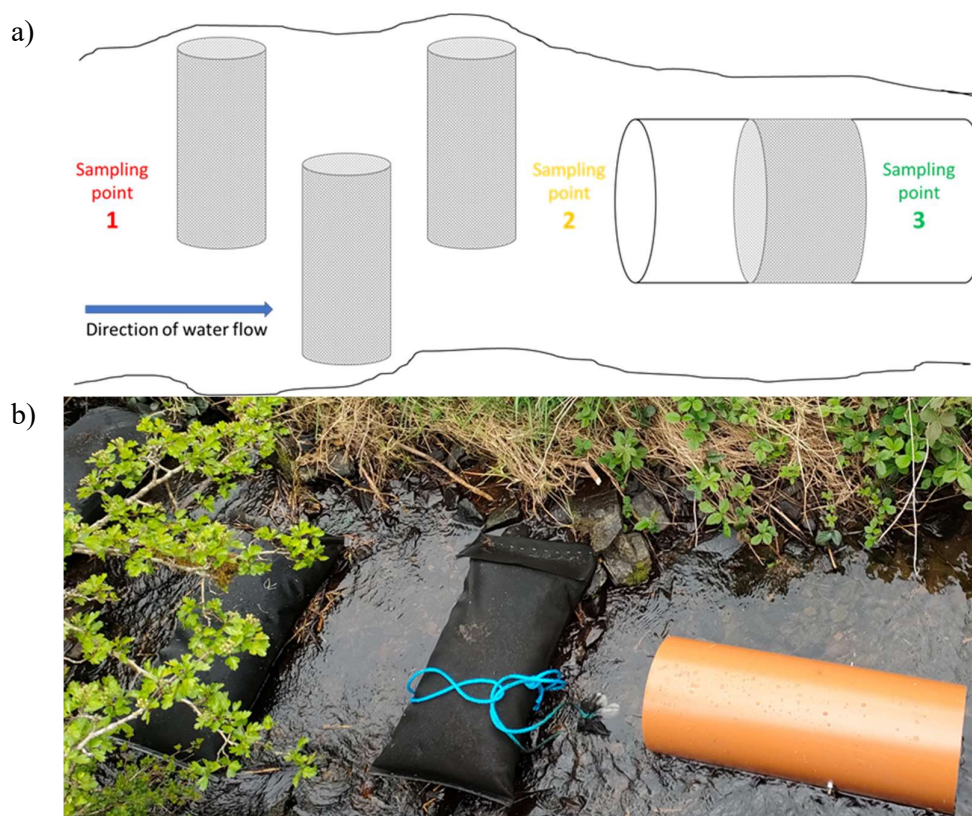


Figure 5.2 a) Schematic of different configurations of the intervention positioned in the stream. The blue arrow indicates direction of water flow. Filter bags are upstream from the filter pipe. Sampling points, colour-coded (see Section 2.4), are also indicated on the diagram. b) Image showing filter bags and filter pipe in position at Corduff stream.

5.2.4 *Herbicide sampling and analysis*

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

Details on the preparation of the Chemcatchers[®] have been previously reported (Grodtko et al., 2021; Taylor et al., 2022). During each deployment, an additional Chemcatcher[®] was exposed to serve as a blank at each site, so that any contamination occurring during deployment of the devices could be readily identified. Once retrieved from the water, they were stored at 4 °C prior to being disassembled for removal of the filter disk. When dry, the herbicides were extracted from the disks with 25 ml of a 9:1 ethyl acetate/formic acid mixture. Chromatographic separation was carried out on a C18 LC Column using a Thermo scientific Dionex UlitMate 3000 system equipped with a binary pump, a vacuum degasser and an autosampler. The column oven was maintained at 25 °C. Samples were analysed using a Thermo scientific Exactive Plus LC-MS Orbitrap[®] mass spectrometer. TraceFinder 4.1 EFS LC software was used for data acquisition and analysis.

At each study location, a suite of eighteen acid herbicides were analysed (limit of detection (ng.l⁻¹) is given in brackets): 2,3,6-trichlorobenzoic acid (3.571); 2,4-D (0.446); 2,4-DB (2.143); 2,4,5-T (0.5); benazolin (5.714); bentazone (5); bromoxynil (5); clopyralid (1.623); dicamba (2.435); dichlorprop (0.478); fenoprop (0.714);

fluroxypyr (0.978); MCPA (1.325); MCPB (1.728); mecoprop (0.759); pentachlorophenol (1.429); picloram (1.429) and triclopyr (0.876).

5.2.5 *Statistical analysis*

MS Excel™ 2016 was used for all statistical analysis, including calculations of the means and standard error of replicated herbicide data, and the analysis of the variance. Data were initially tested to determine the normality and homogeneity of variances. A one-tailed *t*-test was used to determine statistical significance of the reduction of herbicide concentration by the interventions. Results were considered significant at $p \leq 0.05$.

5.3 Results and Discussion

5.3.1 *Outlet monitoring*

Table 1 shows the minimum, maximum, mean and frequency of detection of the detected herbicides at the catchment outlets over the two-year study period. In total, 298 detections of individual herbicides were recorded across all three outlets, of which 131 were over the MAC of 100 ng.l⁻¹ (EU, 1998). The MAC of 500 ng.l⁻¹ (EU, 1998) for total cumulative herbicides was exceeded on 38 occasions (Table 5.1).

Table 5.1. Minimum, maximum and mean concentrations and frequency of detection of the studied herbicides at the outlet points in the sampling areas.

Outlet	Herbicide	Year 1					Year 2				
		Concentration (ng.l ⁻¹)			Frequency		Concentration (ng.l ⁻¹)			Frequency	
		Min	Max	Mean	Detection (%) ^a	Exceedance (%) ^b	Min	Max	Mean	Detection (%) ^a	Exceedance (%) ^b
<i>Corduff</i>	2,4-D	5.02	23.61	10.81	5 (36)	0 (0)	39.29	47.10	39.89	4 (29)	0 (0)
	Clopyralid	21.11	86.04	42.61	8 (57)	0 (0)	14.61	108.77	47.89	4 (29)	1 (7)
	Fluroxypyr	3.43	968.2	200.22	12 (86)	6 (43)	2.45	29.84	12.23	5 (36)	0 (0)
	MCPA	4.67	33973.96	4513.81	14 (100)	6 (43)	5.01	245.33	96.72	11 (79)	4 (29)
	Mecoprop	1.01	4.68	2.33	3 (21)	0 (0)	0	0	0	0 (0)	0 (0)
	Triclopyr	36.86	1630.66	230.51	10 (71)	4 (29)	41.71	131.94	83.84	5 (36)	2 (14)
	Total	111.69	34147.15	4878.79	14 (100)	5 (36)	2.45	357.13	135.38	14 (100)	0 (0)
<i>Dunleer</i>	2,4-D	4.52	2008.04	261.75	14 (100)	5 (36)	28.12	1675.22	449.80	14 (100)	10 (71)
	Clopyralid	28.41	1349.84	427.11	10 (71)	7 (50)	21.92	386.36	125.44	11 (79)	4 (29)
	Fluroxypyr	156.56	1215.75	358.19	13 (93)	13 (93)	43.05	3593.44	949.12	14 (100)	11 (79)
	MCPA	3.05	724.37	118.38	9 (64)	2 (14)	12.15	1540.55	474.21	14 (100)	10 (71)
	Mecoprop	4.55	81.61	16.38	10 (71)	0 (0)	4.84	47.25	15.84	6 (43)	0 (0)
	Triclopyr	106.47	1139.08	426.67	10 (71)	10 (71)	13.34	772.78	173.92	10 (71)	3 (21)
	Total	364.63	4356.87	1295.66	14 (100)	11 (79)	174.31	5712.19	2104.26	14 (100)	12 (86)
<i>Urban</i>	2,4-D	9.88	319.81	100.76	12 (86)	4 (29)	6.64	6697.88	2488.47	14 (100)	10 (71)
	Clopyralid	7.31	819.81	271.79	8 (57)	4 (29)	1070.62	1070.62	1070.62	1 (7)	1 (7)
	Fluroxypyr	5.38	113.50	44.81	9 (64)	2 (14)	6.36	384.54	103.29	8 (50)	2 (14)
	MCPA	5.47	155.99	47.64	10 (71)	2 (14)	5.07	41.13	18.84	9 (64)	0 (0)
	Triclopyr	19.14	5057.55	1358.89	8 (57)	6 (43)	9.84	2629.58	760.39	7 (50)	2 (14)
	Total	33.34	5259.4	1228.00	12 (86)	4 (29)	37.84	9317.88	3016.79	14 (100)	6 (43)

^a Number of positive samples with percentage of positive samples from a total number of 14 sampled in parentheses.

^b Number of exceedances (MAC = 100 ng.l⁻¹ for individual herbicides and 500 ng.l⁻¹ for total herbicides), with percentage of exceedances from a total of 14 sampled in parentheses.

At the three sites, the most frequent herbicide exceedances at the outlets over both years were, from highest to lowest, fluroxypyr ($n = 34$), 2,4-D ($n = 29$), triclopyr ($n = 27$), and MCPA ($n = 24$). Herbicide persistence is categorised by DT_{50} values, which is the time required for the chemical concentration under defined conditions to decline to 50% of the amount at application. The DT_{50} values of the detected herbicides ranges from 3 days (fluroxypyr) to 28.8 days (2,4-D) under field conditions (Lewis et al., 2016). All of the herbicides detected in the current study were categorised as non-persistent (defined as having a $DT_{50} < 30$ days; Silva et al., 2019). There are two potential reasons why these herbicides were detected: (1) the detection of the herbicides in the waterways can be attributed to their desorption from soils or sediments, where they may have accumulated during previous applications (Postigo et al., 2021; McGinley et al., 2023), and (2) the detection can be indicative of recent herbicide application. DT_{50} values do not consider the organic carbon-water partitioning coefficient (K_{OC}) of herbicides, so a more accurate parameter to use when considering herbicide movement from soil to water would be the Groundwater Ubiquity Score (GUS) leaching values. The GUS score is an indicator of the potential leaching of a chemical into groundwater, based on the herbicides' K_{OC} and DT_{50} (Gustafson, 1989), and is one of the most used indicators for herbicide leaching from soil to water. A value above 2.8 indicates that the herbicide is a potential leacher, below 1.8 indicates non-leacher, and those between 1.8 and 2.8 represent moderate mobility in soil or a transition between leacher and non-leacher (Gustafson, 1989). The GUS scores of 2,4-D, MCPA, and triclopyr are >2.8 (Table 5.2), indicating that they are potential leachers, while fluroxypyr was <1.8 , indicating that it was a non-leacher. This implies that 2,4-D, MCPA, and triclopyr would be more likely to be found in waterways than in soils, while the opposite would be the case for fluroxypyr. This further suggests that, particularly in the case of fluroxypyr, the detection of the herbicide in the waterways was due to recent application. This is in agreement with the work of Prosser et al. (2020), who reported that surface run-off following rain events, which is one of the main drivers for herbicide discharge from soil to waterways, occurs mainly with soils having low porosity and low water draining capacity (Prosser et al., 2020). Given the prevalence of slopes within the topography of both Corduff and Dunleer, surface run-off is a likely pathway for herbicide transport from the application site to these water courses. Overall, the balance between the impact of topography and GUS index must be considered, as the GUS index does not

take into account electrostatic interactions, and may not fully correlate with observed mobility of herbicides (Butkovskiy et al., 2021).

Table 5.2 Physico-chemical properties of detected herbicides^a

Herbicide	Water solubility (mg.l⁻¹)	Log Pow (pH 7, 20°C)	DT₅₀ (Field, days)	GUS leaching potential	EU Status
2,4-D	24,300	-0.82	28.8	3.82	Approved
Clopyralid	7,850	-2.63	8.2	3.02	Approved
Fluroxypyr	6,500	0.04	3	1.03	Approved
MCPA	250,000	-0.81	25	3.13	Approved
Mecoprop	250,000	-0.19	-	2.29	Not approved*
Triclopyr	8,100	-0.45	30	3.30	Approved

^a Pesticide properties database online (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>). * Approval removed in 2017.

Fig. 5.3 shows the exceedances at the outlets, as well as the rainfall over the two years of sampling. The majority of the exceedances occurred during the early part (April to June) of each year, with several also observed in early autumn (September/October). This corresponds to the application times for herbicides, which should occur in early to mid-spring of each year, where there is rapid growth of the weeds, as well as in early autumn, at which point weeds are transporting food from their foliage to their roots in preparation for the winter (Turf and Till, 2023). The herbicides that had exceedances are used to control broadleaf weeds, as well as rushes and thistles. They are commonly used on grasslands and where cereal crops are grown (Lewis et al., 2016), and would be expected to be found at the both Corduff and Dunleer sites, as well as a recreational space such as the urban golf course site. Table D.1 shows the optimal spraying time and conditions for the herbicides with exceedances found at the outlets.

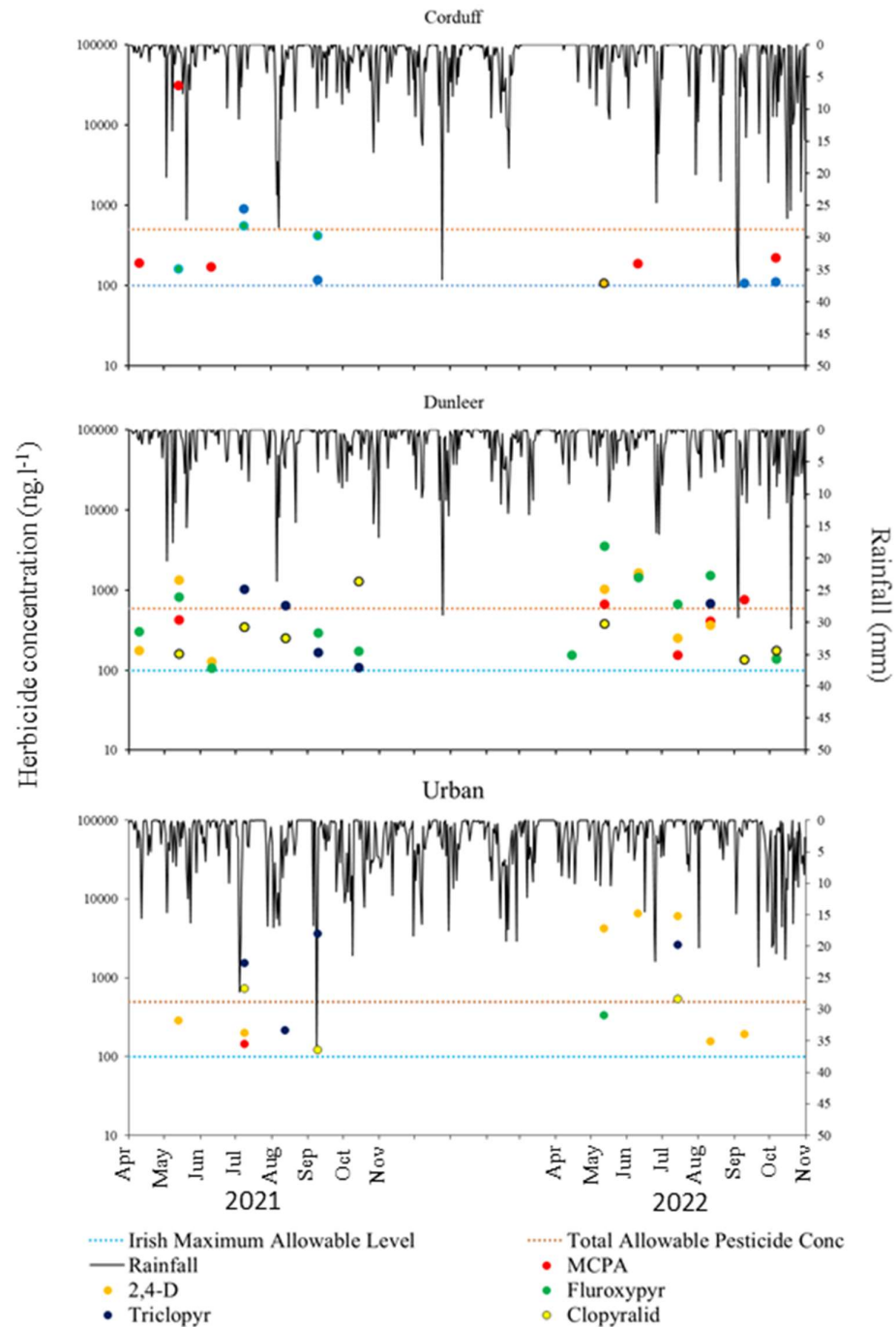


Figure 5.3 Exceedances of herbicides at outlet points in Corduff, Dunleer and Urban sampling areas for Year 1 (2021) and Year 2 (2022) of the study.

The rainfall distribution was similar between the Corduff and Dunleer catchments, but different for the Urban site (Fig. 5.3), which was not surprising given that the latter was located on the western side of Ireland (Fig. 5.1). The average rainfall for Belmullet

weather station in Co. Mayo (on the west coast of Ireland) over the 30 year period 1981-2020 was 1245 mm.y⁻¹, while that for Dublin Airport (on the east coast of Ireland) over the same period was 758 mm.y⁻¹ (Met Éireann, 2023). In all cases, where rainfall exceeded 15 mm.day⁻¹, the concentrations of herbicides detected at the outlets greatly exceeded the MAC value of 100 ng.l⁻¹. This supports evidence that heavy rainfall triggers an increase in overland flow, causing loss of applied herbicides and contamination of surface waterways (Khan et al, 2020; Prosser et al, 2020; Liu et al., 2021).

5.3.2 Media characterisation

We have previously shown that GAC is capable of removal of the herbicides, 2,4-D, fluroxypyr, MCPA, mecoprop-P, and triclopyr, from aqueous solutions with >95% removal reported (McGinley et al., 2022). We have also found that CAC is as efficient at removal of the same suite of herbicides as GAC, with >97% removal observed (Fig. D.1). The surface of the GAC was not smooth but, instead, had small clusters distributed over smooth platelets (Fig. D.2a and b). The surface of CAC, on the other hand, was smooth, with visible indentations in the surface (Fig. D.2c and d). Adsorbent materials can be categorised according to pore size distribution, as macroporous (>50 nm), mesoporous (2-50 nm) or microporous (<2 nm) (Feng et al, 2022; Gao et al., 2023). Mesoporous materials have large specific surface areas (>500 m².g⁻¹; Xu et al., 2020; Plohl et al., 2021; Kouchakinejad et al., 2022), which facilitate the adsorption of guest molecules. GAC is at the lower end of the mesoporous range, with a pore diameter of ca. 6 nm, resulting in a high surface area (579 m².g⁻¹) and a high pore volume (ca. 0.496 cm³.g⁻¹), which is optimal for adsorption (McGinley et al., 2022). On the other hand, CAC has a lower surface area (10.52 m².g⁻¹) and pore volume (0.028 cm³.g⁻¹) than GAC, which would suggest reduced adsorption capacity. However, CAC has a larger pore diameter than GAC (ca. 14.5 nm), which would better facilitate herbicide adsorption. EDX imaging of GAC and CAC is shown in Fig. D.2e and f. While both materials primarily contained carbon and oxygen, GAC also contained the elements aluminium, silicon, sodium and titanium, while CAC also contained calcium. As CAC and GAC had comparable abilities to adsorb herbicides, but CAC was more cost-effective than GAC, it was selected as the adsorbent for the interventions in Year 2.

5.3.3 Herbicide removal by filter bag configuration

Fig. 5.4 shows the herbicide detections before and after the filter bags at each site, thereby indicating the ability of the filter bags to remove the investigated herbicides, while Table D.2 (a-c) shows the minimum, maximum, mean and frequency of detection of the detected herbicides before and after the filter bags in the three sampling areas. In Corduff stream, there were 31 detections of herbicides and one exceedance before the filter bags, compared to 29 detections of herbicides and three exceedances after the filter bags (Fig. 5.4a; Table D.2a), while in Dunleer stream, there were 17 detections of herbicides and no exceedances before the filter bags, compared to 22 detections of herbicides and no exceedances after the filter bags (Fig. 4b; Table S2b). In the majority of samples at the Corduff and Dunleer streams, the concentrations of the herbicides before the filter bags was less than the MAC of 100 ng.l⁻¹. Overall, in the two streams, there was a slight, but not statistically significant ($p > 0.05$), decrease in the average concentrations detected after the filter bags, with a reduction of 24% and 17% in Corduff and Dunleer streams across all measured herbicides (Fig. 5.4a and b; Table D.2a and b). Incomplete removal of the herbicides is probably due to the wide body of water (< 1m in width) in both streams, which meant that a single filter bag could not span the stream. Although the three filter bags were put in a staggered position, there was still room for the water to flow around the filter bags, rather than passing through the adsorbent material. This ability to circumvent the filter bags could account for the incomplete removal of herbicides by this configuration.

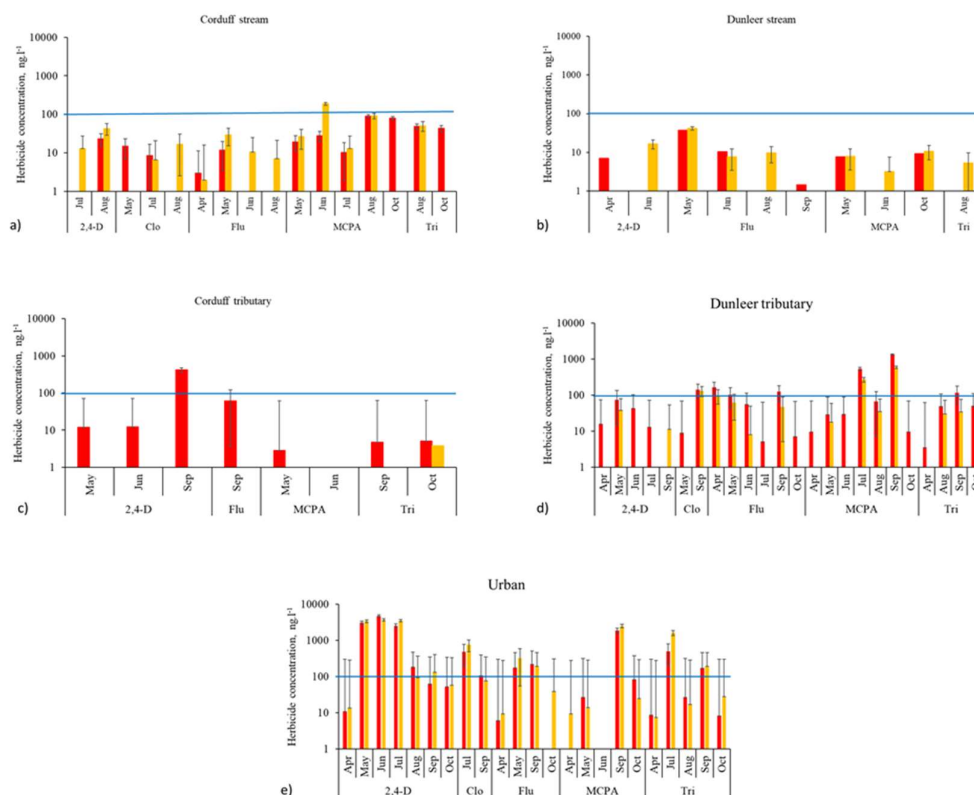


Figure 5.4 Herbicide detections for the filter bag interventions across all sampling areas. Clo = clopyralid, Flu = fluroxypyr and Tri = triclopyr. Red columns indicate herbicide concentrations before the filter bag interventions, and yellow columns indicate herbicide concentrations after the filter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

In the Corduff tributary, there were 12 detections of herbicides and three exceedances before the filter bags, compared to one detection of herbicides and no exceedances after the filter bags (Fig. 5.4c; Table D.2a). The filter bags were very effective in the Corduff tributary (average 89% reduction, $p > 0.05$), with only one detection of triclopyr after the filter bags, which was below the MAC of 100 ng.l^{-1} (Fig. 5.4c; Table D.2a). There was a complete removal of 2,4-D from an average initial concentration of 422.6 ng.l^{-1} (Fig. 5.4c; Table D.2a), indicating that the CAC adsorbent was capable of dealing with incoming herbicide concentrations up to 500 ng.l^{-1} . Zafra-Lemos et al. (2021) reported that coconut-based activated carbon completely removed the herbicide 2,4-D, at a concentration of 10 mg.l^{-1} , from water, but no pilot-scale

experiments were undertaken. Two possible reasons for this complete removal were (1) the low level of water that was present in the tributary, with the level of water never rising above 0.15 m over the base of the stream from April to October, and (2) the tributary was also only 0.40 m wide at its widest point, so that the bag interventions completely filled the path of the stream, thereby forcing the polluted water through the CAC-filled bags and allowing time for the adsorption of the herbicides to occur. The height of the filter bags was approximately 0.15 m, which meant that the water could not flow over the bags. Furthermore, the flow of water in the tributary was quite slow, so that the water had time to flow through the bag and allow adsorption to take place.

In the Dunleer tributary (Fig. 5.4d; Table D.2b), the number of detections before the filter bags was 56, of which seventeen were exceedances, while, after the bags, there were 39 detections and eight exceedances. At the Dunleer tributary, the filter bags were effective for herbicide removal on the majority of occasions (an average reduction, across all herbicides of 67.1%; Fig. 5.4d), with either small or no detections of herbicides being observed after the bags ($p > 0.05$). However, for MCPA in July and September, the incoming concentrations of 536.8 and 1334 ng.l⁻¹, respectively, were reduced to 270.1 and 593.7 ng.l⁻¹, which are considerably above the MAC. This would suggest that the CAC adsorbent is not able to deal with very high concentrations of herbicides in the waterways. The tributary was also slow moving and the filter bags were able to almost completely span the width of the waterway, with only a few centimetres on either side available for the water to circumvent the filter bags.

The number of herbicides detected in the Urban area before the filter bags was 53, of which 29 were exceedances, while after the bags, there were 56 detections and 27 exceedances (Fig. 5.4e; Table D.2c). Across all herbicides measured in the Urban area, there was no significant difference ($p > 0.05$) between detections before and after the filter bags (Fig. 5.4e; Table D.2c). The water was slow moving, which helps the removal of the herbicide by the treatment system. However, the drain was over 1 m in depth, and the water level was consistently >0.5 m, even during the summer months. This reduced the amount of water that was passing through the filter bags and making contact with the CAC material. Overall, the filter bags reduced the exceedances from $n=50$ to $n=38$ (Tables D.2(a-c)).

Based on these observations, the filter bags adsorbed the herbicides most efficiently when (1) the water flow was slow, (2) the filter bags spanned the width of the waterway, and (3) the height of water present in the waterway was lower than the height of the filter bags. In the cases where the water covered the filter bags, or where the water can easily bypass above or around the bags, then the filter bags did not reduce the herbicides concentrations as effectively. Fig. 5.4 also shows that, where the concentrations of herbicides before the bags are $<500 \text{ ng.l}^{-1}$, then the media are better able to remove those herbicides completely in the majority of cases. However, where the concentrations are higher than 500 ng.l^{-1} , particularly in the case of the Urban area, then complete adsorption is more difficult to obtain.

5.3.4 Herbicide removal by filter pipe configuration

Fig. 5.5 shows the herbicide detections before and after the filter pipes at each site, indicating the ability of the filter pipe to remove the herbicides under investigation, while Table D.2 (a-c) shows the minimum, maximum, mean and frequency of detection of the detected herbicides before and after the filter pipes in the three sampling areas. The filter pipes typically had a lower challenge concentration as the water had already been passed by the filter bags. In the Corduff stream (Fig. 5.5a; Table D.2a), there were 29 detections of herbicides before the filter pipes, of which three were exceedances, which were reduced to 14 detections and no exceedances after the filter pipes, while in Dunleer stream (Fig. 5.5b; Table D.2b) there were 22 detections and no exceedances before the filter pipes, which were reduced to 5 detections and no exceedances after the filter pipes. Except for the case of the detection of MCPA at the Corduff stream, the concentrations of the herbicides before the filter pipes in both Corduff and Dunleer streams were below the MAC of 100 ng.l^{-1} . Overall, in the two streams, there was a large, statistically significant ($p < 0.05$), decrease in the concentrations of herbicides, with an average reduction of 83% and 88%, respectively, across the herbicides measured (Fig. 5.5a and b). These reductions included a 95% reduction for MCPA from 186.9 ng.l^{-1} to 8.4 ng.l^{-1} in the Corduff stream (Fig. 5.5a).

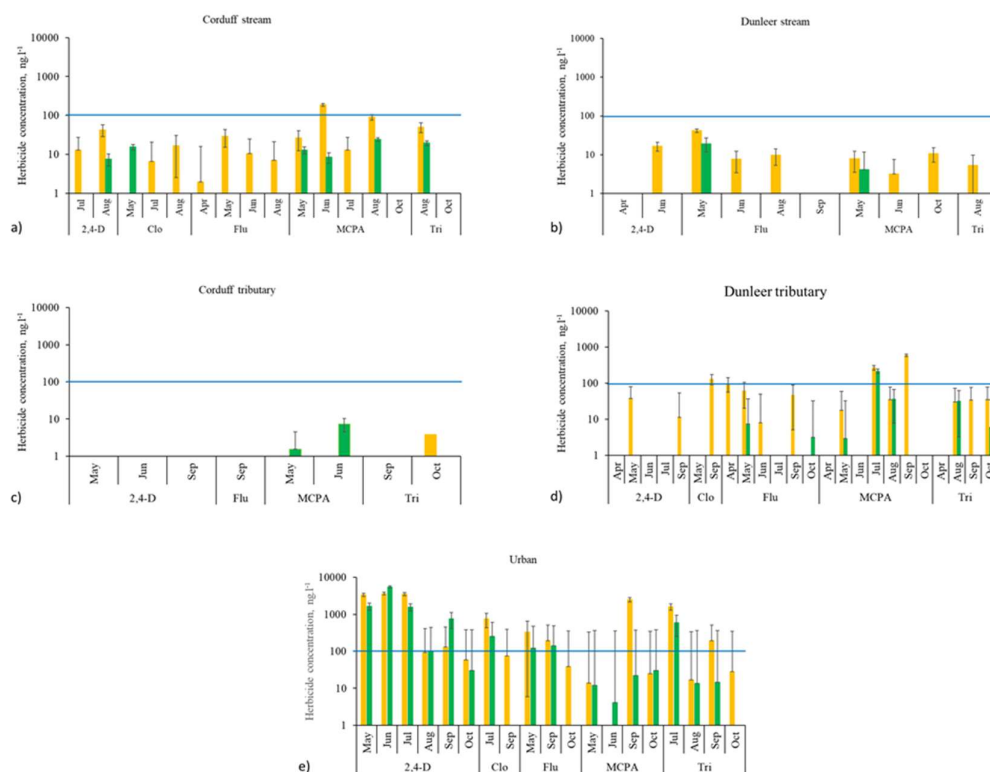


Figure 5.5 Herbicide detections for the filter pipe interventions across all sampling areas. Clo = clopyralid, Flu = fluroxypyr and Tri = triclopyr. Yellow columns indicate herbicide concentrations before the filter pipe interventions, and green columns indicate herbicide concentrations after the filter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

In the Corduff tributary, only one detection was measured before the pipe while two detections were measured after the pipe (Fig. 5.5c). None of these detections were above the MAC. In the Dunleer tributary, there were 39 detections of herbicides before the pipe, of which eight were exceedances, while there were only 14 detections and two exceedances after the filter pipe (Fig. 5.5d; Table D.2b). The filter pipes greatly reduced the herbicide concentrations ($p < 0.05$), with an average reduction of 64% (Fig. 5.5d). In almost all the cases, the starting herbicide concentration was lower than the MAC, except for MCPA in July and September, and clopyralid in September. There was a measured reduction of MCPA in July from 270.1 ng.l^{-1} to 216.7 ng.l^{-1} (which was above the MAC; Fig. 5.5d). However, in September, the pipe was moved

from its original position by the force of water coming down the tributary as a result of heavy prolonged rainfall early that month, so no readings were obtained after the pipe for that month. This month was, as a result, discounted from the overall reduction calculations. In the case of the Dunleer tributary, the herbicide concentrations before the filter pipe were reduced ($p < 0.05$) from 8.1 – 593.7 ng.l⁻¹ to between below the LOD and 216.7 ng.l⁻¹.

At the Urban site, the number of herbicides detected decreased from 56 to 42, while the number of exceedances decreased from 27 to 22 after the filter pipes (Fig. 5.5e; Table D.2c). There was a decrease in concentration detection ($p > 0.05$), after the filter pipe, with an average reduction of 47% (no herbicides were detected after the filter pipe on several occasions; Fig. 5.5e). The herbicide concentrations varied from 7.5 – 3645.4 ng.l⁻¹ before the filter pipe to between below the LOD and 5503 ng.l⁻¹ after the pipe. When the concentrations of the herbicides were greater than 3000 ng.l⁻¹, the filter pipe was unable to reduce the concentration to below the MAC (Fig. 5.5e).

Overall, the filter pipes reduced the exceedances from $n=38$ to $n=24$ (Table D.2 (a-c)). The pipe containing the intervention was 0.3 m in diameter and so could easily fit into all the waterways. The filter pipes adsorbed the herbicides most efficiently when the water flow was slow. From Fig. 5.5, it is clear that, when the concentration of herbicides is < 2500 ng.l⁻¹, the pipe intervention is quite capable of reducing the concentration to below the MAC.

5.3.5 Comparison of the filter bag and filter pipe configurations

There are both similarities and differences between the filter bags and the filter pipes. In terms of similarities, both configurations adsorb herbicides most effectively when the water flow is slow and when the incoming herbicide concentration is low (< 500 ng.l⁻¹). Since both are using the same adsorption based process, this is not surprising. The major difference between both types of intervention is that the filter pipe is better at removing herbicides than the filter bags. The filter bags reduced the number of detections and exceedances across all sampling sites from 169 detections and 50 exceedances to 147 detections and 38 exceedances. The filter pipes brought the detections and exceedances down to 77 detections and 24 exceedances. When the

detections across all the filter bags were compared to the detections across the filter pipes, the number of reductions was significant ($p < 0.05$).

Varying the shape and size of the filter pipe may be an option to improve the configuration of the interventions: they could be smaller and have a rectangle-shape rather than a circular shape, so that multiple pipes could be used across the streams. Alternatively, having a bigger bag within the pipe could also have advantages, as the increased volume of adsorbent would increase the operational life span of the system prior to requiring replacement. A second option could be to physically adapt the stream environment to suit the filter pipe, by creating a narrow section of the stream in order to funnel the water through the intervention.

5.4 Conclusions

This study showed that herbicides are present in high concentrations (frequently above the MAC) in two agricultural catchments and one urban area in Ireland, and that the majority of the exceedances occurred in April to June and September/October, corresponding to the application times for herbicides.

Two different CAC-based *in situ* remediation systems, filter bags and filter pipes, capable of herbicide removal close to the source of contamination, were designed and installed in two agricultural catchment areas and one urban area. Both systems operated effectively when the water flow in the waterways was slow, which allowed time for the adsorption of the herbicides to occur. The reduction in herbicide concentrations was better for the filter pipes than for the filter bags ($p < 0.05$).

While further work on the design of the interventions is envisaged, including increasing the size of the filter bags and modifying the shape of the pipe, this investigation into the use of a CAC-based adsorption system for the removal of herbicides at source, rather than treatment at a drinking water treatment facility, has shown good potential.

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Chapter 6 – Conclusions and Recommendations

6.1 Overview

The inefficient and over-use of pesticides in agriculture, in order to produce foodstuffs to cater for the current global population, is having a profound environmental effect on waterways, soil, ecosystems, and, ultimately, human health. Pesticides are, as a result, widespread in both soils, where crops have been planted and grown, and waterway sediments, where the pesticides have been transported to the waterways and adsorbed. An assessment of the prevalence of pesticides, especially legacy pesticides, in European waterways has not been explored to date; this was the first knowledge gap identified in this study. Hence, the first aim of this study was to review the prevalence of legacy pesticides in waterways, which were reported in the literature between the years 2011 and 2020. This review, presented in **Chapter 2**, found that unapproved pesticides continue to be detected in European surface and ground waters at levels exceeding the legal limits. In the time period reviewed, 233 legacy pesticide detections were observed from 71 pesticides, after they had been prohibited for use in the EU. The remediation of these legacy pesticides was also investigated. It was found that Metal Organic Frameworks (MOFs) and vegetated buffer strips (VBS) are the most promising mitigation methods with the latter being the most cost-effective. The current EU food production strategy aims to reduce the overall use of chemical pesticides by 50 % by 2030. However, the omission of legacy pesticides from this strategy may result in that target not being achieved.

The transport of pesticides to waterways after application are primarily by means of surface run-off, leaching, spray-drift, or subsurface drainage. Mathematical models are used to predict the fate and transport of pesticides in the environment. However, these models are both complex and complicated, and can take a considerable amount of time to run for a single pesticide. A quick and easily applied screening tool to assess the potential risk of loss of pesticides to waterways is required. The second aim of this study was to develop such a screening tool, which would be based on soil texture and various pesticide properties. **Chapter 3** developed a screening tool based on soil texture-specific adsorption isotherm data and the pesticide properties of water

solubility, soil half-life and soil permeability. The tool offers the end user either (1) the opportunity to choose the pesticide that will lower the potential risk of pesticide transmission for a given soil texture, or (2) for a given pesticide, the ability to analyse which soil textures are most likely to increase the potential transmission risk. The screening tool, therefore, allows the farmer to see if the pesticide of choice for the required job was environmentally friendly or if, through its use, there was a potential threat to the environment.

Chapter 4 identified granulated activated carbon (GAC), a coal-based activated carbon, to be the medium of choice for the adsorption of pesticides. Given the life expectancy of fossil fuels, the search for other adsorbent materials, which give comparable results to GAC, is ongoing. Alternative low-cost, renewable media may include agricultural and industrial waste materials. Their use as adsorbent material for pesticides requires further study. This was identified as the third knowledge gap in this study. Therefore, the third aim of this study was to assess the potential of several raw and pyrolysed low-cost industrial and agricultural materials as pesticide adsorbents for the removal of commonly used herbicides in Ireland. **Chapter 4** addresses this aim. In this chapter, twelve materials were chosen as adsorbents, including four biochars and GAC, for the removal of five herbicides from aqueous solutions. The herbicides chosen were 2,4-D, fluroxypyr, MCPA, mecoprop-P and triclopyr, which are among the top ten selling herbicides in Ireland. Initial screening showed that GAC removed all the herbicides with >95 % efficiency over 72 hr, while the raw materials demonstrated little capacity for herbicide adsorption. Adsorption kinetic and isotherm experiments were then undertaken for each of the herbicides with GAC. From the kinetic data, chemisorption was the rate-limiting step for both MCPA and mecoprop-P, intraparticle diffusion was the rate-limiting step for both fluroxypyr and triclopyr, and transport of the herbicide to the adsorbent was the rate-limiting step for 2,4-D. In all cases, the adsorption process followed the Freundlich isotherm model, verifying monolayer and multilayer adsorption.

Many batch adsorption studies use source water, environmentally-relevant aqueous solutions, or spiked samples to demonstrate the potential of the adsorbent media for the removal of pesticides. There is a scarcity of field/pilot studies investigating the use of these materials in intervention systems. This was identified as the fourth knowledge

gap in this study. The fourth aim of this study was to assess, in the field, the potential of the medium which showed the greatest promise in the batch adsorption study by using filter bags containing the medium in two agricultural catchments and one urban area. **Chapter 5** addresses this aim by investigating two configurations of interventions. One configuration used filter bags containing 16 kg of sieved coconut-based activated carbon (CAC), while the second configuration used the same filter bags, but in this case filled with 12 kg of sieved CAC, and fitted into a polyethylene pipe to fill the full diameter of the centre section of the pipe. Overall, the filter pipes were more efficient at achieving a reduction in herbicide concentrations than the filter bags.

6.2 Conclusions

The main study conclusions are as follows:

- The detection of unapproved pesticides continues to occur in European surface and ground waters at levels exceeding the MAC of 100 ng.l⁻¹. Current remediation methods employed at drinking water facilities, consisting of GAC filters, are not widely used in Ireland. Of the current remediation methods for legacy pesticides, a VBS system is the most cost-effective method to protect streams and waterways.
- The screening tool developed in this study, based on soil texture-specific adsorption isotherm data and the pesticide properties of water solubility, soil half-life and soil permeability, offers farmers the opportunity to see if the pesticide of choice for the required job was environmentally friendly or if, through its use, there was a potential threat to the environment.
- The evaluation of twelve materials, including seven industrial and agricultural waste materials, four biochars and GAC, as potential absorbents for the removal of five commonly used herbicides in Ireland showed that GAC removed all the herbicides with >95 % efficiency, while the industrial and agricultural materials demonstrated little or no capacity for herbicide adsorption. Given that biochars

have been reported in the literature as good adsorbents for herbicides, they showed poor adsorption capacities in this study, but CAC, on the other hand, adsorbed the herbicides with >97% efficiency (data not published) and so is a good sustainable alternative to GAC.

- A field study, using two types of intervention systems containing CAC as the adsorbent medium, namely filter bags and filter pipes, demonstrated that the filter pipes reduced the herbicide concentrations more efficiently than the filter bags. Where the water flow was slow and when the water was not able to flow around either the filter bags or pipe, then substantial reductions in the herbicide concentrations in the streams and drains were observed.

6.3 Recommendations

The recommendations arising from this project may be summarised as follows:

- It is recommended that further work on the design of the intervention systems, including modifying the size of the filter bags and the shape of the pipe, should be explored. Given that the width and depth of streams and drains at the sides of fields vary considerably, having a number of different sized filter bags/pipes should be considered. Rather than targeting pesticides alone, chemicals of emerging concern, such as pharmaceuticals, antibiotics, personal care products, and veterinary products could also be investigated.
- Further testing of the *in situ* remediation system, including practical considerations such as ecological impacts and economic costs, should be undertaken.
- As CAC is a relatively expensive adsorbent, the possibility of removing the adsorbed herbicides from the spent CAC, in order to recover the CAC, should be investigated. This desorption process should be carried out at room temperature, as otherwise, unwanted chemical reactions involving the herbicides and desorption solvent could occur.

- Closely linked to this third recommendation, the fourth recommendation in an effort to reduce costs is the possibility of using Irish agricultural waste materials as the activated carbon adsorbent system, as CAC requires transport to Ireland. One such waste material that could be used for this purpose could be wood from forestry waste.
- Identify key stakeholders and work with them to identify and circumvent any barriers to the implementation of this system in the field at a national scale. These stakeholders would include the Department of Agriculture, Food and the Marine, Teagasc, Inland Fisheries Ireland, non-governmental organisations, fisheries owners, as well as the various farming communities.
- The further development and testing with farmers of the pesticide screening tool, with the potential aim of incorporated the tool into a decision-support system, should be undertaken.

Appendix A

Supplementary Information to Chapter 2

Table A.1 Herbicide usage (t) per country from 2011 to 2020.^a

	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Austria	1,505	1,545	1,227	1,376	1,317	1,281	1,297	1,277	1,151	1,153
Belgium	2,611	2,853	2,508	2,534	2,391	2,258	2,334	2,648	2,328	1,944
Bulgaria	-	774	706	652	636	2,007	1,699	2,607	4,340	1,988
Croatia	-	-	829	889	821	743	669	718	700	730
Cyprus	170	137	128	140	122	158	139	161	168	181
Czechia	3,473	3,607	3,145	2,755	2,890	2,893	2,562	2,572	2,399	2,002
Denmark	3,692	4,564	2,936	1,239	1,903	1,914	1,954	2,012	2,025	2,454
Estonia	357	437	434	426	472	604	463	428	531	511
Finland	1,452	1,224	1,133	1,305	1,368	1,264	1,006	982	1,107	1,155
France	29,252	27,801	27,883	31,035	30,596	30,156	30,253	34,354	22,484	29,156
Germany	17,955	19,907	17,670	17,877	16,063	15,038	16,752	14,570	13,946	14,589
Greece	1,455	2,139	2,571	1,195	1,315	1,744	1,674	1,833	1,830	1,910
Hungary	3,668	3,824	3,562	4,011	4,270	4,580	4,270	3,824	3,906	4,265
Ireland	2,812	1,808	2,005	2,392	2,482	2,243	1,916	1,833	1,845	2,262
Italy	8,327	8,056	7,751	7,799	7,950	7,486	7,114	6,880	8,524	9,750
Latvia	722	789	728	847	861	987	801	965	972	1,167
Lithuania	1,773	1,715	1,422	1,394	1,372	1,433	1,251	1,053	1,199	1,487
Luxembourg	102	96	83	89	83	61	61	54	49	60
Malta	6	8	7	8	5	6	2	3	2	3
Netherlands	3,011	3,029	2,751	3,247	2,865	2,733	2,883	2,961	2,721	2,607
Poland	12,408	12,654	12,518	12,073	12,190	12,693	13,655	11,371	11,705	12,809
Portugal	1,996	1,769	1,311	2,411	2,122	1,905	1,899	1,939	2,222	2,402
Romania	6,771	6,614	6,034	5,025	6,353	5,066	5,486	5,188	4,012	4,125
Slovakia	1,080	1,257	1,157	1,215	1,218	1,080	1,105	1,329	1,107	1,155
Slovenia	264	257	223	238	224	247	235	257	172	181
Spain	13,835	13,985	14,720	14,908	15,587	15,224	16,077	16,593	17,023	20,199
Sweden	2,136	2,087	1,773	2,104	1,829	1,633	1,731	1,483	1,544	1,708

^a Data taken from Eurostat (https://ec.europa.eu/eurostat/web/products-datasets/-/aei_fm_salpest09)

Table A.2 Fungicide usage (t) per country from 2011 to 2020.^a

	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Austria	1,544	1,634	1,493	1,641	2,131	2,006	1,992	2,269	2,068	1,931
Belgium	2,452	2,725	2,520	3,131	2,611	2,856	2,496	2,458	2,449	2,203
Bulgaria	-	474	380	186	619	1,049	1,287	1,798	1,578	1,698
Croatia	-	-	945	1,005	1,315	932	727	767	656	701
Cyprus	895	837	805	773	781	804	818	823	867	863
Czechia	1,627	1,410	1,662	1,782	2,109	1,785	1,854	1,755	1,651	1,545
Denmark	633	891	884	417	504	407	484	438	436	503
Estonia	50	60	66	88	109	104	117	106	105	-
Finland	165	189	210	198	225	3,212	3,228	3,814	2,832	3,698
France	24,496	27,581	30,376	34,442	27,374	31,971	29,786	39,065	24,483	26,001
Germany	10,473	9,062	10,507	12,920	12,817	12,141	13,266	11,682	10,217	9,505
Greece	2,256	2,007	5,521	1,867	1,927	1,804	1,686	1,729	1,756	1,802
Hungary	2,997	3,141	3,238	3,674	3,868	3,835	4,170	3,535	2,796	3,372
Ireland	620	650	594	635	688	597	633	602	922	440
Italy	43,574	37,358	33,303	37,226	39,187	36,852	32,687	31,539	24,286	31,644
Latvia	148	202	214	225	270	262	266	213	295	304
Lithuania	361	485	534	601	737	741	690	677	575	593
Luxembourg	92	91	-	-	-	-	-	-	-	-
Malta	95	125	122	97	119	83	102	82	70	90
Netherlands	4,246	4,657	4,321	4,896	4,410	4,867	4,721	4,290	3,882	3,962
Poland	6,081	6,131	6,474	7,442	7,742	7,534	6,927	7,992	6,867	9,278
Portugal	9,975	8,498	7,202	8,244	5,193	5,474	4,181	4,335	5,767	6,402
Romania	3,482	3,541	3,631	4,132	4,142	4,526	4,600	4,541	4,021	3,878
Slovakia	541	497	531	567	639	640	685	676	652	662
Slovenia	797	700	647	724	759	860	795	849	752	731
Spain	31,343	26,793	32,393	38,380	36,423	38,905	37,982	38,067	34,073	37,916
Sweden	218	235	332	302	398	249	265	223	164	222

^a Data taken from Eurostat (https://ec.europa.eu/eurostat/web/products-datasets/-/aei_fm_salpest09)

Table A.3 Insecticide usage (t) per country from 2011 to 2020.^a

	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Austria	248	244	238	240	1956	936	1,186	1,569	1,613	2,363
Belgium	695	584	625	572	578	553	550	476	359	390
Bulgaria	-	83	110	163	286	703	374	596	727	503
Croatia	-	-	135	143	139	134	115	127	122	119
Cyprus	159	168	177	167	104	113	124	151	135	91
Czechia	291	288	270	344	336	375	174	292	307	151
Denmark	45	77	74	37	41	42	44	45	57	32
Estonia	19	21	19	25	28	-	26	29	33	16
Finland	31	31	25	13	18	18	25	21	23	12
France	2,190	2,363	2,283	2,539	2,570	3,651	3,786	4,861	4,367	5,845
Germany	11,831	12,995	12,143	14,636	14,875	15,463	14,549	16,237	18,665	21,248
Greece	109	911	1,287	589	695	921	893	1,009	965	861
Hungary	522	609	606	917	827	842	860	787	690	583
Ireland	47	41	46	51	58	33	53	29	23	10
Italy	2,494	2,365	1,978	2,047	2,279	2,022	2,726	1,653	1,683	4,705
Latvia	34	44	44	64	17	32	33	36	39	44
Lithuania	26	45	44	47	33	45	54	57	76	86
Luxembourg	-	-	-	-	-	-	-	-	-	-
Malta	4	5	5	4	4	5	3	3	3	3
Netherlands	1,898	1,863	1,657	1,715	2,180	2,603	2,476	1,591	1,959	2,372
Poland	991	1,286	1,306	1,479	1,538	1,481	1,819	1,770	2,724	619
Portugal	878	810	746	733	561	766	878	674	812	417
Romania	808	828	626	569	676	744	944	1,012	809	454
Slovakia	64	65	90	106	100	110	139	151	149	138
Slovenia	38.5	42	27	33	38	40	50	55	36	39
Spain	8,062	7,641	6,822	7,515	6,691	7,501	6,549	6,488	7,636	8,165
Sweden	29	29	28	34	30	28	31.4	94	45	32

^a Data taken from Eurostat (https://ec.europa.eu/eurostat/web/products-datasets/-/aei_fm_salpest09)

Table A.4 Pesticide usage (kg) per hectare (Ha) per country from 2011 to 2020.

Austria								
Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)	
2011	1,505,163	1,544,218	247,982	2878170	0.522958	0.536528	0.08616	
2012	1,544,519	1,634,371	244,079	2878170	0.536632	0.567851	0.084804	
2013	1,227,017	1,492,799	238,252	2726890	0.449969	0.547436	0.087371	
2014	1,375,815	1,641,055	240,298	2726890	0.504536	0.601805	0.088122	
2015	1,317,219	2,130,973	195,649	2726890	0.483048	0.781466	0.071748	
2016	1,281,493	2,006,542	936,405	2669750	0.480005	0.751584	0.350746	
2017	1,296,943	1,991,638	1,185,853	2669750	0.485792	0.746002	0.444181	
2018	1,276,929	2,268,659	1,568,970	2669750	0.478295	0.849765	0.587684	
2019	1,150,741	2,068,059	1,612,713	2669750	0.431029	0.774626	0.604069	
2020	1,152,793	1,931,277	2,362,720	2669750	0.431798	0.723392	0.884997	
Belgium								
Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)	
2011	2,610,565	2,452,096	694,606	1358020	1.922332	1.805641	0.511484	
2012	2,853,151	1,724,804	582,728	1358020	2.100964	1.270087	0.429101	
2013	2,508,253	2,519,857	625,325	1307900	1.917771	1.926643	0.478114	
2014	2,533,628	3,131,351	572,087	1307900	1.937173	2.394182	0.437409	
2015	2,390,780	2,611,185	577,880	1307900	1.827953	1.996471	0.441838	
2016	2,257,767	2,856,228	553,003	1354250	1.667171	2.109085	0.408346	
2017	2,334,151	2,495,880	549,859	1354250	1.723575	1.842998	0.406025	
2018	2,648,068	2,457,618	476,237	1354250	1.955376	1.814745	0.351661	
2019	2,327,710	2,449,418	359,000	1354250	1.718819	1.80869	0.265091	
2020	1,944,731	2,203,245	389,567	1354250	1.436021	1.626912	0.287663	

Bulgaria		Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
Year								
2011	-	-	-	4475530	-	-	-	-
2012	773,569	474,395	83,058	4475530	0.172844	0.105998	0.018558	
2013	705,944	380,174	110,152	4650940	0.151785	0.081741	0.023684	
2014	652,446	186,142	163,439	4650940	0.140283	0.040022	0.035141	
2015	636,209	619,022	286,100	4650940	0.136791	0.133096	0.061514	
2016	2,007,428	1,048,879	702,831	4491860	0.446904	0.233507	0.156468	
2017	1,698,979	1,287,452	373,564	4491860	0.378235	0.286619	0.083165	
2018	2,606,572	1,798,029	596,356	4491860	0.580288	0.400286	0.132764	
2019	4,340,168	1,578,538	727,307	4491860	0.96623	0.351422	0.161917	
2020	1,987,695	1,697,663	502,890	4491860	0.44251	0.377942	0.111956	
Croatia		Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
Year								
2011	-	-	-	1316010	-	-	-	-
2012	-	-	-	1316010	-	-	-	-
2013	829440.0	945126.0	135128.0	1571200	0.527902	0.601531	0.086003	
2014	889121.0	1004779.0	143090.0	1571200	0.565887	0.639498	0.091071	
2015	820899.0	1315186.0	139197.0	1571200	0.522466	0.837058	0.088593	
2016	742557.0	932012.0	134603.0	1562980	0.475091	0.596304	0.086119	
2017	668739.0	727129.0	115247.0	1562980	0.427862	0.46522	0.073735	
2018	717673.0	767227.0	126562.0	1562980	0.45917	0.490874	0.080975	
2019	699638.0	656073.0	122342.0	1562980	0.447631	0.419758	0.078275	
2020	729914.0	700973.0	119186.0	1562980	0.467001	0.448485	0.076256	

Cyprus

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	169986.0	894770.0	158669.0	118400	1.435693	7.557179	1.34011
2012	137002.0	837480.0	168179.0	118400	1.157111	7.073311	1.420431
2013	127677.0	804761.0	176869.0	109330	1.167813	7.360843	1.617754
2014	140379.0	772662.0	166763.0	109330	1.283993	7.067246	1.525318
2015	121756.0	781151.0	103927.0	109330	1.113656	7.144892	0.950581
2016	157649.0	803815.0	112985.0	111930	1.408461	7.181408	1.009426
2017	138932.0	817955.0	124258.0	111930	1.24124	7.307737	1.11014
2018	160580.0	823467.0	151083.0	111930	1.434647	7.356982	1.349799
2019	168342.0	867436.0	134635.0	111930	1.503994	7.749808	1.20285
2020	181319.0	862578.0	91154.0	111930	1.619932	7.706406	0.814384

Czechia

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Herbicide per hectare (kg/Ha)	Herbicide per hectare (kg/Ha)
2011	3,473,231.0	1,626,666.0	290967.0	3483500	0.997052	0.466963	0.083527
2012	3,606,879.0	1,410,021.0	287724.0	3483500	1.035418	0.404771	0.082596
2013	3,144,886.0	1,661,560.0	270033.0	3491470	0.900734	0.475891	0.077341
2014	2,755,336.0	1,782,187.0	343824.0	3491470	0.789162	0.51044	0.098475
2015	2,889,375.0	2,109,337.0	336549.0	3491470	0.827553	0.60414	0.096392
2016	2,892,771.0	1,785,207.0	375294.0	3455410	0.837172	0.516641	0.108611
2017	2,562,124.0	1,853,685.0	174044.0	3455410	0.741482	0.536459	0.050369
2018	2,572,338.0	1,755,138.0	291603.0	3455410	0.744438	0.507939	0.08439
2019	2,399,082.0	1,650,880.0	307083.0	3455410	0.694297	0.477767	0.08887
2020	2,002,231.0	1,544,879.0	151212.0	3455410	0.579448	0.44709	0.043761

Denmark

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (kg)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	3,692,148.0	632925.0	44940.0	2646860	1.394916	0.239123	0.016979
2012	4,563,850.0	890573.0	77174.0	2646860	1.724251	0.336464	0.029157
2013	2,935,904.0	883737.0	73780.0	2619340	1.120856	0.337389	0.028167
2014	1,238,594.0	416805.0	36949.0	2619340	0.472865	0.159126	0.014106
2015	1,903,399.0	504012.0	41440.0	2619340	0.726671	0.192419	0.015821
2016	1,914,299.0	406713.0	42063.0	2614600	0.732158	0.155555	0.016088
2017	1,953,712.0	483731.0	44329.0	2614600	0.747232	0.185011	0.016954
2018	2,011,748.0	438345.0	45541.0	2614600	0.769429	0.167653	0.017418
2019	2,025,547.0	436363.0	57266.0	2614600	0.774706	0.166895	0.021902
2020	2,453,588.0	502607.0	31612.0	2614600	0.938418	0.192231	0.012091

Estonia

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	357091.0	50529.0	19382.0	940930	0.379509	0.053701	0.020599
2012	436888.0	60032.0	20607.0	940930	0.464315	0.063801	0.021901
2013	434251.0	66163.0	19544.0	957510	0.453521	0.069099	0.020411
2014	425845.0	88227.0	25283.0	957510	0.444742	0.092142	0.026405
2015	472279.0	109267.0	27633.0	957510	0.493237	0.114116	0.028859
2016	604150.0	104386.0	-	995100	0.607125	0.1049	-
2017	462644.0	117032.0	26102.0	995100	0.464922	0.117608	0.026231
2018	428200.0	106542.0	28749.0	995100	0.430309	0.107067	0.028891
2019	531268.0	104924.0	32565.0	995100	0.533884	0.105441	0.032725
2020	510774.0	-	16375.0	995100	0.513289	-	0.016456

Finland

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (kg)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	1452126.0	165151.0	31419.0	1895500	0.766091	0.087128	0.016576
2012	1223838.0	188895.0	30876.0	1895500	0.645654	0.099654	0.016289
2013	1132945.0	209572.0	25484.0	1901610	0.595782	0.110208	0.013401
2014	1305390.0	198523.0	12839.0	1901610	0.686466	0.104397	0.006752
2015	1367912.0	224679.0	18620.0	1901610	0.719344	0.118152	0.009792
2016	1264470.0	3212359.0	18405.0	1889820	0.669095	1.699823	0.009739
2017	1006413.0	3227750.0	24998.0	1889820	0.532544	1.707967	0.013228
2018	982359.0	3814408.0	20947.0	1889820	0.519816	2.018398	0.011084
2019	1106760.0	2831862.0	23190.0	1889820	0.585643	1.498482	0.012271
2020	1154997.0	3698298.0	11666.0	1889820	0.611168	1.956958	0.006173

France

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	29,252,304.0	24,495,844.0	2,190,206.0	27837290	1.050832	0.879965	0.078679
2012	27,800,650.0	27,580,733.0	2,363,015.0	27837290	0.998684	0.990784	0.084887
2013	27,882,963.0	30,376,030.0	2,282,569.0	27739430	1.005174	1.095049	0.082286
2014	31,034,696.0	34,441,873.0	2,538,625.0	27739430	1.118794	1.241622	0.091517
2015	30,595,770.0	27,373,707.0	2,579,970.0	27739430	1.10297	0.986816	0.093007
2016	30,155,584.0	31,971,200.0	3,650,742.0	27814160	1.084181	1.149458	0.131255
2017	30,252,649.0	29,786,228.0	3,785,871.0	27814160	1.087671	1.070902	0.136113
2018	34,354,391.0	39,064,721.0	4,861,340.0	27814160	1.23514	1.40449	0.174779
2019	22,483,780.0	24,483,508.0	4,366,791.0	27814160	0.808357	0.880253	0.156999
2020	29,155,642.0	26,001,474.0	5,845,201.0	27814160	1.04823	0.934829	0.210152

Germany

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	17,955,168.0	10,472,846.0	11,831,541.0	16704040	1.0749	0.626965	0.708304
2012	19,907,265.0	9,062,328.0	12,994,621.0	16704040	1.191763	0.542523	0.777933
2013	17,669,877.0	10,506,875.0	12,142,564.0	16699580	1.058103	0.62917	0.727118
2014	17,876,678.0	12,919,599.0	14,635,638.0	16699580	1.070487	0.773648	0.876408
2015	16,062,592.0	12,817,362.0	14,874,901.0	16699580	0.961856	0.767526	0.890735
2016	15,038,215.0	12,140,886.0	15,463,481.0	16715320	0.899667	0.726333	0.925108
2017	16,752,409.0	13,266,132.0	14,549,184.0	16715320	1.002219	0.793651	0.87041
2018	14,570,146.0	11,681,855.0	16,236,728.0	16715320	0.871664	0.698871	0.971368
2019	13,945,889.0	10,217,440.0	18,665,370.0	16715320	0.834318	0.611262	1.116662
2020	14,589,317.0	9,504,733.0	21,248,295.0	16715320	0.872811	0.568624	1.271187

Greece

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	1,454,632.0	2,256,372.0	109297.0	5177510	0.280952	0.435803	0.02111
2012	2,139,107.0	2,006,725.0	910678.0	5177510	0.413154	0.387585	0.175891
2013	2,571,536.0	5,520,830.0	1287010.0	4856780	0.529473	1.136726	0.264992
2014	1,194,605.0	1,866,378.0	588794.0	4856780	0.245966	0.384283	0.121231
2015	1,315,133.0	1,926,970.0	694354.0	4856780	0.270783	0.396759	0.142966
2016	1,744,039.0	1,803,566.0	921033.0	4553830	0.382983	0.396055	0.202255
2017	1,673,681.0	1,685,867.0	892763.0	4553830	0.367533	0.370209	0.196047
2018	1,833,052.0	1,728,709.0	1008807.0	4553830	0.40253	0.379616	0.221529
2019	1,830,175.0	1,755,818.0	964556.0	4553830	0.401898	0.38557	0.211812
2020	1,910,455.0	1,801,712.0	860835.0	4553830	0.419527	0.395648	0.189035

Hungary

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	3,668,067.0	2,997,436.0	522094.0	4686340	0.782715	0.639611	0.111408
2012	3,824,104.0	3,140,952.0	609383.0	4686340	0.816011	0.670236	0.130034
2013	3,562,125.0	3,238,478.0	606210.0	4656520	0.764976	0.695472	0.130185
2014	4,011,143.0	3,674,173.0	916538.0	4656520	0.861404	0.789038	0.196829
2015	4,270,176.0	3,867,891.0	826643.0	4656520	0.917032	0.83064	0.177524
2016	4,580,315.0	3,835,024.0	841828.0	4670560	0.980678	0.821106	0.180241
2017	4,269,854.0	4,170,518.0	859884.0	4670560	0.914206	0.892937	0.184107
2018	3,824,089.0	3,535,072.0	787295.0	4670560	0.818765	0.756884	0.168565
2019	3,905,683.0	2,796,084.0	690025.0	4670560	0.836234	0.598661	0.147739
2020	4,264,633.0	3,371,876.0	582594.0	4670560	0.913088	0.721943	0.124738

Ireland

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	2,811,899.0	619971.0	47513.0	4991350	0.563354	0.124209	0.009519
2012	1,807,584.0	650159.0	41502.0	4991350	0.362143	0.130257	0.008315
2013	2,004,814.0	594101.0	45941.0	4959450	0.404241	0.119792	0.009263
2014	2,391,861.0	635509.0	50651.0	4959450	0.482284	0.128141	0.010213
2015	2,482,278.0	687731.0	58068.0	4959450	0.500515	0.138671	0.011709
2016	2,243,469.0	596570.0	32759.0	4883640	0.459385	0.122157	0.006708
2017	1,916,141.0	633474.0	52821.0	4883640	0.392359	0.129713	0.010816
2018	1,833,054.0	601996.0	29244.0	4883640	0.375346	0.123268	0.005988
2019	1,844,951.0	922282.0	23000.0	4883640	0.377782	0.188851	0.00471
2020	2,262,447.0	440434.0	9958.0	4883640	0.463271	0.090186	0.002039

Italy

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	8,327,293.0	43,574,469.0	2,493,839.0	12856050	0.647733	3.389413	0.193982
2012	8,055,924.0	37,358,123.0	2,364,839.0	12856050	0.626625	2.905879	0.183948
2013	7,750,988.0	33,302,885.0	1,978,144.0	12098890	0.640636	2.752557	0.163498
2014	7,798,745.0	37,226,295.0	2,046,631.0	12098890	0.644584	3.076836	0.169159
2015	7,950,433.0	39,186,665.0	2,279,343.0	12098890	0.657121	3.238864	0.188393
2016	7,486,496.0	36,851,936.0	2,021,704.0	12598160	0.594253	2.925184	0.160476
2017	7,114,263.0	32,686,887.0	2,725,868.0	12598160	0.564707	2.594576	0.21637
2018	6,880,130.0	31,538,590.0	1,652,991.0	12598160	0.546122	2.503428	0.131209
2019	8,524,270.0	24,285,678.0	1,682,583.0	12598160	0.676628	1.927716	0.133558
2020	9,749,762.0	31,644,123.0	4,705,180.0	12598160	0.773904	2.511805	0.373482

Latvia

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	722050.0	148222.0	34164.0	1796290	0.401967	0.082516	0.019019
2012	789139.0	202514.0	44516.0	1796290	0.439316	0.11274	0.024782
2013	728065.0	214274.0	43892.0	1877720	0.387739	0.114114	0.023375
2014	847474.0	224735.0	63998.0	1877720	0.451331	0.119685	0.034083
2015	861076.0	269836.0	16782.0	1877720	0.458575	0.143704	0.008937
2016	986892.0	261967.0	32190.0	1930880	0.51111	0.135672	0.016671
2017	801179.0	266538.0	32984.0	1930880	0.414929	0.13804	0.017082
2018	965291.0	212650.0	35679.0	1930880	0.499923	0.110131	0.018478
2019	972018.0	295355.0	39368.0	1930880	0.503407	0.152964	0.020389
2020	1167424.0	303793.0	44008.0	1930880	0.604607	0.157334	0.022792

Lithuania

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (kg)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	1,772,873.0	361502	26359	2742560	0.64643	0.131812	0.009611
2012	1,715,221.0	485437	44898	2742560	0.625409	0.177001	0.016371
2013	1,421,923.0	534444	43707	2861250	0.496959	0.186787	0.015275
2014	1,394,236.0	601198	47213	2861250	0.487282	0.210117	0.016501
2015	1,371,539.0	736752	33217	2861250	0.47935	0.257493	0.011609
2016	1,432,729.0	741166	45316	2924600	0.489889	0.253425	0.015495
2017	1,251,548.0	690115	53837	2924600	0.427938	0.235969	0.018408
2018	1,053,599.0	676667	56622	2924600	0.360254	0.231371	0.019361
2019	1,199,217.0	575042	75758	2924600	0.410045	0.196622	0.025904
2020	1,487,050.0	592648	85720	2924600	0.508463	0.202642	0.02931

Luxembourg

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	102073	92080		131110	0.778529	0.702311	
2012	96467	91039		131110	0.735771	0.694371	
2013	82778			131040	0.6317		
2014	88601			131040	0.676137		
2015	83354			131040	0.636096		
2016	61078			130650	0.467493		
2017	60765			130650	0.465098		
2018	54178			130650	0.41468		
2019	49073			130650	0.375607		
2020	60225			130650	0.460964		

Malta	Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
	2011	6223	95040.0	4377	11450	0.543493	8.300437	0.382271
	2012	7959	124625.0	4710	11450	0.695109	10.88428	0.411354
	2013	7006	122070.0	5131	10880	0.643934	11.21967	0.471599
	2014	7632	97370.0	4406	10880	0.701471	8.949449	0.404963
	2015	4748	118644.0	4449	10880	0.436397	10.90478	0.408915
	2016	5609	83523.0	4972	11180	0.501699	7.470751	0.444723
	2017	2244	101943.0	3078	11180	0.200716	9.118336	0.275313
	2018	3247	82509.0	3492	11180	0.290429	7.380054	0.312343
	2019	2234	69779.0	2918	11180	0.199821	6.241413	0.261002
	2020	2899	89777.0	2634	11180	0.259302	8.030143	0.235599

Netherlands	Year	Herbicide	Fungicide	Insecticide	Land	He/Ha	Fu/Ha	In/Ha
	2011	3011210	4246282	1,898,289.0	1872350	1.608252	2.267889	1.013854
	2012	3029202	4657134	1,862,550.0	1872350	1.617861	2.48732	0.994766
	2013	2750607	4321344	1,657,403.0	1847570	1.48877	2.338934	0.897072
	2014	3246596	4896459	1,715,026.0	1847570	1.757225	2.650216	0.92826
	2015	2864819	4410071	2,179,912.0	1847570	1.550588	2.386957	1.179881
	2016	2732946	4867484	2,603,093.0	1796260	1.521465	2.709788	1.449174
	2017	2882972	4721461	2,476,494.0	1796260	1.604986	2.628495	1.378695
	2018	2960908	4289681	1,591,333.0	1796260	1.648374	2.388118	0.885915
	2019	2721182	3882326	1,959,010.0	1796260	1.514915	2.161339	1.090605
	2020	2606603	3962227	2,371,589.0	1796260	1.451128	2.20582	1.320293

Poland

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	12,408,486.0	6,080,802.0	991,418.0	1872350	6.627226	3.247684	0.529505
2012	12,654,357.0	6,130,813.0	1,286,326.0	1872350	6.758542	3.274395	0.687012
2013	12,518,197.0	6,474,339.0	1,305,890.0	1847570	6.775493	3.504246	0.706815
2014	12,073,411.0	7,442,470.0	1,479,061.0	1847570	6.534752	4.028248	0.800544
2015	12,189,714.0	7,742,020.0	1,537,818.0	1847570	6.597701	4.19038	0.832346
2016	12,693,320.0	7,534,406.0	1,481,486.0	1796260	7.066527	4.194496	0.824761
2017	13,655,478.0	6,927,315.0	1,819,059.0	1796260	7.602172	3.856521	1.012692
2018	11,370,744.0	7,991,707.0	1,770,071.0	1796260	6.330233	4.449081	0.98542
2019	11,705,375.0	6,867,376.0	2,724,266.0	1796260	6.516526	3.823153	1.516632
2020	12,809,348.0	9,278,129.0	618,821.0	1796260	7.131121	5.165248	0.344505

Portugal

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	1,995,991.0	9,974,797.0	877774.0	3668150	0.544141	2.719299	0.239296
2012	1,768,622.0	8,498,465.0	809679.0	3668150	0.482156	2.316826	0.220732
2013	1,311,016.0	7,201,606.0	745785.0	3641590	0.360012	1.977599	0.204797
2014	2,410,804.0	8,244,381.0	732935.0	3641590	0.66202	2.263951	0.201268
2015	2,122,471.0	5,193,428.0	561450.0	3641590	0.582842	1.426143	0.154177
2016	1,905,180.0	5,473,568.0	766106.0	3641690	0.523158	1.50303	0.210371
2017	1,899,471.0	4,181,275.0	877782.0	3641690	0.521591	1.148169	0.241037
2018	1,938,900.0	4,335,173.0	674521.0	3641690	0.532418	1.190429	0.185222
2019	2,222,363.0	5,767,487.0	812172.0	3641690	0.610256	1.583739	0.223021
2020	2,401,922.0	6,401,932.0	416627.0	3641690	0.659562	1.757956	0.114405

Romania

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	6,770,904.0	3,481,611.0	807,802.0	13306130	0.508856	0.261655	0.060709
2012	6,614,042.0	3,540,974.0	827,576.0	13306130	0.497067	0.266116	0.062195
2013	6,034,253.0	3,630,952.0	626,348.0	13055850	0.462188	0.278109	0.047975
2014	5,025,373.0	4,131,916.0	569,046.0	13055850	0.384914	0.31648	0.043586
2015	6,353,159.0	4,142,494.0	676,494.0	13055850	0.486614	0.31729	0.051815
2016	5,066,293.0	4,525,812.0	743,763.0	12502540	0.405221	0.361991	0.059489
2017	5,486,476.0	4,600,276.0	944,523.0	12502540	0.438829	0.367947	0.075546
2018	5,187,911.0	4,541,509.0	1,012,398.0	12502540	0.414949	0.363247	0.080975
2019	4,012,721.0	4,020,810.0	808,700.0	12502540	0.320952	0.321599	0.064683
2020	4,125,502.0	3,877,891.0	453,939.0	12502540	0.329973	0.310168	0.036308

Slovakia

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	1,079,871.0	540820	63693	1895500	0.569702	0.285318	0.033602
2012	1,257,380.0	496655	65157	1895500	0.66335	0.262018	0.034375
2013	1,157,477.0	531417	90226	1901610	0.608683	0.279456	0.047447
2014	1,215,096.0	567191	106509	1901610	0.638983	0.298269	0.05601
2015	1,218,222.0	639212	99629	1901610	0.640627	0.336143	0.052392
2016	1,080,278.0	640143	109875	1889820	0.57163	0.338732	0.05814
2017	1,105,104.0	685325	138965	1889820	0.584767	0.36264	0.073533
2018	1,328,923.0	676108	151264	1889820	0.703201	0.357763	0.080041
2019	1,159,510.0	652509	148628	1889820	0.613556	0.345276	0.078647
2020	1,107,929.0	662310	138094	1889820	0.586262	0.350462	0.073073

Slovenia

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	264289	797046.0	38493	482650	0.547579	1.651395	0.079753
2012	257007	700223.0	41621	482650	0.532491	1.450788	0.086234
2013	223472	647491.0	26749	485760	0.460046	1.332944	0.055066
2014	238502	723695.0	33453	485760	0.490987	1.48982	0.068867
2015	224430	759238.0	37821	485760	0.462018	1.56299	0.077859
2016	246996	859603.0	40310	488400	0.505725	1.760039	0.082535
2017	235302	794727.0	50079	488400	0.481781	1.627205	0.102537
2018	256840	849032.0	54584	488400	0.52588	1.738395	0.111761
2019	171761	751777.0	36298	488400	0.351681	1.539265	0.07432
2020	180872	731011.0	38684	488400	0.370336	1.496747	0.079206

Spain

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	13,834,600.0	31,343,389.0	8,061,915.0	23752690	0.582444	1.319572	0.339411
2012	13,984,903.0	26,792,750.0	7,640,732.0	23752690	0.588771	1.127988	0.321679
2013	14,719,759.0	32,393,012.0	6,821,991.0	23300220	0.631743	1.390245	0.292787
2014	14,908,032.0	38,379,663.0	7,515,055.0	23300220	0.639824	1.64718	0.322532
2015	15,586,625.0	36,423,289.0	6,690,752.0	23300220	0.668948	1.563217	0.287154
2016	15,224,454.0	38,905,110.0	7,500,979.0	23229750	0.655386	1.674797	0.322904
2017	16,077,356.0	37,982,029.0	6,549,043.0	23229750	0.692102	1.63506	0.281925
2018	16,592,907.0	38,067,058.0	6,488,405.0	23229750	0.714296	1.63872	0.279314
2019	17,022,958.0	34,073,450.0	7,636,039.0	23229750	0.732808	1.466802	0.328718
2020	20,199,361.0	37,915,957.0	8,165,124.0	23229750	0.869547	1.632215	0.351494

Sweden

Year	Herbicide (kg)	Fungicide (kg)	Insecticide (kg)	Land (Ha)	Herbicide per hectare (kg/Ha)	Fungicide per hectare (kg/Ha)	Insecticide per hectare (kg/Ha)
2011	2,136,107.0	218458	28829	3066320	0.696635	0.071244	0.009402
2012	2,087,116.0	234589	28990	3066320	0.680658	0.076505	0.009454
2013	1,772,813.0	332073	27569	3035920	0.583946	0.109381	0.009081
2014	2,103,771.0	302337	34126	3035920	0.69296	0.099587	0.011241
2015	1,829,323.0	398169	29804	3035920	0.60256	0.131153	0.009817
2016	1,633,008.0	249029	27868	3021350	0.54049	0.082423	0.009224
2017	1,731,236.0	264768	31421	3021350	0.573001	0.087632	0.0104
2018	1,482,790.0	222579	93803	3021350	0.490771	0.073669	0.031047
2019	1,543,585.0	164279	45218	3021350	0.510892	0.054373	0.014966
2020	1,707,955.0	222207	32111	3021350	0.565295	0.073546	0.010628

Table A.5 Reported legacy pesticides in Europe between 2011 and 2020.

Water Source	Group	Pesticide	Concentration ($\mu\text{g.l}^{-1}$) ^a	Year not approved in EU ^b	Country	Reference
Surface water	Fungicide	Hexachlorobenzene	0.042	2004	Strymonas river basin, Greece	Papadakis et al., 2018
		Quintozene	0.564	1985	Nestos river basin, Greece	Papadakis et al., 2018
		Diphenylamine	0.688	2013		
		Hexachlorobenzene	0.040	2004	Turia river basin, Spain	Ccancapa et al., 2019
		Butoxycarboxim	0.061	1998		
		Carbendazim	0.047	2015		
		Etaconazole	0.041	2009		
		Fenarimol	0.037	2008		
		Hexaconazole	0.029	2009		
		Oxadixyl	0.077	2002	Llobregat river basin, Spain	Postigo et al., 2021
		Tricyclazole	0.051	2016		
		Carbendazim	0.379	2015		
		Pentachlorophenol	0.115	2015		
		Propiconazole	0.067	2018	Aspropotamos river, Greece	Papadakis et al., 2015
		Hexachlorobenzene	0.033	2004		
		Quintozene	0.148	1985	Kompsatos river, Greece	Papadakis et al., 2015
		Hexachlorobenzene	0.048	2004		
		Quintozene	0.229	1985	Lissos river, Greece	Papadakis et al., 2015
		Hexachlorobenzene	0.035	2004		
		Quintozene	0.056	1985		
Hexachlorobenzene	0.029	2004				
Quintozene	0.224	1985	Kosynthos river, Greece	Papadakis et al., 2015		

Herbicide	2,4,5-T	0.062	1985	Strymonas river basin, Greece	Papadakis et al., 2018
	Alachlor	0.049	2006		
	Atrazine	0.410	2003		
	Chlorthal-dimethyl	0.285	2009		
	Dimethenamid	0.625	2006		
	Molinate	0.510	2004		
	Prometryn	0.696	2004		
	Atrazine	0.086	2003	Nestos river basin, Greece	Papadakis et al., 2018
	Chloridazon	0.225	2008		
	Chlorthal-dimethyl	0.016	2009		
	Dimethenamid	0.157	2006		
	Molinate	0.485	2004		
	Prometryn	0.967	2004	Sjaelland, Denmark	McKnight et al., 2015
	DNOC	0.310	1998		
	TCA	0.950	1991		
	Dinoseb	0.013	1986		
	Hexazinone	0.011	2004		
	Dichlorprop	0.230	2007		
	Dichlobenil	0.051	2008		
	Simazine	0.110	2004		
Diuron	0.150	2008			
Terbutryn	0.031	2002	Ebro river basin, Spain		
Diuron	0.024	2008			
Terbumeton	0.010	2002	Júcar river basin, Spain	Ccanccapa et al., 2016b	
Diuron	0.009	2008			
Metolachlor	0.058	2002	Turia river basin, Spain	Ccanccapa et al., 2016b	
Atrazine	0.007	2003			
Simazine	0.056	2004			

Terbutryn	0.020	2002	Turia river basin, Spain	Ccanccapa et al., 2019
Isoproturon	0.041	2016		
Mefenacet	0.025	2002		
Neburon	0.031	2002		
Tebuthiuron	0.030	2002		
Terbutryn	0.005	2002	Louros river basin, Greece	Kapsi et al., 2019
EPTC	0.157	2004		
Molinate	0.144	2004		
Propachlor	0.139	2008		
Trifluralin	0.084	2010		
Atrazine	0.077	2003	Llobregat river basin, Spain	Postigo et al., 2021
Metolachlor	0.077	2002		
Diuron	0.578	2008		
Fenuron	0.032	2002		
Isoproturon	0.016	2016		
Terbutryn	0.105	2002	Llobregat river basin, Spain	Proia et al., 2013
Alachlor	0.001	2006		
Atrazine	0.003	2003		
Simazine	0.004	2004		
Diuron	0.031	2008		
Molinate	0.004	2004	Alpine Glaciers, Italy	Rizzi et al., 2019
Alachlor	0.001	2006		
Propazine	0.103	2002		
Simazine	0.207	2004		
Atrazine	0.214	2003		
Terbutryn	2.749	2002		
Diuron	5.008	2008		
Metolachlor	0.263	2002		

Chloridazon	0.028	2008	La Rioja Alta area, Spain	Herrero-Hernández et al., 2017
Alachlor	8.928	2006		
Propazine	0.648	2002		
Simazine	0.114	2004		
Atrazine	0.110	2003		
Terbutryn	0.164	2002		
Diuron	0.607	2008		
Metolachlor	0.276	2002		
Chloridazon	0.039	2008		
Alachlor	0.648	2006	La Rioja Baja area, Spain	Herrero-Hernández et al., 2017
Propazine	0.194	2002		
Simazine	0.085	2004		
Atrazine	0.333	2003		
Terbutryn	0.107	2002		
Diuron	0.247	2008		
Metolachlor	1.106	2002		
Chloridazon	0.034	2008		
Alachlor	11.98	2006		
Diuron	0.015	2008	Arade river estuary, Portugal	Gonzalez-Rey et al., 2015
Simazine	0.003	2004	Aspropotamos river, Greece	Papadakis et al., 2015
Terbutryn	0.005	2002		
Atrazine	0.003	2003		
2,4,5-T	0.026	1985		
Atrazine	0.037	2003		
Chlorthal dimethyl	0.025	2009		
Atrazine	0.026	2003	Kompsatos river, Greece	Papadakis et al., 2015

Chlorthal dimethyl	0.209	2009		
Prometryn	0.031	2004	Lissos river, Greece	Papadakis et al., 2015
Chlorthal dimethyl	0.045	2009	Kosynthos river, Greece	Papadakis et al., 2015
Dimethenamid	0.027	2006		
Atrazine	0.019	2003	Alqueva reservoir, Portugal	Palma et al., 2014
Cyanazine	0.007	2002		
Simazine	0.034	2004		
Diuron	0.020	2008		
Alachlor	0.019	2006		
Metolachlor	0.291	2002		
Propanil	0.009	2008		
Molinate	0.352	2004		
Atrazine	0.010	2003	Llobregat river basin, Spain	Köck-Schulmeyer et al., 2012
Simazine	0.038	2004		
Cyanazine	0.009	2002		
Diuron	0.818	2008		
Alachlor	0.011	2006		
Metolachlor	0.013	2002		
Atrazine	0.001	2003	Guadalquivir river basin, Spain	Masiá et al., 2013
Terbutryn	0.003	2002		
Diuron	0.058	2008		
Atrazine	0.002	2003	Guadalquivir river, Spain	Robles-Molina et al., 2014.
Simazine	0.195	2004		
Alachlor	0.012	2006	Ria Formosa lagoon, Portugal	Cruzeiro et al., 2015.
Atrazine	0.004	2003		
Cyanazine	0.020	2002		
Metolachlor	0.001	2002		

Simazine	0.013	2004
Terbutryn	0.013	2002
Trifluralin	0.009	2010
Atrazine	0.006	2003
Diuron	0.024	2008
Metolachlor	0.013	2002
Propazine	0.009	2002
Simazine	0.003	2004
Terbutryn	0.010	2002

Llobregat river basin, Spain

Masiá et al., 2013

Insecticide	Carbaryl	0.171	2006	Strymonas river basin, Greece	Papadakis et al., 2018
	Carbofuran	0.087	2006		
	Lindane	0.252	2000		
	Methomyl	0.028	2009		
	Mirex	0.060	2002		
	Permethrin	0.259	2000		
	Carbaryl	0.049	2006	Nestos river basin, Greece	Papadakis et al., 2018
	Lindane	0.115	2000		
	Methomyl	0.069	2009		
	Pirimiphos-ethyl	0.161	2002		
	Chlorfenvinphos	0.008	1991	Júcar river basin, Spain	Ccancapa et al., 2016b
	Diazinon	0.002	2006		
	Ethion	0.005	2000		
	Carbofuran	6.845	2006	Turia river basin, Spain	Ccancapa et al., 2016b
	Azinphos-methyl	0.002	2007		
	Chlorfenvinphos	0.047	1991		
	Diazinon	0.037	2006		
	Ethion	0.350	2000		

Fenitrothion	0.018	2006		
Butoxycarboxim	0.061	1998	Turia river basin, Spain	Ccancapa et al., 2019
Ethiprole	0.032	1991		
Chlorfenvinphos	0.008	1991	Júcar river basin, Spain	Pascual Aguilar et al., 2017
Diazinon	0.002	2006		
Ethion	0.005	2000		
Quinalphos	0.142	2002	Louros river basin, Greece	Kapsi et al., 2019
Endosulfan- α	0.241	2005		
Endosulfan- β	0.205	2005		
Endosulfan-sulphate	0.194	2005		
Azinphos-ethyl	0.250	2002		
Diazinon	0.145	2006	Llobregat river basin, Spain	Postigo et al., 2021
Lindane	0.038	2000		
Carbofuran	0.025	2006	Aspropotamos river, Greece	Papadakis et al., 2015
Fipronil	0.061	2010		
Lindane	0.411	2000		
Fipronil	0.047	2010	Kompsatos river, Greece	Papadakis et al., 2015
Lindane	0.230	2000		
Lindane	0.055	2000	Lissos river, Greece	Papadakis et al., 2015
Dichlorvos	0.027	2006	Kosynthos river, Greece	Papadakis et al., 2015
Chlorfenvinphos	0.002	1991	Guadalquivir river basin, Spain	Masiá et al., 2013
Diazinon	0.079	2006	Llobregat river basin, Spain	Proia et al., 2013
Carbaryl	1.865	2006	La Rioja Alavesa area, Spain	Herrero-Hernández et al., 2017
Carbaryl	0.503	2006	La Rioja Alta area, Spain	Herrero-Hernández et al., 2017
Carbaryl	0.450	2006	La Rioja Baja area, Spain	Herrero-Hernández et al., 2017

Diazinon	0.018	2006	Alqueva reservoir, Portugal	Palma et al., 2014
Chlorfenvinphos	0.022	1991		
Diazinon	0.132	2006	Llobregat river basin, Spain	Köck-Schulmeyer et al., 2012
Diazinon	0.006	2006	Volturno river	Triassi et al., 2019
Fenitrothion	0.004	2006		
Methidathion	0.002	2006		
Diazinon	0.056	2006	Amvrakia lake, Greece	Thomatou et al., 2013
Fenitrothion	0.021	2006		
Diazinon	0.235	2006	Guadalquivir river, Spain	Robles-Molina et al., 2014.
Diphenylamine	0.220	2013		
Chlorfenvinphos	0.002	1991		
Azinphos-methyl	0.076	2007	Ria Formosa lagoon, Portugal	Cruzeiro et al., 2015.
Chlorfenvinphos	0.098	1991		
Cyfluthrin	0.025	2003		
Cyhalothrin	0.079	1994		
Diazinon	0.139	2006		
Dichlorvos	0.030	2006		
Dieldrin	0.164	2002		
Heptachlor	0.021	1999		
Lindane	0.042	2000		
Parathion-methyl	0.190	2002		
Azinphos-ethyl	0.003	2002	Llobregat river basin, Spain	Masiá et al., 2015
Azinphos-methyl	0.009	2007		
Carbofuran	0.007	2006		
Chlorfenvinphos	0.004	1991		
Diazinon	0.014	2006		
Fenitrothion	0.047	2006		

Ground water	Fungicide	Chloropicrin	1.400	2011	France	Lopez et al., 2015
		Dichlorophen	0.340	2002		
		Dinocap	0.300	2009		
		Oxadixyl	0.080	2002		
		Carbendazim	0.060	2014	Llobregat river basin, Spain	Postigo et al., 2021
Herbicide		Diuron	0.036	2008	Llobregat river basin, Spain	Postigo et al., 2021
		Simazine	0.005	2004		
		Terbutryn	0.006	2002		

^a Maximum concentration of pesticides detected

^b Data obtained from EU pesticides database (<https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/active-substances>)

Table A.6 Mitigation systems for removal of pesticides.

Mitigation System	Reference
Activated Carbon	Jjagwe et al., 2021 Larasati et al., 2021
Graphene/Graphene Oxide	Rana et al., 2021 Soleimani et al., 2021
Biochar	Ogura et al., 2021 Lima et al., 2022
Clays	Granetto et al., 2021 Novikau and Lujanienė, 2022
Chitosan / Zeolite	Pal et al., 2021 Sharma et al., 2021 Zhang et al., 2022a
Metal-Organic Frameworks	Wagner et al., 2021 Lunardi et al., 2022
Nanoparticles	Nguyen et al., 2022a Intisar et al., 2022
Membranes	Khoo et al., 2022 Jankowski et al., 2022
Semiconductors	Zeshan et al., 2022 de Oliveira et al., 2022
Vegetated Buffers	Lorenz et al., 2022 Tepes et al., 2021
Nanocatalysts	Akash et al., 2022 Jabbar and Ebrahim, 2022

Fenton process	Silva et al., 2021
	Dihingia and Tiwari, 2022
Ozonation	Martínez-Escudero et al., 2023
	Zheng et al., 2022
Photocatalysts	Andronnic et al., 2022
	Elango et al., 2023
Constructed Wetlands	Yang et al., 2022
	Lei et al., 2022
Biomass-based materials	Zhang et al., 2022b
	Nguyen et al., 2022b

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Appendix B

Supplementary Information to Chapter 3

A number of properties influence the transport of pesticides and were scored in order to facilitate the ranking of the transport potential of pesticides in different soil types. Properties such as half-life, solubility in water and adsorption capacity vary in orders of magnitude for each pesticide and so existing arbitrary grouping systems were used to score such properties. There are three commonly used arbitrary systems for grouping solubility values in threshold levels as described in the Pesticide Properties Database (PPDB) (FOOTPRINT, 2006), the National Pesticide Information Centre (NPIC) (NPIC, 2016), and a system used in publications by the Food and Agriculture Organisation of the United Nations (FAO, 2000). By amalgamating these, a novel system was generated for ranking the solubility values in our study (Table B.1).

Table B.1 Solubility ranking

Solubility [mg.l ⁻¹]	Class	Ranking
> 15000	Very High	12
500 - 15000	High	10
50 - 500	Moderate	8
10 - 50	Moderately Low	6
1 - 10	Low	4
< 1	Very Low	2

Half-life is used to determine the persistence of pesticides in the environment. Persistence thresholds below are described by FOOTPRINT PPDB, based on half-life in soil and modified to account for the variations of values in this study, are in line with EU Guidance Document 9188/VI/97 rev 8 (European Commission, 2000) on Persistence in Soil.

Table B.2 Soil half-life ranking

Soil half-life [days]	Class	Ranking
< 15	Not persistent	2
15 - 30	Slightly Persistent	4
30 - 50	Moderately Persistent	6
50 - 100	Persistent	8
100 – 365	Very Persistent	10
> 365	Extremely Persistent	12

There is no available classification of adsorption capacity coefficients in the literature. Therefore, the grouping scheme used (Table B.3) is based on the spread of the adsorption coefficient data calculated for this paper (Table B.4).

Table B.3 Adsorption capacity ranking

Adsorption Capacity Values	Class	Ranking
0 – 5	Extraordinarily High	12
5 – 12.5	Extremely High	11
12.5 – 15	Very High	10
15 – 20	High	9
20 – 25	Moderately High	8
25 – 30	Slightly High	7
30 – 50	Moderate	6
50 – 100	Slightly Low	5
100 – 200	Moderately Low	4
200 – 500	Low	3
500 – 1000	Very Low	2
> 1000	Extremely Low	1

Table B.4 Median pesticide adsorption values^a (mg g⁻¹) by soil texture.

Pesticide	Group	Soil Textures												
		Sand	Loamy Sand	Sandy Loam	Sandy Loam	Clay Loam	Sandy Clay	Silt Loam	Silt	Clay Loam	Silty Clay Loam	Silty Clay	Clay	
2,4-D	H			37.53		103.46		56.49		46.89		54	46.46	50.89
Bensulfuron-methyl	H					202.88						126.8	216.8	
Bentazone	H			13		12.53		13.21		12.28		14	13	13
Chlorotoluron	H	3.13	90.5	25.41	20.84	17.46		27.73		116.61		106.3	119.05	125.98
Dimethenamid-P	H							14.01						
Ethofumesate	H	39.21	23.93	18.67				40.34						30.06
Glyphosate	H	550	1144.46	281.2		1370.82		671.87				1269.77		1039.37
Isoxaflutole	H					41.31		1.32		1.56		2.1	80.67	
Lenacil	H													9.99
MCPA	H			18.61				5.63		10.29				38.70
Mecoprop-P	H			13.8										
Metamitron	H	24.78	17.07	5.18				14.58						19.55
Metribuzin	H			2.7										
Metsulfuron-methyl	H				3.06			2.3		4.66				3.64
Pendimethalin	H			787.8		535.96				2048.92				
Phenmedipham	H	442.44	45.98	28.35						73.12				102.73
Terbuthylazine	H	8.11	18.11	23.27		26.62				22.29		18.72		3993.59
Azoxystrobin	F	23.6	49.2	50.79		57.78				109.35				
Metalaxyl	F			0.03	8.37	19.43				155.18		56.57		42.56
Metalaxyl-M	F			31.38	27.03	317.74				3.19				
Myclobutanil	F									47.13				29.01
Penconazole	F			0.5										
Pyrimethanil	F	74.83		69.27										
Tebuconazole	F	355.08	146.65	481.64	2900.69	748.45								
Thiabendazole	F									384.45				
Abamectin	I	341.12		514.47				625.31						925.48
α -Cypermethrin	I									6413.53				
Deltamethrin	I		3139.59									9067.33		

^a The soil adsorption capacity q_e was calculated for the median value, using an equilibrium pesticide concentration (C_e) of 10 mg L⁻¹. H = Herbicide, F = Fungicide, I = Insecticide.

Table B.5 Risk ranking of pesticide solubility, half-life (DT₅₀), permeability and adsorption^a values.

Pesticide	Group	Solubility Ranking ^b	DT ₅₀ Ranking ^c	Soil Textures											
				Sand	Loamy Sand	Sandy Loam	Sandy Clay Loam	Loam	Sandy Clay	Silt Loam	Silt	Clay Loam	Silty Clay Loam	Silty Clay	Clay
				12 ^d	11	10	9	8	7	6	5	4	3	2	1
2,4-D	H	12	2			6		4		5		6	5	6	5
Bensulfuron-methyl	H	8	4					3				4	3		
Bentazone	H	10	4			10		10		10		11	10	10	10
Chlorotoluron	H	8	4	12	5	7	8	9		7		4	4	4	4
Dimethenamid-P	H	10	2							10					
Ethofumesate	H	6	4	6	8	9				6					6
Glyphosate	H	10	4	2	1	3		1		2			1		1
Isoxaflutole	H	4	2					6		12		12	12	5	
Lenacil	H	4	6												11
MCPA	H	12	4			9				11		11			6
Mecoprop-P	H	12	2			10									
Metamitron	H	10	4	8	9	11				10					9
Metribuzin	H	10	2			12									
Metsulfuron-methyl	H	8	6				12		12			12			12
Pendimethalin	H	2	10			2		2		1					
Phenmedipham	H	4	2	3	6	7				5					4
Terbutylazine	H	4	8	11	9	8		7		8			9		1
Azoxystrobin	F	4	8	8	6	5		5		4					
Metalaxyl	F	10	6			12	11	9		4		5			6
Metalaxyl-M	F	12	2			6	7	3				12			
Myclobutanil	F	8	12			12									
Penconazole	F	8	10	3	4	3	1	2							
Pyrimethanil	F	8	8							6					7
Tebuconazole	F	6	8	5		5									
Thiabendazole	F	6	12									3			
Abamectin	I	2	4	3		2			2						2
α-Cypermethrin	I	2	4							1					
Deltamethrin	I	2	8		1							1			

^a: Values are the scores given to the q_e values in Table 7A in accordance with ranking in Table S3 (adsorption) of the Supplementary Information.

^b: Solubility ranking based on S_w values (Table 2) for each of the 17 herbicides in accordance with ranking in Table S1 of the Supplementary Information.

^c: DT₅₀ ranking based on DT₅₀ values (Table 2) for each of the 17 herbicides in accordance with ranking in Table S2 of the Supplementary Information.

^d: Permeability ranking based on the number of soil textures (12) within each textural triangle, with the highest score = highest permeability. H = Herbicide, F = Fungicide, I = Insecticide.

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Appendix C

Supplementary Information to Chapter 4

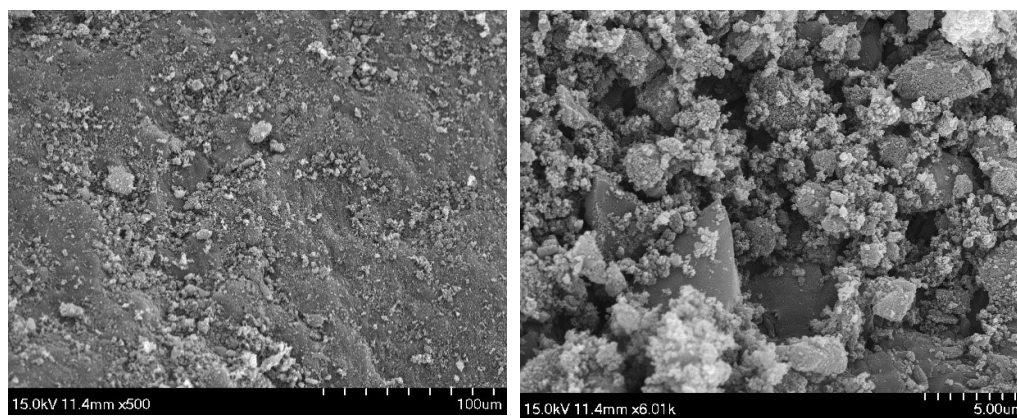


Figure C.1. SEM images of GAC at a resolution of 100 μm (left) and 5 μm (right).

Table C.1 Kinetic Isotherm equations.

Model	Equation	Plot
First order	$\ln q_t = \ln q_0 - k_1 t$	$\ln q_t$ vs t
Second order	$1/q_t = 1/q_0 - k_2 t$	$1/q_t$ vs t
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1' t$	$\ln(q_e - q_t)$ vs t
Pseudo-second order	$t/q_t = 1/k_2' q_e^2 + (1/q_e)t$	t/q_t vs t
Elovich	$q_t = 1/\beta \ln(\alpha\beta) + (1/\beta) \ln t$	q_t vs $\ln t$
Intraparticle diffusion	$q_t = c + k_{id} t^{0.5}$	q_t vs $t^{0.5}$

t is the equilibrium time (h); q_t is the amount of herbicide adsorbed at time t (mg.g⁻¹); q_0 is the amount of herbicide adsorbed at time 0 (mg.g⁻¹); k_1 is the first order rate constant; k_2 is the second order rate constant; q_e is the sorption capacity at equilibrium (mg.g⁻¹); k_1' is the pseudo-first order rate constant; k_2' is the pseudo-second order rate constant; α is the initial sorption rate (mg.g⁻¹.h⁻¹); β is the Elovich sorption constant; k_{id} is the rate constant for Intraparticle diffusion ([mg.g⁻¹]^{-0.5}); c is the boundary layer diffusion effects.

Table C.2 Kinetic model parameters of herbicides on GAC.

	First Order		Second Order		Pseudo-first order		Pseudo-second order			Elovich		Intraparticle diffusion	
	k_1		k_2		k'_1	q_e	k'_2	q_e	h	α	β	k_{id}	c
MCPA	0.307		-0.032		0.722	34.213	0.009	32.678	9.569	16.301	0.113	11.437	-5.273
Mecoprop-P	0.213		-0.018		0.677	25.529	0.013	28.345	10.270	20.232	0.148	8.731	-0.777
2,4-D	0.141		-0.020		0.136	12.680	0.034	13.343	6.088	13.946	0.349	3.629	1.120
Triclopyr	0.145		-0.020		0.153	11.860	0.034	13.489	6.128	13.512	0.338	3.715	1.025
Fluroxypyr	0.173		-0.031		0.086	16.203	0.025	12.700	4.090	8.699	0.354	3.566	-0.163
	r^2	SEE	r^2	SEE	r^2	SEE	r^2	SEE		r^2	SEE	r^2	SEE
MCPA	0.804	0.276	0.687	0.039	0.986	0.155	0.995	0.004		0.996	0.431	0.967	1.186
Mecoprop-P	0.879	0.144	0.803	0.017	0.981	0.172	0.996	0.004		0.996	0.305	0.981	0.685
2,4-D	0.989	0.030	0.959	0.008	0.965	0.054	0.942	0.039		0.916	0.642	0.969	0.389
Triclopyr	0.975	0.049	0.938	0.011	0.993	0.026	0.966	0.029		0.950	0.504	0.988	0.242
Fluroxypyr	0.978	0.054	0.923	0.018	0.993	0.016	0.935	0.043		0.937	0.543	0.983	0.283

Where: k_1 is the rate constant for the first order reaction; k_2 is the rate constant for the second order reaction; k'_1 is the rate constant for the pseudo-first order reaction; q_e is the adsorption capacity at equilibrium (mg.g^{-1}); k'_2 is the rate constant for the pseudo-second order reaction; h is the initial sorption rate determined by the pseudo-second order model ($\text{mg.g}^{-1}.\text{min}^{-1}$); α is the initial sorption rate determined by the Elovich model ($\text{mg.g}^{-1}.\text{min}^{-1}$); β is the Elovich sorption constant; k_{id} is the diffusion rate constant ($[\text{mg.g}^{-1}]^{0.5}$); c is the intraparticle diffusion constant; r^2 is the coefficient of determination; SEE is the standard error of estimates.

Table C.3 Adsorption Isotherm Equations.

Model	Non-linear equation	Linear equation	Plot
Langmuir	$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}}$	$\frac{C_e}{q_e}$ vs C_e
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$
Temkin	$q_e = q_{max} \ln(K_T C_e)$	$q_e = q_{max} \ln K_T + q_{max} \ln C_e$	q_e vs $\ln C_e$
Dubinin-Radushkevich	$q_e = q_{max} \exp(-D\varepsilon^2)$ where: $\varepsilon = RT \ln(1 + C_e^{-1})$	$\ln q_e = \ln q_{max} - D\varepsilon^2$	$\ln q_e$ vs ε^2
Koble-Corrigan	$q_e = \frac{A_{KC} C_e^p}{1 + B_{KC} C_e^p}$	$\frac{1}{q_e} = \frac{q}{A_{KC} C_e^p} + \frac{B_{KC}}{A_{KC}}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e^p}$

Where: q_e is the quantity of herbicide adsorbed per gram of media ($\text{mg}\cdot\text{g}^{-1}$); q_{max} is the maximum amount of herbicide that can be adsorbed onto the media ($\text{mg}\cdot\text{g}^{-1}$); K_L is the Langmuir constant related to the affinity between herbicide and the media ($\text{l}\cdot\text{mg}^{-1}$); C_e is the concentration of herbicide in the liquid phase at equilibrium ($\text{mg}\cdot\text{l}^{-1}$); K_F is the Freundlich adsorption capacity factor ($\text{mg}\cdot\text{g}^{-1}(\text{mg}\cdot\text{l}^{-1})^{-1/n}$); $1/n$ is the intensity parameter; K_T is the Temkin constant ($\text{l}\cdot\text{mg}^{-1}$); D is the Dubinin-Radushkevich constant ($\text{mol}^2 \text{kJ}^{-2}$); R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$); T is temperature in K; A_{KC} , B_{KC} and p are Koble-Corrigan constants where A_{KC} is expressed in $(\text{mg}\cdot\text{g}^{-1})(\text{l}\cdot\text{mg}^{-1})^p$ and B_{KC} in $(\text{l}\cdot\text{mg}^{-1})^p$.

Table C.4 Parameters of adsorption isotherms for herbicides onto GAC.

	Linear					Non-linear				
	MCPA	Mecoprop-P	2,4-D	Triclopyr	Fluroxypyr	MCPA	Mecoprop-P	2,4-D	Triclopyr	Fluroxypyr
Langmuir										
Q_{max} (mg.g ⁻¹)	116.82	103.392	78.092	116.759	110.557	107.05	84.381	77.252	111.431	110.783
K_L (L.g ⁻¹)	0.153	0.204	0.479	0.160	0.164	0.205	1.242	0.422	0.157	0.122
r^2	0.967	0.937	0.986	0.973	0.942	0.879	0.688	0.826	0.829	0.694
χ^2	-	-	-	-	-	19.918	112.54	94.564	70.890	3054.9
Freundlich										
K_F (mg.g ⁻¹ (mg.l ⁻¹) ^{-1/n})	28.565	21.455	33.654	30.933	42.343	29.881	40.134	35.287	30.753	34.646
n	3.096	2.757	4.859	3.351	5.557	3.254	4.933	5.270	3.327	3.949
r^2	0.997	0.989	0.999	0.997	0.997	0.971	0.893	0.942	0.979	0.911
χ^2	-	-	-	-	-	3.562	8.454	2.455	3.635	14.775
Temkin										
Q_{max} (mg.g ⁻¹)	17.927	9.635	9.099	16.449	8.995	19.110	11.53	9.099	16.449	8.995
K_T (L.mg ⁻¹)	4.484	139.504	60.635	6.827	252.463	3.362	38.056	60.637	6.827	252.464
r^2	0.916	0.833	0.886	0.926	0.755	0.936	0.687	0.936	0.926	0.755
χ^2	-	-	-	-	-	11.302	10.642	3.337	8.128	34.527
Dubinin-Radushkevich										
Q_{max} (mg.g ⁻¹)	72.753	66.804	60.451	74.218	66.957	86.026	81.579	62.690	81.778	91.588
D (mol ² kJ ⁻²)	1.256	0.099	0.195	0.885	0.058	5.465	1.010	0.224	1.850	30.841
r^2	0.728	0.672	0.739	0.753	0.627	0.618	0.638	0.552	0.382	0.493
χ^2	-	-	-	-	-	32.917	19.699	21.199	34.194	
Koble-Corrigan										
A_{kc} (mg.g ⁻¹)(L.mg ⁻¹) ^p	47.655	63.677	296.14	66.685	2929.46	31.486	40.134	46.006	30.753	34.645
B_{kc} (L.mg ⁻¹) ^p	0.578	0.447	4.950	0.827	46.871	0	0	0.328	0	0
p	0.924	0.286	0.577	0.984	0.999	0.293	0.203	0.314	0.301	0.253
r^2	0.969	0.975	0.643	0.948	0.843	0.965	0.893	0.951	0.979	0.911
χ^2	-	-	-	-	-	2.204	8.451	1.893	3.635	14.776

Where: q_{max} is the maximum amount of herbicide that can be adsorbed onto the media (mg.g⁻¹); K_L is the Langmuir constant related to the affinity between herbicide and the media (l.mg⁻¹); r^2 is the coefficient of determination; R_L is the equilibrium parameter; χ^2 is the non-linear chi-square value; K_F is the Freundlich adsorption capacity factor (mg.g⁻¹); n is a Freundlich parameter related to linearity; K_T is the Temkin constant (l.mg⁻¹); D is the Dubinin-Radushkevich constant (mol² kJ⁻²); A_{kc} , B_{kc} and p are Koble-Corrigan constants, where A_{kc} is expressed as (mg.g⁻¹)(l.mg⁻¹)^p and B_{kc} in (l.mg⁻¹)^p.

Appendix D

Supplementary Information to Chapter 5

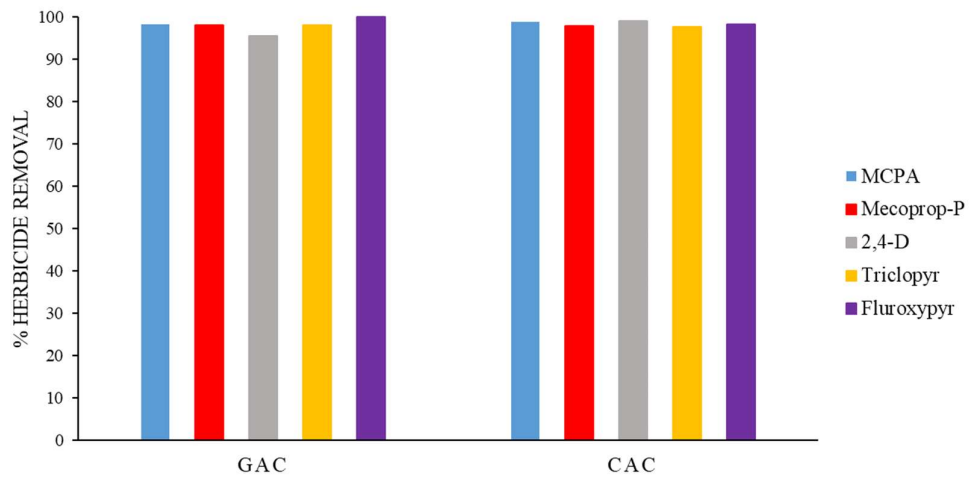
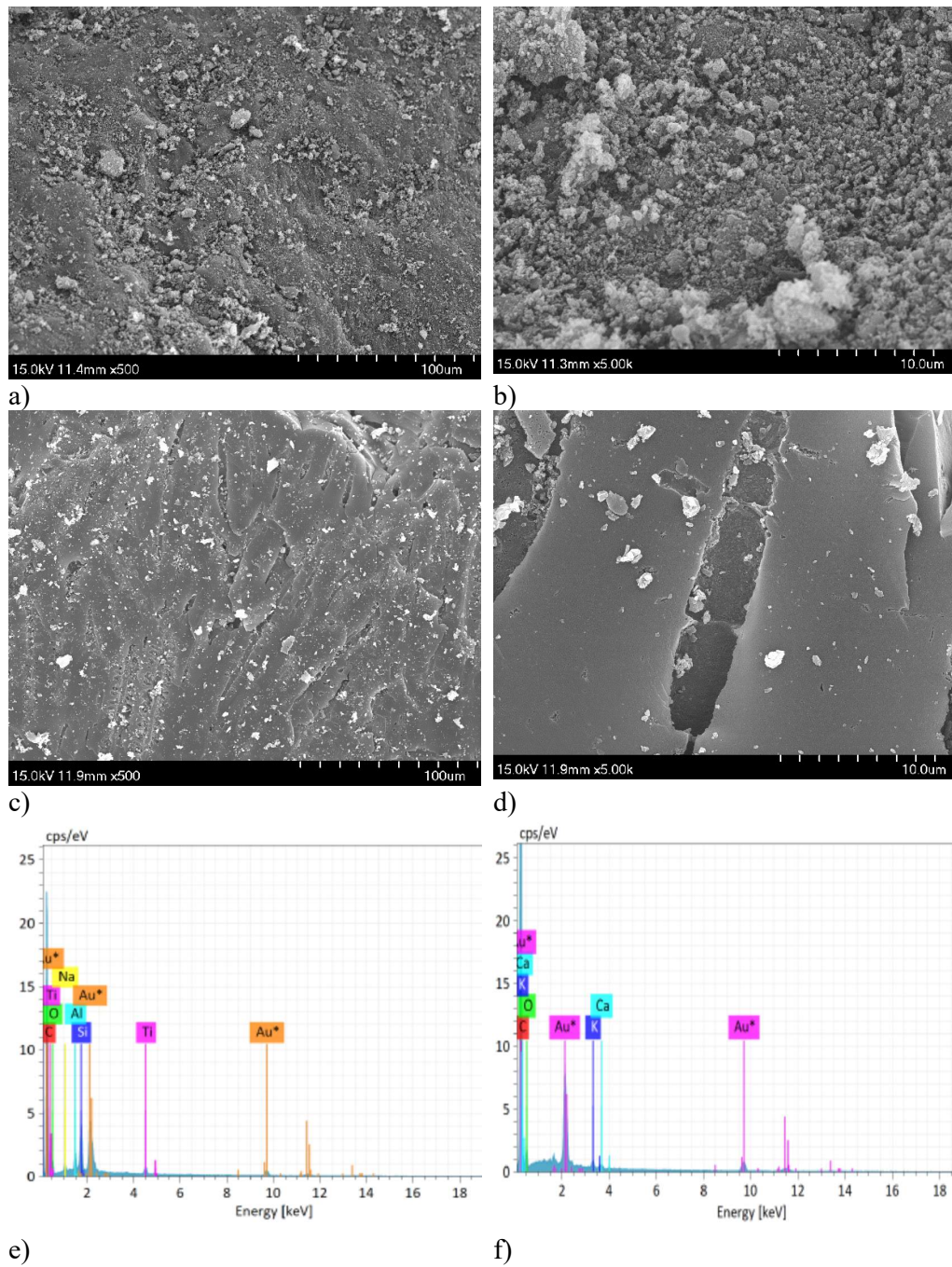


Figure D.1 Comparison of herbicide removal capacity of GAC and CAC against the herbicides MCPA, Mecoprop-P, 2,4-D, Triclopyr and Fluroxypyr.



e) f)
Figure D.2 SEM images of GAC (a and b) and CAC (c and d) at a resolution of 100 μm (left) and 10 μm (right). EDX spectra of e) GAC and f) CAC.

Table D.1 Pests controlled^a and optimal spraying conditions^b for herbicides.

Herbicides	Pests controlled	Crop	Spraying time	Rainfall
2,4-D	Broadleaf weeds	Cereals, grassland	Early Spring / Early Autumn	No rain after spraying or next day
Clopyralid	Thistles and clover	Cereals, grassland, fallow land	Mid Spring / Early Autumn	No rain after spraying or next day
Fluroxypyr	Broadleaf weeds and woody brush	Pasture, grassland, cereals	Early Spring / Early Autumn	No rain after spraying
MCPA	Rushes	Grassland	Early Spring / Early Autumn	No rain after spraying or next two days
Mecoprop	Broadleaf weeds	Cereals, grassland	Early Spring / Early Autumn	No rain after spraying or next two days
Triclopyr	Broadleaf weeds and woody plants	Christmas tree plantations	Spring	No rain after spraying or next day

^a Pesticide properties database online (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>).

^b www.epa.gov/pesticide-labels

Table D.2a Minimum, maximum and mean concentrations and frequency of detection of the studied pesticides before the bag interventions, between the bag interventions and before the pipe intervention, and after the pipe intervention in Corduff.

Herbicide	Position	Stream					Tributary				
		Concentration (ng.l ⁻¹)			Frequency		Concentration (ng.l ⁻¹)			Frequency	
		Min	Max	Mean	Detection (%) ^a	Exceedance (%) ^b	Min	Max	Mean	Detection (%) ^a	Exceedance (%) ^b
2,4-D	Before	46.32	46.32	46.32	1 (7)	0 (0)	24.11	845.15	298.05	3 (21)	1 (7)
	Between	25.22	49.50	36.92	3 (21)	0 (0)	-	-	-	-	-
	After ^{c,d}	15.18	15.18	15.18	1 (13)	0 (0)	-	-	-	-	-
Clopyralid	Before	17.05	28.41	22.73	2 (14)	0 (0)	-	-	-	-	-
	Between	13.00	33.28	23.13	2 (14)	0 (0)	-	-	-	-	-
	After ^{c,d}	29.22	29.22	29.22	1 (13)	0 (0)	-	-	-	-	-
Fluroxypyr	Before	2.94	22.51	9.46	3 (21)	0 (0)	124.27	124.27	124.27	1 (7)	1 (7)
	Between	3.91	31.31	19.28	5 (36)	0 (0)	-	-	-	-	-
	After ^{c,d}	-	-	-	-	-	-	-	-	-	-
MCPA	Before	19.18	159.74	50.29	9 (64)	1 (7)	5.76	5.76	5.76	1 (7)	0 (0)
	Between	25.11	217.63	79.27	8 (57)	3 (21)	-	-	-	-	-
	After ^{c,d}	9.27	30.01	18.11	5 (63)	0 (0)	3.05	14.92	8.99	2 (25)	0 (0)
Triclopyr	Before	44.27	85.71	60.83	3 (21)	0 (0)	9.43	10.24	9.84	2 (14)	0 (0)
	Between	46.02	53.30	49.66	2 (14)	0 (0)	7.68	7.68	7.68	1 (7)	0 (0)
	After ^{c,d}	12.53	26.35	19.44	2 (25)	0 (0)	-	-	-	-	-
Total	Before	2.94	179.59	77.10	13 (93)	0 (0)	32.19	978.85	231.63	5 (36)	1 (7)
	Between	3.91	237.62	113.00	9 (64)	0 (0)	5.71	15.71	10.71	0 (0)	0 (0)
	After ^{c,d}	16.48	71.54	34.77	5 (63)	0 (0)	3.05	14.92	8.99	2 (25)	0 (0)

^a Number of positive samples with percentage of positive samples from a total number of 14 sampled in parentheses.

^b Number of exceedances, with percentage of exceedances from a total of 14 sampled in parentheses.

^c Number of positive samples with percentage of positive samples from a total number of 8 sampled in parentheses.

^d Number of exceedances, with percentage of exceedances from a total of 8 sampled in parentheses.

Table D.2b Minimum, maximum and mean concentrations and frequency of detection of the studied pesticides before the bag interventions, between the bag interventions and before the pipe intervention, and after the pipe intervention in Dunleer.

Herbicide	Position	Stream					Tributary				
		Concentration (ng.l ⁻¹)			Frequency		Concentration (ng.l ⁻¹)			Frequency	
		Min	Max	Mean	Detection (%) ^a	Exceedance (%) ^b	Min	Max	Mean	Detection (%) ^a	Exceedance (%) ^b
2,4-D	Before	6.36	7.92	7.14	2 (14)	0 (0)	14.12	84.04	41.61	7 (50)	0 (0)
	Between	9.99	23.49	16.74	2 (14)	0 (0)	22.55	42.75	32.92	3 (21)	0 (0)
	After ^{c,d}	-	-	-	-	-	-	-	-	-	-
Clopyralid	Before	-	-	-	-	-	17.86	155.03	99.57	3 (21)	2 (14)
	Between	-	-	-	-	-	75.49	188.31	131.9	2 (14)	1 (7)
	After ^{c,d}	-	-	-	-	-	-	-	-	-	-
Fluroxypyr	Before	2.94	37.67	19.67	5 (36)	0 (0)	4.89	204.50	84.02	11 (79)	5 (36)
	Between	8.32	47.46	23.97	5 (36)	0 (0)	16.15	107.14	67.61	7 (50)	1 (7)
	After ^{c,d}	13.21	25.44	19.32	2 (17)	0 (0)	6.36	14.68	10.52	2 (17)	0 (0)
MCPA	Before	6.22	18.78	11.48	3 (21)	0 (0)	7.83	1348.96	287.77	14 (100)	4 (29)
	Between	6.22	11.29	8.79	5 (36)	0 (0)	16.65	752.02	229.15	8 (57)	4 (29)
	After ^{c,d}	8.30	8.30	8.30	1 (8)	0 (0)	4.67	243.03	102.52	5 (42)	2 (17)
Triclopyr	Before	-	-	-	-	-	6.94	119.14	62.53	7 (50)	2 (14)
	Between	10.78	10.78	10.78	1 (7)	0 (0)	7.48	61.32	33.32	6 (43)	0 (0)
	After ^{c,d}	-	-	-	-	-	-	-	-	-	-
Total	Before	6.36	88.89	29.49	7 (50)	0 (0)	59.52	1752.21	435.44	14 (100)	4 (29)
	Between	9.99	60.55	29.07	9 (64)	0 (0)	16.15	999.70	225.44	13 (93)	2 (14)
	After ^{c,d}	13.21	33.74	23.47	2 (17)	0 (0)	4.67	243.03	87.25	7 (58)	0 (0)

^a Number of positive samples with percentage of positive samples from a total number of 14 sampled in parentheses.

^b Number of exceedances, with percentage of exceedances from a total of 14 sampled in parentheses.

^c Number of positive samples with percentage of positive samples from a total number of 12 sampled in parentheses.

^d Number of exceedances, with percentage of exceedances from a total of 12 sampled in parentheses.

Table D.2c Minimum, maximum and mean concentrations and frequency of detection of the studied pesticides before the bag interventions, between the bag interventions and before the pipe intervention, and after the pipe intervention in Urban.

Herbicide	Position	Stream				
		Concentration (ng.l ⁻¹)			Frequency	
		Min	Max	Mean	Detection (%) ^a	Exceedance (%) ^b
2,4-D	Before	9.26	4774.28	1528.74	14 (100)	9 (64)
	Between	8.15	4412.22	1551.73	14 (100)	9 (64)
	After ^{c,d}	1.67	5674.28	1661.64	11 (92)	8 (67)
Clopyralid	Before	210.23	517.05	393.40	3 (21)	3 (21)
	Between	150.97	889.61	551.41	3 (21)	3 (21)
	After ^{c,d}	229.71	276.79	253.25	2 (17)	2 (17)
Fluroxypyr	Before	4.89	333.17	132.257	6 (43)	4 (29)
	Between	3.91	397.26	142.18	8 (57)	3 (21)
	After ^{c,d}	86.60	178.57	131.97	4 (33)	3 (25)
MCPA	Before	19.47	3479.32	656.62	6 (43)	2 (14)
	Between	4.67	4992.22	725.91	7 (50)	1 (7)
	After ^{c,d}	8.18	38.71	19.61	7 (58)	0 (0)
Mecoprop	Before	14.47	149.11	81.80	2 (14)	1 (7)
	Between	203.63	203.63	203.63	1 (7)	1 (7)
	After ^{c,d}	-	-	-	-	-
Triclopyr	Before	7.61	1002.90	182.19	8 (57)	2 (14)
	Between	5.93	1892.72	412.69	9 (64)	3 (21)
	After ^{c,d}	6.20	653.50	209.14	6 (50)	2 (17)

Total	Before	31.79	4727.68	2081.26	14 (100)	8 (57)
	Between	23.15	7001.19	2404.83	14 (100)	7 (50)
	After ^{c,d}	22.41	5682.46	1802.80	12 (100)	7 (58)

^a Number of positive samples with percentage of positive samples from a total number of 14 sampled in parentheses.

^b Number of exceedances, with percentage of exceedances from a total of 14 sampled in parentheses.

^c Number of positive samples with percentage of positive samples from a total number of 12 sampled in parentheses.

^d Number of exceedances, with percentage of exceedances from a total of 12 sampled in parentheses.

Appendix E

Published papers



Contents lists available at ScienceDirect

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Review

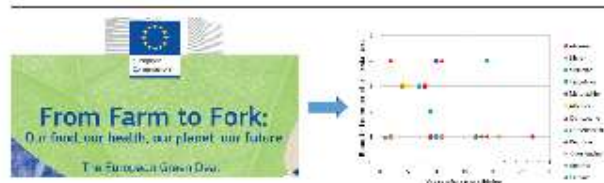
Impact of historical legacy pesticides on achieving legislative goals in Europe

J. McGinley^{a,b}, M.G. Healy^{a,b}, P.C. Ryan^{c,d}, Harmon O'Driscoll^c, P.-E. Mellander^e, L. Morrison^{h,f}, A. Siggins^{h,g,*}^a Civil Engineering, University of Galway, Ireland^b Ryan Institute, University of Galway, Ireland^c Discipline of Civil, Structural and Environmental Engineering, School of Engineering, University College Cork, Ireland^d Environmental Research Institute, University College Cork, Cork, Ireland^e Agricultural Catchments Programme, Teagasc Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland^f Earth and Ocean Sciences, Earth and Life Sciences, School of Natural Sciences, University of Galway, Ireland^g School of Biological and Chemical Sciences, University of Galway, Ireland

HIGHLIGHTS

- 2030 targets for pesticide reduction may be missed due to static pesticide use.
- Detection of legacy pesticides will compromise achievement of EU targets.
- MOB and VRS are promising methods of legacy pesticide remediation.
- Improvement of future EU strategies required for targeting legacy pesticides.

GRAPHICAL ABSTRACT



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ABSTRACT

Pesticides are widely used in agriculture to optimise food production. However, the movement of pesticides into water bodies negatively impacts aquatic environments. The European Union (EU) aims to make food systems fair, healthy and environmentally friendly through its current Farm to Fork strategy. As part of this strategy, the EU plans to reduce the overall use and risk of chemical pesticides by 50 % by 2030. The attainment of this target may be compromised by the prevalence of legacy pesticides arising from historical applications to land, which can persist in the environment for several decades. The current EU Farm to Fork policy overlooks the potential challenges of legacy pesticides and requirements for their remediation. In this review, the current knowledge regarding pesticide use in Europe, as well as pathways of pesticide movement to waterways, are investigated. The issues of legacy pesticides, including exceedances, are examined, and existing and emerging methods of pesticide remediation, particularly of legacy pesticides, are discussed. The fact that some legacy pesticides can be detected in water samples, more than twenty-five years after they were prohibited, highlights the need for improved EU strategies and policies aimed at targeting legacy pesticides in order to meet future targets.

Contents

1. Introduction	2
2. Methodology	3
3. Pesticide usage and pathways of loss	3
3.1. Usage of pesticides in the EU-27	3
3.2. Pathways of pesticide loss	4

* Corresponding author at: School of Biological and Chemical Sciences, University of Galway, Ireland.
E-mail address: sina.siggins@universityofgalway.ie (A. Siggins).

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RESEARCH ARTICLE

Soil Use and Management  WILEY

An assessment of potential pesticide transmission, considering the combined impact of soil texture and pesticide properties: A meta-analysis

John McGinley¹  | Jenny Harmon O'Driscoll²  | Mark G. Healy¹  |
Paraic C. Ryan²  | Per Eric Mellander³  | Liam Morrison⁴  | Oisín Callery⁴  |
Alma Siggins^{1,3} 

¹Civil Engineering and Ryan Institute, National University of Ireland Galway, Galway, Ireland

²Civil and Environmental Engineering, University College Cork, Cork, Ireland

³Teagasc Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland

⁴Earth and Ocean Sciences, School of Natural Science/s and Ryan Institute, National University of Ireland Galway, Galway, Ireland

Correspondence

Alma Siggins, Civil Engineering and Ryan Institute, National University of Ireland Galway, Galway, Ireland.
Email: alma.siggins@nuigalway.ie

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Abstract

Pesticides are widely employed as a cost-effective means of reducing the impacts of undesirable plants and animals. The aim of this paper is to develop a risk ranking of transmission of key pesticides through soil to waterways, taking into account physico-chemical properties of the pesticides (soil half-life and water solubility), soil permeability, and the relationship between adsorption of pesticides and soil texture. This may be used as a screening tool for land managers, as it allows assessment of the potential transmission risks associated with the use of specified pesticides across a spectrum of soil textures. The twenty-eight pesticides examined were differentiated into three groups: herbicides, fungicides and insecticides. The highest risk of pesticide transmission through soils to waterways is associated with soils containing <20% clay or >45% sand. In a small number of cases, the resulting transmission risk is not influenced by soil texture alone. For example, for Phenmedipham, the transmission risk is higher for clay soils than for silt loam. The data generated in this paper may also be used in the identification of critical area sources, which have a high likelihood of pesticide transmission to waterways. Furthermore, they have the potential to be applied to GIS mapping, where the potential transmission risk values of the pesticides can be layered directly onto various soil textures.

KEYWORDS

adsorption, Freundlich, half-life, pesticides, soil texture

1 | INTRODUCTION

A pesticide is any substance, plant protection product or biocide, that is used to repel, control or kill organisms that are considered to be pests (DAFM, 2017). The umbrella

term "pesticides" includes herbicides, fungicides, insecticides, molluscicides, bactericides and rodenticides (Mojiri et al., 2020). In Europe, total annual pesticide sales during the period 2011 to 2016 rose from 386,400 to 439,400 tonnes of active ingredients, with France, Spain, Italy and

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Research article

Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon

J. McGinley^a, M.G. Healy^a, P.C. Ryan^{b,c}, P.-E. Mellander^d, L. Morrison^e,
J. Harmon O'Driscoll^b, A. Siggins^{a,d,*}

^a Civil Engineering and Ryan Institute, National University of Ireland Galway, Galway, Ireland

^b Discipline of Civil, Structural and Environmental Engineering, School of Engineering, University College Cork, Ireland

^c Environmental Research Institute, University College Cork, Cork, Ireland

^d Teagasc Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland

^e Earth and Ocean Sciences, School of Natural Sciences and Ryan Institute, National University of Ireland Galway, Galway, Ireland

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ABSTRACT

This study reports the kinetics and isotherms of the adsorption of five herbicides, MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr, from aqueous solutions onto a range of raw and pyrolysed waste materials originating from an industrial setting. The raw waste materials investigated demonstrated little capability for any herbicide adsorption. Granulated activated carbon (GAC) was capable of the best removal of the herbicides, with >95% removal observed. A first order kinetic model fitted the data best for GAC adsorption of 2,4-D, while a pseudo-first order model fitted the data best for GAC adsorption of fluroxypyr and triclopyr, indicating that adsorption was via physisorption. A pseudo-second order kinetic model fitted the GAC adsorption of MCPA and mecoprop-P, which is indicative of chemisorption. The adsorption of the herbicides in all cases was best described by the Freundlich model, indicating that adsorption occurred onto heterogeneous surfaces.

1. Introduction

A global population increase has necessitated an intensification of agricultural practices in order to achieve improved crop yields and production rates (Morillo and Villaverde, 2017). This has been accomplished, in part, by increased pesticide usage (Gavrilescu, 2005; Morillo and Villaverde, 2017; Khalid et al., 2020). Total annual pesticide sales in Europe during the period 2011 to 2016 rose by approximately 14% from 386,400 to 439,400 tonnes of active ingredients (Peña et al., 2020). In the United States, the use of the broad spectrum herbicide glyphosate has risen by approximately 19,700% from 635 tonnes in 1974 to 125,000 tonnes in 2014 (Zhang et al., 2019). While increased pesticide application has been beneficial in preventing hazardous diseases in crops, improving yields, and maintaining the economic viability of agriculture (Maggi et al., 2020), it has also increased the risk of subsequent human exposure, resulting in human health issues, such as neurological, respiratory and carcinogenic effects (Van Maele-Fabry et al., 2017; Ye et al., 2017; Pouchieu et al., 2018). It has also intensified the contact of these compounds with aquatic environments (Burr et al., 2019; Liu et al., 2019; Sahin and Karpuzcu, 2020). Mojiri et al.

(2020) reported on pesticide concentrations in various aquatic environments across the world and found that pesticide levels ranged from 7 ng l⁻¹ to 121222 ng l⁻¹, often well above the maximum allowable concentration of pesticides in drinking water (100 ng l⁻¹; Council of the European Union, 1998). As herbicides account for the biggest proportion of pesticide usage (Mojiri et al., 2020), their removal from aqueous environments is, therefore, an important scientific and environmental objective, according to the Food and Agriculture Organization of the United Nations (Food and Agricultural Organization of the United Nations).

Many media have been used as adsorbents for herbicides (Bayat et al., 2018; Papanlatani et al., 2019; Amoah-Antwi et al., 2020). Granulated activated carbon (GAC) is often used as an adsorbent for pesticides in Water Treatment Plants (Environmental Protection Agency / Health Service Executive, 2019), due to its large surface area (300–2500 m² g⁻¹) and highly microporous structure (Jusoh et al., 2011). Typical adsorption capacities for the herbicides MCPA and 2,4-D on GAC range from 174.2 mg g⁻¹ to 181.8 mg g⁻¹, respectively (Ocampo-Pérez et al., 2012; Salman and Hameed, 2010). Biochar, a carbon-rich, porous material, has been used as a soil amendment

* Corresponding author. Civil Engineering and Ryan Institute, National University of Ireland Galway, Galway, Ireland.
E-mail address: ama.siggins@nuigalway.ie (A. Siggins).

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