



Terms and Conditions of Use of Digitised Theses from Trinity College Library Dublin

Copyright statement

All material supplied by Trinity College Library is protected by copyright (under the Copyright and Related Rights Act, 2000 as amended) and other relevant Intellectual Property Rights. By accessing and using a Digitised Thesis from Trinity College Library you acknowledge that all Intellectual Property Rights in any Works supplied are the sole and exclusive property of the copyright and/or other IPR holder. Specific copyright holders may not be explicitly identified. Use of materials from other sources within a thesis should not be construed as a claim over them.

A non-exclusive, non-transferable licence is hereby granted to those using or reproducing, in whole or in part, the material for valid purposes, providing the copyright owners are acknowledged using the normal conventions. Where specific permission to use material is required, this is identified and such permission must be sought from the copyright holder or agency cited.

Liability statement

By using a Digitised Thesis, I accept that Trinity College Dublin bears no legal responsibility for the accuracy, legality or comprehensiveness of materials contained within the thesis, and that Trinity College Dublin accepts no liability for indirect, consequential, or incidental, damages or losses arising from use of the thesis for whatever reason. Information located in a thesis may be subject to specific use constraints, details of which may not be explicitly described. It is the responsibility of potential and actual users to be aware of such constraints and to abide by them. By making use of material from a digitised thesis, you accept these copyright and disclaimer provisions. Where it is brought to the attention of Trinity College Library that there may be a breach of copyright or other restraint, it is the policy to withdraw or take down access to a thesis while the issue is being resolved.

Access Agreement

By using a Digitised Thesis from Trinity College Library you are bound by the following Terms & Conditions. Please read them carefully.

I have read and I understand the following statement: All material supplied via a Digitised Thesis from Trinity College Library is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of a thesis is not permitted, except that material may be duplicated by you for your research use or for educational purposes in electronic or print form providing the copyright owners are acknowledged using the normal conventions. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone. This copy has been supplied on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.

PESTICIDE OCCURRENCE IN IRISH GROUNDWATER

**Presented in fulfilment
of the requirements for the degree of
Doctor of Philosophy
December 2012**

By: Sarah-Louise McManus



Supervised by:

Dr. C.E. Coxon,
Department of Geology,
School of Natural Sciences,
Trinity College Dublin.

Dr. K.G. Richards,
Teagasc Environmental
Research Centre,
Johnstown Castle.

DECLARATION

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work.

I agree to deposit this thesis in the University's open access institutional repository or allow the library to do so on my behalf, subject to Irish Copyright Legislation and Trinity College Library conditions of use and acknowledgement.



Thesis 1026 T

SUMMARY

Groundwater pesticide occurrence was investigated within agricultural catchments and at the national scale across Ireland. Seven intensive agricultural catchments were selected, each with different physical characteristics representing common scenarios within Ireland. Six catchments were dominated by arable farming and one by grassland. At each site monitoring points were installed to target groundwater at different depths. Springs, drains, and streams were also monitored where present, to gain insight into potential pesticide transport pathways. Groundwater was sampled monthly between March 2010 to March 2012, using low-flow purging methods. Water quality parameters were measured *in-situ* and samples collected for both physico-chemical variables and pesticide analysis. Three external methods were used to quantify for phenoxyacid and organophosphorus herbicides. Two in-house methods were developed using gas chromatography- and liquid chromatography- mass spectrometry and validated according to European Union legislation (2002/657/EC) to determine five organochlorine pesticides, 16 phenoxyacid herbicide parent active ingredients and their relevant transformation products, and two benzonitrile transformation products. 61 pesticide compounds in groundwater, including transformation products, from 835 samples, were analysed throughout the study.

The most frequently detected parent active ingredients in groundwater from these agricultural catchments were mecoprop and 2,4-D which were present in 36% and 26%, of all samples collected. The most frequently detected transformation products in groundwater within the agricultural catchments were phenoxyacetic acid and 4-chloro-2-methylphenol in 33% and 26% of samples, respectively. The most commonly detected compounds in breach of the European Union drinking water standard of 0.1 µg/L for individual compounds (98/83/EC) were the transformation products 2,6-dichlorobenzoic acid and phenoxyacetic acid. This is the first report of the widespread occurrence of these two transformation products in groundwater. The toxicity, persistence and source of these products in groundwater are unknown.

The effect of land use on pesticide occurrence was investigated by comparing pesticide occurrence on karst dominated by arable and grassland farming. The results suggest that groundwater pesticides were more associated with arable land use compared to grassland farming due to higher pesticide usage in arable.

The relationship between groundwater pesticide occurrence and physico-chemical groundwater parameters was statistically evaluated. Significant positive associations were found between pesticide occurrence in groundwater and calcium, manganese, sodium, magnesium, and total nitrogen. Significant negative associations were found with redox potential, turbidity and pH.

Groundwater pesticide occurrence at the national and catchment scales was found to be significantly associated with site physical characteristics. Monitoring point type, aquifer type, subsoil type, and soil drainage class were all significantly associated with pesticide occurrence, at the national scale. At the catchment scale pesticides were associated with sample type, sample depth, soil association, soil texture, soil drainage class, subsoil type, subsoil thickness, subsoil permeability, aquifer type, and groundwater vulnerability.

Risk of pesticide occurrence was associated with groundwater vulnerability as classified by the national methodology, providing a useful risk assessment tool. The study has highlighted that the risk of groundwater pesticide occurrence varies nationally and that mitigation measures maybe required in arable farming areas dominated in high risk catchments.

At the national scale, a two year database from the Environmental Protection Agency's groundwater monitoring campaign for pesticides was analysed, reported and interpreted. The main pesticide compounds detected were MCPA and mecoprop. Comparing this national monitoring campaign with the catchment scale campaign revealed more detections during the catchment scale, which also had a higher temporal resolution. There were also more detections in breach of the European Union drinking water standard for individual compounds during catchment scale monitoring.

This thesis is dedicated to my Mother
Jacqueline Eleanor Curry

“Groundwater is always on the move, sometimes at a pace so slow that it travels no more than fifty feet a year, sometimes rapidly, by comparison, so that it moves nearly a tenth of a mile in a day. It travels by unseen waterways until here and there it comes to the surface as a spring, or perhaps it is tapped to feed a well. But mostly it contributes to streams and so to rivers. Except for what enters streams directly as rain or surface runoff, all the running water of the earth’s surface was at one time groundwater. And so, in a very real and frightening sense, pollution of the groundwater is pollution of water everywhere”

Rachel Carson 1907-1964.

ACKNOWLEDGEMENTS

I would sincerely like to thank both my supervisors Dr. Catherine E. Coxon and Dr. Karl G. Richards for their knowledge, support, and understanding throughout the four years of this Ph.D. My gratitude also goes to Dr. Martin Danaher at The Food Research Centre at Teagasc Ashtown. Also at The Food Research Centre I would like to thank Dr. Mary Moloney, Paddy Byrne, and Dr. Anita Radovnikovic for their help and assistance.

This project would not have been possible without funding and I wish to thank the National Development Plan, through the Research Stimulus Fund, administered by the Department of Agriculture, Food and Marine for the first three years and for the final year I wish to thank Teagasc for providing the project with funding through the Walsh Fellowship award. I would also like to thank the International Association of Hydrogeologists (IAH) for awarding me a student bursary in 2010.

Acknowledgement is also given to the Northern Ireland Environment Agency (NIEA) in Lisburn for allowing me analytical work experience in their laboratories, especially Raymond Thomas and Leslie Smith. At the Environmental Protection Agency (EPA) in Dublin, I would like to thank Anthony Mannix, Donal Daly, and Matthew Craig for their time. At the Geological Survey of Ireland (GSI) I would like to thank Taly Hunter-Williams, Caoimhe Hickey, and Monica Lee. At the Pesticide Control Service in Backweston I wish to thank Dr. Aidan Moody and Dr. Kenneth Conroy for their assistance.

I would like to thank the collaborators involved in this project for granting me access to their field sites. From the Agricultural Catchment Team (ACP) Dr. Per-Erik Mellander, Ger Shortle, Dr. Alice Melland, Dr. Paul Murphy, Sarah Mechan, Oliver Shine, Edward Burgess, Brian O'Connor, and David Ryan. From the EPA funded Pathways Project Dr. Marie Archbold, Dr. Ray Flynn, and Dr. Jenny Deakin.

I would also like to especially thank the private land owners involved in the project. They all assisted me in every way possible with providing pesticide application records, giving me a farmer's perspective, and making me mobile when I got my vehicle stuck!

At Teagasc Johnstown Castle I would like to thank John B. Murphy for his excellent technical assistance and brilliant work ethic throughout sampling. I would also like to acknowledge Denis Brennan for his advice and analytical instrumentation. I would like to thank Dr. Jim Grant at the Statistics and Applied Physics Research Operations Group in Teagasc Ashtown who provided me with endless statistical advice.

Last but not least I would like to thank my family for their kindness through these past four years. To my Mother whom this thesis is dedicated to, my brother Matthew, his fiancée Amanda, and my sister Michaela: thank you for your positivity and kind words throughout. I would also like to acknowledge the people I have met and the friendships I have made. I would especially like to thank Dr. Sinead O'Keeffe, Eamon Haughey, Marina Carrascosa, Iolanda Simo, Dr. Caroline Sullivan, Uta Priegnitz, and Anna Murphy.

Table of Contents

<i>Title page</i>	<i>i</i>
<i>Declaration and permission to copy</i>	<i>ii</i>
<i>Summary</i>	<i>iii</i>
<i>Acknowledgements</i>	<i>vii</i>
<i>Table of contents</i>	<i>ix</i>
<i>List of figures</i>	<i>xvi</i>
<i>List of tables</i>	<i>xxiii</i>
<i>Units, terminology and abbreviations</i>	<i>xxvii</i>

Chapter 1: INTRODUCTION	1
1.1 Background to the research project	1
1.2 Study aims and objectives	3
1.3 Thesis layout	5
Chapter 2: LITERATURE REVIEW: PESTICIDE TRANSPORT TO GROUNDWATER	6
2.1 Introduction to the pesticide problem	6
2.1.1 Why groundwater contamination from pesticides is of concern	6
2.1.2 Legislation to control pesticide contamination from pesticides	7
2.1.3 International research on extent of the groundwater pesticide problem	11
2.1.4 Pesticide monitoring and research in Ireland	12
2.1.5 Groundwater vulnerability	15
2.2 Sources of pesticides in the environment	17
2.2.1 Agricultural land use	17
2.2.2 Urban land use	18
2.2.3 Aquatic management	19
2.2.4 Amenity uses	19
2.3 Processes affecting pesticide leaching to groundwater	20
2.3.1 Agricultural management	21
2.3.2 Soil type	22
2.3.2.1 Sorption and desorption	23
2.3.2.2 Preferential flow	24
2.3.2.3 Artificial subsurface features	25
2.3.2.4 Colloidally bound transport	25
2.3.2.5 Pesticide degradation	26
2.3.3 Quaternary deposit type	28
2.3.4 Aquifer type	29

2.3.5	Weather and climate	33
2.4	Chapter 2 conclusions	34
Chapter 3: ANALYSIS OF NATIONAL - SCALE GROUNDWATER PESTICIDE OCCURRENCE		35
3.1	Introduction	35
3.2	Materials and methods	36
3.2.1	EPA network summary	36
3.2.2	Zones of contribution (ZOCs)	37
3.2.3	Dataset assembly for statistical analysis with corresponding ZOCs	39
3.2.4	Physical characteristics national dataset summary	40
3.2.5	Statistical methods	42
3.3	Results	46
3.3.1	Frequency of occurrence in groundwater	46
3.3.2	Statistical analysis of occurrence with zone of contribution properties	49
3.4	Discussion	54
3.4.1	Frequency of occurrence in groundwater	54
3.4.2	Frequency of detections at monitoring points	57
3.4.3	Physical characteristics and detections	57
3.5	Chapter 3 conclusions	62
Chapter 4: SITE SELECTION AND INTRODUCTION TO SITE CHARACTERISTICS		63
4.1	Introduction	63
4.1.1	Context	63
4.1.2	Conceptual model	64
4.2	Methods used to select sites across Ireland	65
4.3	Site selection results	67
4.3.1	National physical characteristics results	67
4.3.2	Potential candidate results	70
4.4	Selected sites	73
4.5	Known characteristics of the chosen sites	76
4.5.1	Karst well-drained grassland (KWDg)	76
4.5.1.1	Introduction	76
4.5.1.2	Land use	77
4.5.1.3	Pesticide applications	78
4.5.1.4	Physical characteristics	78

4.5.2	Karst well-drained arable (KWDa)	79
4.5.2.1	Introduction	79
4.5.2.2	Land use	80
4.5.2.3	Pesticide applications	81
4.5.2.4	Physical characteristics	81
4.5.3	Intergranular/karst well-drained arable (I/KWDa)	82
4.5.3.1	Introduction	82
4.5.3.2	Land use	82
4.5.3.3	Pesticide applications	82
4.5.3.4	Physical characteristics	82
4.5.4	Fractured-volcanics well-drained arable (FvWDa)	84
4.5.4.1	Introduction	84
4.5.4.2	Land use	85
4.5.4.3	Pesticide applications	85
4.5.4.4	Physical characteristics	85
4.5.5	Fractured-volcanics poorly-drained arable (FvPDa)	86
4.5.5.1	Introduction	86
4.5.5.2	Land use	88
4.5.5.3	Pesticide applications	88
4.5.5.4	Physical characteristics	89
4.5.6	Fractured-metasediments well-drained arable Site 1 and 2 (FmWDa _{1/2})	89
4.5.6.1	Introduction	89
4.5.6.2	Land use	90
4.5.6.3	Pesticide applications	90
4.5.6.4	Physical characteristics	91
4.5.7	Differences between Fractured-metasediments well-drained arable Site 1 and 2	91
4.6	Chapter 4 conclusions	91
Chapter 5: SITE SOIL, GEOLOGY, HYDROELOGY AND HYDROCHEMICAL CHARACTERISITCS		94
5.1	Introduction	94
5.2	Physical and chemical analysis of soil and subsoil	94
5.2.1	Soil and subsoil analytical methods	94
5.2.2	Soil and subsoil results	95
5.2.3	Soil and subsoil discussion	96

5.3	Geology and hydrogeology	98
5.3.1	Borehole installations	98
5.3.2	Geophysical surveys	99
5.3.2.1	Geophysical survey of the karst well-drained arable (KWDa) site	100
5.3.2.2	Geophysical survey of the fractured-volcanic well-drained arable (FvWDa) site	101
5.3.2.3	Geophysical survey of the fractured-volcanic poorly-drained arable (FvPDa)	102
5.3.2.4	Geophysical survey of the fractured-metasediments well-drained arable site 1 (FmWDa ₁)	106
5.3.2.5	Geophysical survey of the fractured-metasediments well-drained arable site 2 (FmWDa ₂)	107
5.3.3	Summary of subsoil and Quaternary deposits at each site	110
5.4	Effective rainfall	112
5.4.1	Introduction	112
5.4.2	Effective rainfall calculation method	112
5.4.3	Technical note on effective rainfall model comparisons	113
5.4.4	Results of effective rainfall calculations and meteorology	114
5.5	Groundwater level monitoring and spring discharge	116
5.5.1	Methodology	116
5.5.2	Spring flow results	117
5.5.2.1	Spring discharge results from the karst well-drained grassland (KWDg) site	117
5.5.2.2	Spring discharge results from the karst well-drained arable (KWDa) site	118
5.5.3	Groundwater level results	120
5.5.3.1	Groundwater level results for the intergranular/karst well-drained arable (I/KWDa) site	120
5.5.3.2	Groundwater level results for the fractured-metasediments well-drained arable site 1 (FmWDa ₁)	121
5.5.3.3	Groundwater level results for the fractured-metasediments well-drained arable site 2 (FmWDa ₂)	123
5.6	Groundwater flow direction and zones of contribution	126
5.6.1	Groundwater flow direction and the zone of contribution at the karst-well drained grassland (KWDg) site	126
5.6.2	Groundwater flow direction and the zone of contribution at the karst well-drained arable (KWDa) site	128
5.6.3	Groundwater flow direction and the zone of contribution at the	131

	intergranular/karst well-drained arable (I/KWDa) site	
5.6.4	Groundwater flow direction and the zone of contribution at the fractured-volcanics well-drained arable (FvWDa) site	132
5.6.5	Groundwater flow direction and the zone of contribution at the fractured-volcanics poorly-drained arable (FvPDa) site	135
5.6.6	Groundwater flow direction and the zone of contribution at the fractured-metasediments well-drained arable site 1 and 2 (FmWDa _{1/2})	137
5.7	Groundwater age dating	138
5.8	Hydrochemistry	139
5.8.1	Aims of hydrochemical analysis	139
5.8.2	Hydrochemistry methods	140
5.8.2.1	Sample collection and field measurements	140
5.8.2.2	Hydrochemical statistical methods	140
5.8.2.3	Hydrochemical parameters summary	141
5.8.3	Hydrochemical results for individual sites	147
5.8.3.1	Hydrochemistry of the karst well-drained grassland (KWDg) site	149
5.8.3.2	Hydrochemistry of the karst well-drained arable (KWDa) site	150
5.8.3.3	Hydrochemistry of the intergranular/karst well-drained arable (I/KWDa) site	151
5.8.3.4	Hydrochemistry of the fractured-volcanics well-drained arable (FvWDa) site	153
5.8.3.5	Hydrochemistry of the fractured-volcanics poorly-drained arable (FvPDa) site	156
5.8.3.6	Hydrochemistry of the fractured-metasediments well-drained arable site 1 (FmWDa ₁)	157
5.8.3.7	Hydrochemistry of the fractured-metasediments well-drained arable site 2 (FmWDa ₂)	158
5.8.3.8	Hydrochemical comparison between sites	159
5.9	Discussion of site characteristics	160
5.9.1	Karst well-drained grassland (KWDg)	160
5.9.2	Karst well-drained arable (KWDa)	161
5.9.3	Intergranular/karst well-drained arable (I/KWDa)	162
5.9.4	Fractured-volcanics well-drained arable (FvWDa)	163
5.9.5	Fractured-volcanics poorly-drained arable (FvPDa)	164
5.9.6	Fractured-metasediments well-drained arable site 1 (FmWDa ₁)	166
5.9.7	Fractured-metasediments well-drained arable site 2 (FmWDa ₂)	168

5.10	Chapter 5 conclusions	169
Chapter 6: PESTICIDE ANALYTICAL METHODOLOGY		171
6.1	Introduction	171
6.2	Collection and storage of samples for pesticide analysis	171
6.2.1	Collection of groundwater samples from piezometers and springs	171
6.2.2	Technical note on storage of raw groundwater samples and extracted samples	173
6.2.3	Technical note on filtering samples for phenoxy acid and benzonitrile herbicide analysis	174
6.3	Literature review of analytical techniques to quantify pesticides in groundwater	176
6.3.1	Extraction methods	176
6.3.1.1	Solid phase extraction	176
6.3.1.2	Solid phase microextraction	177
6.3.2	Separation methods	179
6.3.2.1	Gas chromatography (GC)	179
6.3.2.2	Liquid chromatography (LC)	180
6.3.3	Mass spectrometry detection	180
6.4	External laboratory analysis	182
6.4.1	Phenoxyacid herbicides	182
6.4.2	Organophosphorous herbicides	184
6.5	Analysis of organochlorine pesticides using gas chromatography	185
6.5.1	Experimental	185
6.5.2	Results and discussion	191
6.5.3	Conclusion	195
6.6	Analysis of phenoxyacid herbicides and benzonitriles using liquid chromatography	195
6.6.1	Experimental	196
6.6.2	Results and discussion	200
6.6.3	Conclusion	206
6.7	Chapter 6 conclusions	206
Chapter 7: CASE STUDY PESTICIDE RESULTS AND DISCUSSION		208
7.1	Introduction	208
7.2	Groundwater pesticide frequency of occurrence	208
7.2.1	Percentage frequency calculation method	208
7.2.2	Percentage frequency results	209
7.3	Within site variation of pesticide occurrence	219

7.3.1	Within site variation at Intergranular/karst well-drained arable	219
7.3.2	Within site variation at Fractured-volcanic well-drained arable	220
7.3.3	Within site variation at Fractured-volcanic poorly-drained arable	221
7.3.4	Within site variation at Fractured-metasediments well-drained arable site 1	224
7.3.5	Within site variation at Fractured-metasediments well-drained arable site 2	226
7.4	Temporal variation of pesticide occurrence at each site	227
7.4.1	Temporal variation at Karst well-drained grassland	227
7.4.2	Temporal variation at Karst well-drained arable	228
7.4.3	Temporal variation at Intergranular/karst well-drained arable	233
7.4.4	Temporal variation at Fractured-volcanic well-drained arable	235
7.4.5	Temporal variation at Fractured-volcanic poorly-drained arable	238
7.4.6	Temporal variation at Fractured-metasediments well-drained arable site 1	239
7.4.7	Temporal variation at Fractured-metasediments well-drained arable site 2	241
7.5	Statistical correlations of variables with pesticide detections	243
7.5.1	Introduction to statistical analysis	243
7.5.2	Sample pre-treatment and statistical materials and methods	243
7.5.3	Results of statistical analysis	246
7.5.3.1	Physical characteristics	246
7.5.3.2	Chemical variables	250
7.5.3.3	Sites most associated with pesticide occurrence in groundwater	251
7.6	Chapter 7 discussion	252
7.6.1	Discussion of parent compounds and transformation products detected in the study	252
7.6.2	Discussion of temporal variations in pesticide occurrence	258
7.6.3	Discussion of the relationship between pesticide occurrence and site characteristics	260
7.7	Chapter 7 conclusions	265
Chapter 8: OVERALL DISCUSSION AND CONCLUSIONS		266
8.1	Main findings	266
8.2	Discussion	270
8.2.1	Comparison between national scale and catchment scale monitoring	270

8.2.2	Discussion of overall study findings	272
8.3	Recommendations for future research	275
8.4	Conclusions	277
REFERENCES		279

APPENDICES

Appendix 1	Active ingredients used on particular land uses within the Republic of Ireland and the percentage of PPP with each particular a.i.	305
Appendix 2	Pesticide application records each site.	308
Appendix 3	Borehole installation logs.	319
Appendix 4	Phi sizes and corresponding soil classification.	331
Appendix 5	Geophysical surveys.	332
Appendix 6	Coefficients of variation (r^2) between modelled potential evapotranspiration (PET) and recorded PET.	340
Appendix 7	Summary of hydrochemical variables for each monitoring point (MP).	341
Appendix 8	Scree plots from Principal Component Analysis (PCA) of hydrochemical composition for each monitoring point (MP) at fractured-metasediments well-drained arable (FmWDa ₁) site 1.	344
Appendix 9	Scree plots from Principal Component Analysis (PCA) of hydrochemical composition for each monitoring point (MP) at fractured-metasediments well-drained arable (FmWDa ₂) site 2.	346
Appendix 10	Compounds quantified for during catchment scale monitoring, their CAS registry number, and their chemical grouping.	348
Appendix 11	List of compounds analysed during external laboratory analysis.	340
Appendix 12	Within laboratory repeatability (WLR) validation results for the organochlorine method.	352
Appendix 13	Within laboratory repeatability (WLR) validation results for the phenoxyacid ad benzonitrile herbicide method.	353
Appendix 14	Raw data for the percentage frequency of occurrence for all seven sites where monthly samples were collected.	354
Appendix 15	Raw data for the percentage frequency of occurrence for each individual site.	356
Appendix 16	List of publications from this work.	363

LIST OF FIGURES

Figure 1.1	Thesis layout.	5
Figure 2.1	Possible pesticide pathways in the environment following land application (adapted from (Rowell, 1993)).	7
Figure 3.1	Examples of zone of contribution (ZOC) boundaries for two	39

monitoring points (MPs) in Co. Meath.

Figure 3.2	Sequence of work undertaken to allow for the assessment of ZOC physical characteristics and pesticide detections in groundwater.	46
Figure 3.3	Frequency of pesticide detections as a percentage of the total number of samples analysed for a particular pesticide compound from the 2007 – 2008 EPA groundwater monitoring dataset: n = 845. Values are adjusted to each compound's limit of detection (LOD) of 0.01 µg/L. The Council Directive 98/83/EC drinking water standard (EU DWS(i*)) is 0.1 µg/L.	47
Figure 3.4	Monitoring points (MPs) with detections exceeding the European Union Drinking Water Standard for individual compounds (EU DWS(i)), MPs with detectable detections of pesticides, and MPs which never had a pesticide detection throughout the two year monitoring campaign.	48
Figure 3.5	Monitoring points (MPs) with detections of MCPA, mecoprop, lindane, and glyphosate on at least one occasion.	49
Figure 3.6	Results from logistic regression based on (a) the type of monitoring point (p=0.0028), (b) aquifer type classified using the GSI classification system based on aquifer importance (p=0.0007), (c) aquifer type classified using the Irish system of flow regime adopted for the WFD (p=0.0002), and (d) acid versus basic subsoil as identified by their reaction with 10 v/v hydrochloric acid (p=0.0048).	53
Figure 3.7	Results from logistic regression for GSI aquifer importance aquifer types with karst aquifer types removed from the count tables (p=0.0030).	59
Figure 4.1	Hydrological conceptual model and potential sampling locations.	64
Figure 4.2	Arable land (non-irrigated arable and complex cultivation patterns) in Ireland from the CORINE Land Cover dataset in 2006 (European Environment Agency, 2011).	66
Figure 4.3	Location of monitoring sites across Ireland used for collecting monthly data.	75
Figure 4.4	The catchment of monitoring point (MP) karst well-drained grassland (KWDg). Map indicates the spring sampled, karst features known by the GSI in the area, tracer lines from studies carried out by Coxon and Drew (1986), and the catchment boundary estimated by the ACP which is finalised in Chapter 5 using water balance and additional tracer studies carried out by the ACP. Land cover from Corine 2006 is also shown.	77
Figure 4.5	Land use at karst well-drained arable (KWDa) in Co. Kilkenny. The purple boundary North West of the Boiling Spring shows an estimation of the Boiling Springs ZOC. Land cover from Corine 2006 is also shown.	80
Figure 4.6	The Sawmills Field at intergranular/karst well-drained arable (I/KWDa), Co. Carlow. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland. The red line	83

indicates the boundary of the Sawmills Field.

Figure 4.7	Fractured-volcanic well-drained arable (FvWDa) site situated in the catchment of Ballycanew showing the five monitoring points (MPs) sampled with the red boundary showing the location of the fields housing the MPs. Land cover from Corine 2006 is also shown.	86
Figure 4.8	The Fractured-volcanic poorly-drained arable (FvPDa) site and approximate field boundaries (red line) situated in the catchment of Ballycanew. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	87
Figure 4.9	The 11 km ² catchment showing the relative locations of the fractured-volcanic well-drained arable (FvWDa) site in the south west and the fractured-volcanic poorly-drained arable (FvPDa) site in the centre-east, each with their approximate field boundaries shown in red. Land use is taken from the CORINE land cover dataset fro 2006 (European Environment Agency, 2011). Approximately 77% of the catchment is in grassland and 20% in arable.	88
Figure 4.10	The fractured-metasediments well-drained arable (FmWDa) catchment showing the location of each site and the monitoring locations within. Land cover from Corine 2006.	90
Figure 5.1	Particle size distribution for soils and subsoils from fractured-volcanics poorly-drained arable (FvPDa) collected during borehole installation in October 2008.	95
Figure 5.2	2D resistivity for karst well-drained arable (KWDa). Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	100
Figure 5.3	2D resistivity for fractured-volcanics well-drained arable (FvWDa). Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	102
Figure 5.4	2D resistivity for fractured-volcanics poorly-drained arable (FvPDa). Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	104
Figure 5.5	Schematical cross section of material encountered at the piezometers drilled using a Giddings Hydraulic Soil Sampling, Coring and Drilling machine at the fractured-volcanics poorly-drained arable (FvPDa) site.	105
Figure 5.6	2D resistivity for fractured-metasediments well-drained arable site 1 (FmWDa ₁). Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	107
Figure 5.7	2D resistivity for fractured-metasediments well-drained arable site 2 (FmWDa ₂). Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	108
Figure 5.8	Schematical summary and comparison of material encountered across each site using information obtained from borehole installation records and geophysical surveys.	109
Figure 5.9	Material encountered 5.5 m b.g.l at piezometer 1b at the fractured-volcanic poorly-drained arable (FvPDa) site during Gidding's Rig	111

drilling.

Figure 5.10	Comparison of recorded potential evapotranspiration (PET) from the fractured-volcanic poorly-drained arable site (FvPDa) with modelled PET obtained from the grassland SMD model by Schulte <i>et al.</i> (2005) with a coefficient of determination (r^2) of 0.91284.	114
Figure 5.11	Cumulative effective rainfall for each site where effective rainfall was modelled.	115
Figure 5.12	Spring discharge and total rainfall from 11 th May 2010 until 21 st March 2011 from the spring at karst well-drained grassland (KWDg) in Co. Mayo which is used to supply water to a group water scheme (GWS) and which is also monitored by the Agricultural Catchments Programme (ACP).	117
Figure 5.13	Daily average discharge from the Rocky Weir located approximately 200 m downstream from where the Boiling Spring enters the River Nuenna and daily total rainfall at karst well-drained arable (KWDa).	119
Figure 5.14	Groundwater table fluctuations and effective rainfall at the intergranular/karst well-drained arable (I/KWDa) site.	120
Figure 5.15	Groundwater table fluctuations and effective rainfall at the lower borehole in fractured-metasediments well-drained arable site 1 (FmWDa ₁).	121
Figure 5.16	Groundwater table fluctuations and effective rainfall at the middle borehole in fractured-metasediments well-drained arable site 1 (FmWDa ₁).	121
Figure 5.17	Groundwater table fluctuations and effective rainfall at the upper borehole in fractured-metasediments well-drained arable site 1 (FmWDa ₁).	122
Figure 5.18	Groundwater table fluctuations and effective rainfall at the lower borehole in fractured-metasediments well-drained arable site 2 (FmWDa ₂).	123
Figure 5.19	Groundwater table fluctuations and effective rainfall at the middle borehole in fractured-metasediments well-drained arable site 2 (FmWDa ₂).	123
Figure 5.20	Groundwater table fluctuations and effective rainfall at the upper borehole in fractured-metasediments well-drained arable site 2 (FmWDa ₂).	124
Figure 5.21	The karst well-drained grassland (KWDg) catchment in Co. Mayo, Ireland with mapped karst features commissioned by the ACP and the new catchment boundary.	128
Figure 5.22	The karst well-drained arable (KWDa) catchment in Co. Kilkenny, Ireland showing the estimated ZOC of the Boiling spring and the estimated ZOC from Walsh (2011) following tracer work from a swallow hole in the south west to the Group Water Scheme spring. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	130

Figure 5.23	Groundwater flow direction at intergranular/karst well-drained arable (I/KWDa).	131
Figure 5.24	The intergranular/karst well-drained arable (I/KWDa) site in Co. Carlow with field boundaries in red and arable areas in the ZOC potentially able to receive pesticide applications in yellow. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	132
Figure 5.25	Groundwater flow direction at fractured-volcanic well-drained arable (FvWDa).	133
Figure 5.26	The fractured-volcanic well-drained arable (FvWDa) site in Co. Wexford with field boundaries in red and the estimated ZOC in yellow. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	134
Figure 5.27	Groundwater flow direction at fractured-volcanic poorly-drained arable (FvPDa).	135
Figure 5.28	The fractured-volcanic poorly-drained arable (FvPDa) site in Co. Wexford with field boundaries in red and the estimated ZOC in yellow. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.	136
Figure 5.29	Groundwater flow direction at fractured-metasediments well-drained arable site 1 (FmWDa ₁).	137
Figure 5.30	Groundwater flow direction at fractured-metasediments well-drained arable site 2 (FmWDa ₂).	138
Figure 5.31	Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the Boiling Spring at karst well-drained arable (KWDa).	151
Figure 5.32	Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the shallow piezometer at MP2 at the intergranular/karst well-drained arable (I/KWDa) site. PCS 1 = turbidity.	152
Figure 5.33	Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the interface piezometer at MP1 at the intergranular/karst well-drained arable (I/KWDa) site. PCS 1 = turbidity.	153
Figure 5.34	Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the deep piezometer at MP1 at the intergranular/karst well-drained arable (I/KWDa) site. PCS 1 = residual dissolved oxygen (RDO).	153
Figure 5.35	Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the deep piezometer at the Lower borehole in the fractured-volcanic well-drained arable (FvWDa) site. PSC 1 = Iron.	155
Figure 5.36	Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the deep piezometer	155

	at the Upper borehole in the fractured-volcanic well-drained arable (FvWDa) site. PCS 1 = Iron.	
Figure 5.37	Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the deep piezometer at the Upper Spring in the fractured-volcanic well-drained arable (FvWDa) site. PCS 1 = turbidity.	155
Figure 6.1	Stability over time of analytes in prepared vials calculated as the percentage of analyte remaining after day 1. Error bars represent standard error of the sample mean.	173
Figure 6.2	Stability over time of (a) phenoxyacid and benzonitrile herbicides and their (b) transformation products (TPs), calculated as the percentage of the analyte remaining after day 1.	175
Figure 6.3	Chromatographic trace, showing the sum of all ions, for each compound at 0.1 µg/L.	188
Figure 6.4	Optimisation of SPME conditions: (a) fibre choice and (b) ionic strength. Error bars represent standard error of the sample mean.	192
Figure 6.5	SPME optimization extraction experiments for (a) temperature and (b) time. Error bars represent standard error of the sample mean.	193
Figure 6.6	Fibre longevity following repeated injections of fortified samples at 0.05 µg/L.	194
Figure 6.7	(a) Absolute recoveries for each compound using samples spiked at 100 µg/L from Strata-X and Bond Elut ENV (200mg in 6ml) SPE cartridges and (b) absolute recoveries for Bond Elut ENV cartridges using 6 mL of acetone as an elution solvent. Error bars represent standard error of the sample mean.	201
Figure 6.8	UHPLC-MS/MS trace for all 18 compounds at 0.4 µg/L after SPE clean up and re-suspension in acetonitrile:ultra pure water (50:50, v/v).	203
Figure 7.1	Percentage frequency of detection for all seven sites sampled monthly from March 2010 to March 2012. The total number of samples analysed for each compound is stated in brackets.	210
Figure 7.2	Percentage frequency of detection for samples collected at karst well-drained grassland (KWDg) between March 2010 to March 2012. The total number of samples analysed for each compound is stated in brackets.	212
Figure 7.3	Percentage frequency of detection for samples collected at the Boiling Spring at karst well-drained arable (KWDa) between March 2010 to March 2012. The total number of sampling dates for each compound that was analysed is stated in brackets.	213
Figure 7.4	Percentage frequency of detection for samples collected at all MPs at I/KWDa between March 2010 to March 2012. The total number of sample dates analysed for each compound is stated in brackets.	214
Figure 7.5	Percentage frequency of detection for samples collected at all MPs at FvWDa between March 2010 to March 2012. The total number of	215

	samples analysed for each compound on separate sampling occasions is stated in brackets.	
Figure 7.6	Percentage frequency of detection for samples collected at all MPs for groundwater at FvPDa between March 2010 and March 2012. The total number of samples analysed on separate sampling occasions for each compound is stated in brackets. Surface water samples collected at FvPDa have not been included for the percentage frequency of occurrence.	216
Figure 7.7	Percentage frequency of detection for all groundwater samples collected at MPs at FmWDa ₁ from March 2010 to March 2012. The total number of samples analysed for each compound is stated in brackets. Surface water samples have not been included for the percentage frequency of occurrence.	217
Figure 7.8	Percentage frequency of detection for samples collected at all MPs at FmWDa ₂ between March 2010 and March 2012. The total number of samples analysed for each compound is stated in brackets. Surface water samples have not been included for the percentage frequency of occurrence.	218
Figure 7.9	Within site distribution of the percentage frequency of pesticide occurrence at FvWDa using graduated symbols based on the number of detections recorded at each MP as a function of the number of samples collected throughout monitoring. Printed under licence No. 6155 from the Ordnance Survey of Ireland.	221
Figure 7.10	Within site distribution of the percentage frequency of pesticide occurrence at FvPDa using graduated symbols based on the number of detections recorded at each MP as a function of the number of samples collected throughout monitoring. Printed under licence No. 6155 from the Ordnance Survey of Ireland.	223
Figure 7.11	Conceptual model showing borehole installations and piezometers to target the shallow, interface, and deep groundwater with areas under the influence of discharge and recharge highlighted.	225
Figure 7.12	Within site distribution of the percentage frequency of pesticide occurrence at FmWDa ₁ and FmWDa ₂ using graduated symbols based on the number of detections recorded at each MP as a function of the number of samples collected throughout monitoring. Printed under licence No. 6155 from the Ordnance Survey of Ireland.	226
Figure 7.13	Temporal variation between total parent pesticide compounds at the karst well-drained grassland (KWDg) spring in Co. Mayo.	228
Figure 7.14	Temporal variation between total parent active ingredient (a.i) and total transformation products (TPs) from monthly samples collected at KWDa with daily average discharge from Rocky weir and total rainfall.	230
Figure 7.15	Total rainfall and stream discharge at the Rocky Weir located approximately 200 m downstream of where the Boiling Spring enters the R. Nuenna at karst well-drained arable site (KWDa) before and after event-based sampling which occurred in May 2012.	231

Figure 7.16	Temporal variation between total parent active ingredient (a.i) and total transformation products (TPs) from event-based samples collected at karst well-drained arable (KWDa) with daily average discharge at Rocky weir and total rainfall.	232
Figure 7.17	Temporal variation between total parent pesticide compounds and TPs from MP1 and MP1 at I/KWDa. Note differences in the y-axis scale between MP1 and MP2.	234
Figure 7.18	Temporal variation between total parent pesticide compounds and TPs from the upper and lower boreholes (BHs) and effective rainfall at FvWDa. Note differences in the y-axis scale. Months marked with an asterisk (*) indicates months when pesticides were applied.	236
Figure 7.19	Temporal variation between total parent pesticide active ingredients (a.i.) and transformation products (TPs) from the three springs (Sp.) and effective rainfall calculated for FvWDa. Months marked with an asterisk (*) indicates the months pesticides were applied. The location of these springs can be found in Figure 4.7 and 5.3 .	237
Figure 7.20	Temporal variation between total parent pesticide compounds at fractured-volcanic poorly-drained arable (FvPDa) and effective rainfall. Months marked with an asterisk (*) indicates that pesticides were applied.	238
Figure 7.21	Temporal variation between total parent pesticide compounds at fractured-metasediments well-drained arable site 1 (FmWDa ₁) and effective rainfall.	240
Figure 7.22	Temporal variation between total parent pesticide compounds at fractured-metasediments well-drained arable site 2 (FmWDa ₂) and effective rainfall.	242
Figure 7.23	A proposed degradation pathway for 2,4-dichlorophenoxyacetic acid (2,4-D) to degrade to phenoxyacetic acid (PAC).	257

LIST OF TABLES

Table 2.1	Groundwater threshold values under S.I. No. 9 of 2010 taken from Ireland (Government of Ireland, 2010) and groundwater quality standards taken from Directive (1998).	10
Table 2.2	Summary of pesticides detected in Irish drinking water supplies in 2006 from Page <i>et al.</i> (2007).	15
Table 2.3	The matrix used to categorise groundwater vulnerability. Adapted from the DELG/EPA/GSI (1999).	17
Table 2.4	Each aquifer categories characteristics. Taken from GSI (1999).	32
Table 3.1	Pesticides quantified during monitoring, their registration status in Ireland in 2007 and use. CAS = Chemical Abstracts Service.	38
Table 3.2	National datasets for physical characteristics selected for the prediction of groundwater pesticide occurrence and categories for	43

each characteristics subsequent associations within each category.

Table 3.3	Statistical analysis p values for Fisher's Exact Test and Logistic Regression. $p \leq 0.05$ infers there is an association between pesticide detections in groundwater and the physical characteristic or amalgamated category (in <i>italics</i>).	52
Table 3.4	Total amounts of active ingredient applied to arable, and grassland & fodder crops in Ireland.	55
Table 4.1	Some physical characteristics which may affect pesticide leaching to groundwater and corresponding national datasets available in Ireland and their source used to assist in selecting suitable sites.	65
Table 4.2	The principal soil types which are associated with arable land use and the area they represent in Ireland.	68
Table 4.3	The aquifer types which are associated with arable land use and the area they represent in Ireland.	68
Table 4.4	The bedrock geology types which are associated with arable land use and the area they represent in Ireland.	69
Table 4.5	The groundwater vulnerability types which are associated with arable land use and the area they represent in Ireland using data sources from 2009. These areas will be subject to change as the GSI groundwater vulnerability map is updated.	70
Table 4.6	The candidates selected and their main physical characteristics. The theoretical risk category is given in brackets (M)=moderate, (L)=low and (H)=high.	72
Table 4.7	Site names.	75
Table 4.8	Characteristics of the final seven sites and their theoretical risk to groundwater based on these characteristics.	93
Table 5.1	Soil and subsoil results from Brookside Laboratories Inc. for fractured-volcanic well-drained arable (FvWDa) and fractured-volcanic poorly-drained arable (FvPDa).	97
Table 5.2	Summary of subsoil and Quaternary deposits at each chosen site.	111
Table 5.3	Coefficient of determination (r^2) results for modelled potential evapotranspiration (PET) and recorded PET.	113
Table 5.4	Total rainfall, potential evapotranspiration, actual evapotranspiration, effective rainfall, maximum and average effective rainfall and the number of days of effective rainfall for each site in 2011.	115
Table 5.5	Meteorological summary information between sites.	116
Table 5.6	Discharge flow measured from the Boiling Spring at karst well-drained arable (KWDa) site in Co. Kilkenny.	118
Table 5.7	Summary of each sites hydrogeological properties.	125
Table 5.8	The monitoring points sampled to determine the age of groundwater and results.	139
Table 5.9	The variables (n=15) used for input into GenStat for principal	141

component analysis (PCA) of each monitoring points (MP) hydrochemical composition.

Table 5.10	Major elements and some of their mineral sources in unpolluted fresh water (Appelo and Postma, 2006).	146
Table 5.11	Typical groundwater hydrochemistry values for inorganic variables in Ireland. Source: EPA (2003) and units are in mg/L.	147
Table 5.12	Descriptive statistics for hydrochemical variables at each site.	147
Table 5.13	Summary of the hydrochemical composition from the output of principal component analysis (PCA) for each monitoring point (MP) at fractured-metasediments well-drained arable (FmWDa) site 1 and 2.	159
Table 6.1	Solid phase extraction (SPE) cartridge conditioning steps for phenoxyacetic acid herbicides analysed at the NIEA.	182
Table 6.2	Mobile phase gradient programme used for the NIEA phenoxyacid herbicide method.	184
Table 6.3	Parent and daughter transitions used for identification and quantification during the NIEA phenoxyacid herbicide method.	184
Table 6.4	Average compound retention time from 18 replicates, characteristic ions, and the quantification ions monitored using selective ion storage (SIS).	189
Table 6.5	Specific compound settings applied during both electrospray ionisation (ESI) positive and negative mode with m/z ratios for the precursor and product ion transitions.	199
Table 6.6	External laboratory results for blank matrices spiked at two fortification levels (n=2).	204
Table 6.7	Comparison between other methods on performance.	205
Table 6.8	Summary of limits of detection (LOD) for the compound classes used for catchment scale monitoring across the seven sites.	207
Table 7.1	Compound frequency of occurrence, the maximum, mean, median, and 90 th percentile observed concentration monitored monthly throughout the catchment scale study for all seven sites. Compounds are listed in order of decreasing frequency of occurrence.	211
Table 7.2	Summary of detections at each piezometer at the Sawmills Field at Intergranular/karst well-drained arable (I/KWDa).	220
Table 7.3	Breakdown of detections at fractured-metasediments well-drained arable (FmWDa ₁).	225
Table 7.4	Breakdown of detections at fractured-metasediments well-drained arable 2 (FmWDa ₂).	227
Table 7.5	Variables tested statistically against the pesticide categories (A)-(D).	245
Table 7.6	Association (P value) of site physical characteristics in groundwater total pesticides, parent active ingredients (a.i.), and transformation products.	247
Table 7.7	The chemical variables which are associated with pesticide occurrence	250

from the mixed model in SAS[®] 9.3 with their significance level and trend.

Table 7.8	Site estimates for total pesticides in groundwater from a mixed model	251
Table 7.9	Sites which are more likely to have higher detections of parent active ingredients (a.i.) in groundwater.	252
Table 7.10	The number of transformation products (TPs) detected at each site from samples collected from monthly monitoring between March 2010 to March 2012 and the percentage frequency of occurrence of TPs at each site.	257
Table 7.11	Pesticide frequency of occurrence, absolute numbers greater than the limit of detection (LOD), absolute numbers greater than the European Union Drinking Water Standard for individual pesticides EU DWS(i), and the total number of samples processed at each site.	264
Table 8.1	Differences in sample detection frequency between national- and catchment- scale monitoring.	271
Table 8.2	Comparison of statistically significant physical characteristics at the catchment- and national-scale.	272

UNITS, TERMINOLOGY AND ABBREVIATIONS

PESTICIDES	
a.i.	active ingredient
2,4-D	2,4-dichlorophenoxyacetic acid
4C2MP	4-chloro-2-methylphenol
BAM	3,5-dichlorobenzamide
BrAc	3,5-dibromo-4-hydroxybenzoic acid
DBA	2,6-dichlorobenzoic acid
DCP	2,4-dichlorophenol
endo- hep. epo.	<i>endo</i> -heptachlor epoxide (Isomer A)
exo- hep. epo.	<i>exo</i> -heptachlor epoxide (Isomer B)
MCPA	MCPA acid
MCPA-D6	deuterated MCPA acid
MCPP	mecoprop
MCPP-P	mecoprop-p
PAC	phenoxyacetic acid
PPP	Plant protection product
T2P	3,5,6-trichloro-2-pyridinol
TBA	2,3,6-trichlorobenzoic acid
TCP	2,4,5-trichlorophenol

CHEMISTRY

ALK	Alkalinity
NH₄⁺	Ammonium
C	Carbon
Ca	Calcium
CaCO₃	Bicarbonate fraction as calcium carbonate
Cl	Chloride
μS/cm	Conductivity (microSiemens per centimetre)
Fe	Iron
FA	Formic acid
HCl	Hydrochloric acid
Mg	Magnesium
Mn	Manganese
μg/L	micrograms per litre
mg/L	milligram per litre
MTBE	methyl tert-butyl ether
NO₃⁻	Nitrate
NO₂	Nitrite
N	Nitrogen
PO₄³⁻	Phosphate (orthophosphate)
K	Potassium
Na	Sodium
NPOC	Non-purgeable organic carbon
PA	polyacrylate SPME fibre coating
TN	Total nitrogen
TOC	Total organic carbon

WATER QUALITY AND LEGISLATION

EU DWS(i)	Drinking water permitted limit for individual pesticides (Council Directive, 98/83/EC)
EU DWS(t)	Drinking water permitted limit for total pesticides (Council Directive, 98/83/EC)
GWD	Groundwater directive (European Parliament, 2006/118/EC)
WFD	Water framework directive (European Parliament, 2000/60/EC)

STATISTICAL AND ANALYTICAL

EI	Electron impact
ESI	Electrospray ionisation
GC-MS	Gas-chromatography mass-spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
MDL	Method detection limit
PCA	Principal Component Analysis
PCS	Principal Component Score
QC	Quality control
r²	co-efficient of determination
S:N	Signal-to-noise ratio
SIM	Selective ion monitoring
SIS	Selective ion storage
SPE	Solid phase extraction
SPME	Solid phase micro extraction
UHPLC- MS/MS	Ultra high performance liquid chromatography triple quadrupole mass spectrometry

MISCELLANEOUS

ACP	Agricultural Catchments Programme
b.g.l	below ground level
BH	borehole
c.	circa/approximately
CEC	cation exchange capacity
GWS	group water scheme
K_d	distribution coefficient
kg/a.i.	kilograms of active ingredient
K_{OC}	organic carbon partition coefficient
Lg	locally productive extensive sand and gravel
LI	bedrock which is generally moderately productive only in local zones
Lm	bedrock which is generally moderately productive
m	metre(s)
mAOD	metres above ordnance datum
m b.g.l	metres below ground level
OC	organic carbon
OM	organic matter
PET	potential evapotranspiration
PI	bedrock which is generally unproductive except for local zones
PL	permitted limit
Pu	bedrock which is generally unproductive
Rf	regionally productive fissured bedrock
Rg	regionally productive extensive sand and gravel
Rk	regionally productive karstified bedrock
Rkc	regionally productive karstified bedrock conduit in nature
Rkd	regionally productive karstified bedrock diffuse in nature
SMD	soil moisture deficit
Sp.(s)	spring(s)
TP(s)	transformation product(s)
ZOC	zone of contribution

CHAPTER 1

INTRODUCTION

1.1 Background to the research project

Pesticides can be natural or synthetic substances used to kill various types of animals and plants in agriculture, veterinary, household, and hygiene products (Rowell, 1993). The name pesticide is derived from the Latin word *pestis* (pestilence, plague) and *caedere* – to kill. Throughout this thesis pesticide encompasses herbicides, insecticides, growth regulators, and fungicides. Although pesticides are required to fulfil the World's quota for food, pesticides have the ability to cause unintended damage to non-target organisms. Chronic exposure can lead to ill health, some pesticides are endocrine disruptors, and have mutagenic or intergenerational effects (Mostafalou *et al.*, 2013). Furthermore, once pesticides are present in the ecosystem they can be very difficult to remove (Reichenberger *et al.*, 2007).

It was once believed that after pesticides were applied they degraded to harmless compounds, remained dormant in the soil, and never had the opportunity to leach to groundwater (Rowell, 1993). This is not the case, as pesticides have been detected in groundwater in considerable concentrations by many authors e.g. Arias-Estévez *et al.* (2008), Haarstad and Ludvigsen (2007), and Papadopoulou-Mourkidou *et al.* (2004). Although pesticides degrade in the environment, they can degrade to more toxic transformation products (TPs) or metabolites than the parent compound, as discussed in section 2.3.2.5. which has been reported by Clausen *et al.* (2004), Fava *et al.* (2006), and Kolpin *et al.* (1998b). Worrall *et al.* (2002) and Lindsey *et al.* (2006) report that physical characteristics at the site of application will influence a pesticides ability to leach to groundwater. The physical attributes associated with pesticide occurrence in groundwater were examined by Worrall and Kolpin (2004) using molecular descriptors derived solely from the structural formula of the compound and the properties of the immediate monitoring point (MP). Using binary logistic regression, they found pesticide occurrence was related to water table depth, soil organic matter content, and particle size distribution.

See section 2.3 for more detail on the processes affecting pesticide leaching to groundwater.

Groundwater is an important source of water throughout the world with more than 1.5 billion people across the globe relying on groundwater as their primary source of drinking water (Alley *et al.*, 2002). Legislation relating to groundwater pesticides is reviewed in section 2.1.2. The main pieces of legislation include the Drinking Water Directive 98/83/EC (Council Directive, 1998) which has set individual and total permitted limits (PL) for active ingredients (a.i.) present in plant protection product (PPP) formulations. Individual pesticides must not exceed 0.1 µg/L and total pesticides should not exceed 0.5 µg/L (98/83/EC). In December 2000 the European Union (EU) Water Framework Directive (WFD) (2000/60/EC) (European Parliament, 2000) was implemented across all member states. By 2015 all member states must achieve 'good status' for all water bodies, including compounds present as a.i.s in PPPs.

Hydrologically groundwater is connected to other water bodies (Fetter, 2001) and its contamination can lead to the deterioration of drinking water supplies. In the Republic of Ireland approximately 26% of public and private drinking water supplies are from groundwater sources, with groundwater acting as the main drinking water source in counties such as Co. Roscommon, where it can contribute up to 75% (Lucey, 2009). Ireland has a reputation across the globe as a green country with unpolluted resources, and this gives Ireland a potential advantage over its competitors as regards agricultural exports. However, water quality as regards pesticide occurrence has never been studied in detail until now. Groundwater monitoring studies, through the Environmental Protection Agency (EPA), have been carried out since 2008 to determine which potable water supplies have pesticides present, although detailed analysis has not been carried out until the present study (see Chapter 3). A modelling study by Moe (2008) predicted the impact on Irish groundwater quality from diffuse mobile organics (see section 2.1.4) but this study did not verify predicted results with observed field data. At the time no field data was available for use. This study aimed to provide insight into pesticide occurrence in groundwater and produce a reliable groundwater dataset for pesticides in Irish groundwaters.

1.2 Study aims and objectives

The overall aim of this doctoral thesis was to determine whether a range of pesticide compounds were present in Irish groundwaters and, if so, what physical characteristics of catchments are associated with their occurrence. Subsequently, the study aims and objectives were to identify sites at the catchment scale more at risk of pesticide occurrence in groundwater. Sites were selected based on their physical characteristics e.g. bedrock geology, and which were represented across the Island of Ireland (see Chapter 4). Since the project investigated diffuse agricultural sources, the aim was to choose an agricultural source which is a high user of pesticides with the subsequent aim of investigating pesticide compounds not widely studied across the international community. Thus another aim was to determine if certain active herbicides within the European Union (EU) were present in detectable concentrations in groundwater and if their relevant transformation products (TPs) were also detected. Chemical characteristics in association with pesticide occurrence in groundwater were also identified.

The project hypotheses are listed below:

Hypothesis 1:

Pesticides and their respective transformation products are more prevalent in Irish groundwater than was hitherto understood to be the case.

Hypothesis 2:

The occurrence of pesticides and their transformation products in Irish groundwaters is associated with certain physical characteristics of the catchment.

A summary of the project objectives are listed below:

1. To determine which pesticide compounds are present in Irish groundwater.
2. To determine if pesticide a.i.s that are currently used within the EU can be detected in Irish groundwater and, if so, at what concentrations.
3. To determine if TPs are present in Irish groundwater and, if so, at what concentration.
4. To determine the physical characteristics of catchments that are associated with pesticide occurrence in groundwater at both the catchment and national scale.
5. To compare national scale monitoring data on pesticides in groundwater with catchment scale pesticide monitoring data.
6. To determine the influence of land use on the occurrence of pesticides in groundwater.
7. To develop improved analytical methods to quantify a range of currently used and prohibited pesticide a.i.s and their TPs in groundwater samples.
8. To describe any temporal patterns of pesticide occurrence in Irish groundwaters that can be discerned from the datasets in this study.

1.3 Thesis structure

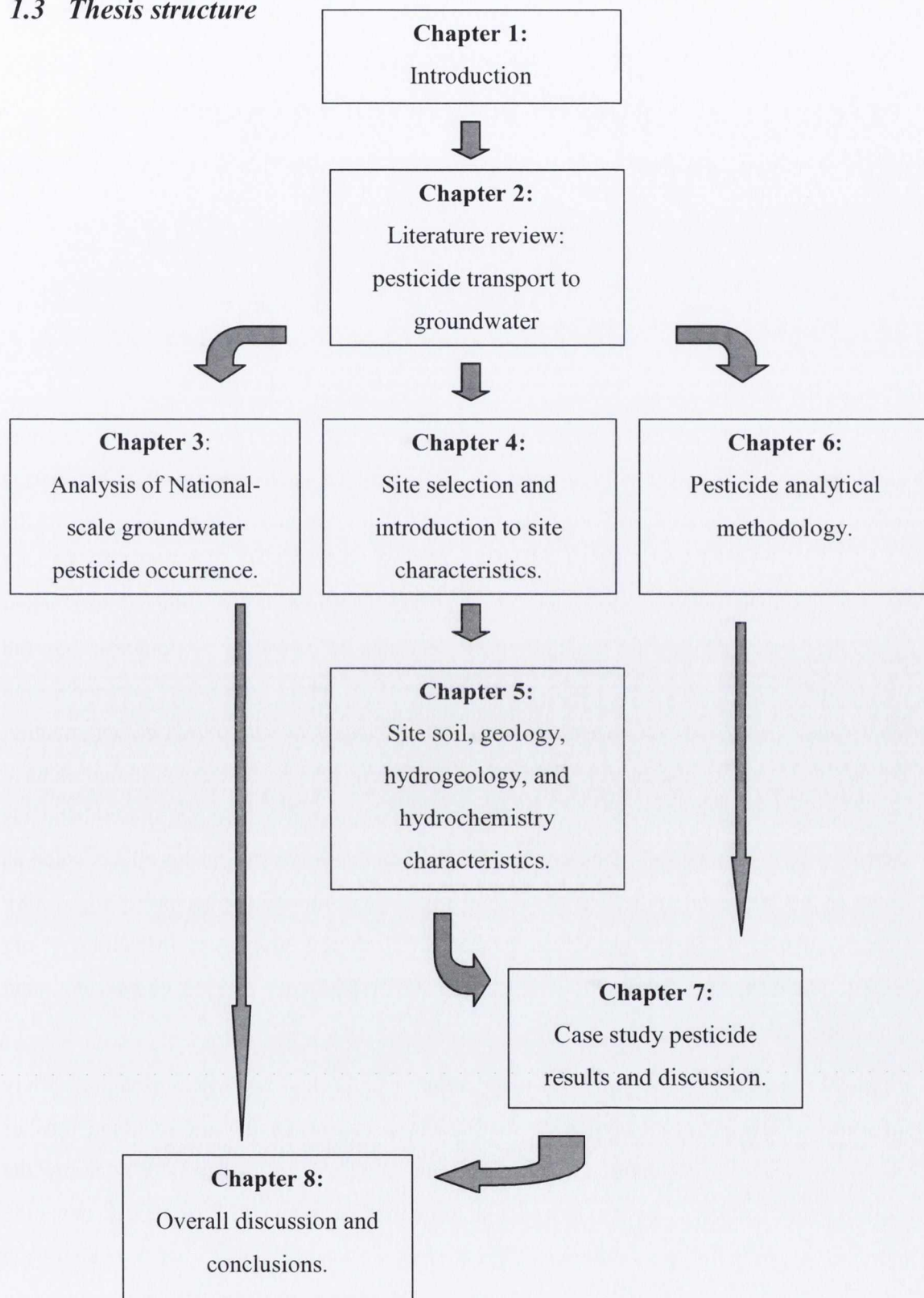


Figure 1.1 Thesis layout.

CHAPTER 2

LITERATURE REVIEW: PESTICIDE TRANSPORT TO GROUNDWATER

2.1 Introduction to the pesticide problem

2.1.1 Why groundwater contamination from pesticides is of concern

Although pesticides are indispensable in modern agriculture, they can produce a wide range of toxic side effects that pose a potential hazard to the environment. Possible effects include cancer, tumours, infertility, suppression of the immune system, disruption of the endocrine system, cellular DNA damage, physical deformities, and physiological and intergenerational effects (McKinlay *et al.*, 2008). It was once believed that when pesticides were applied to the land they degraded to harmless compounds, but the ubiquitous, poisonous, and accumulating nature of DDT and other organochlorine compounds has proven this wrong (Carson, 1962; Yang *et al.*, 2010) and drawn attention to pesticides as potential causes of concern in the environment. Endocrine disruptors have also received a great deal of attention because exposure to low levels of these chemicals and their bioaccumulation potential in the body, can cause adverse health effects (such as poor endocrine functionality) to the organism and its progeny (McKinlay *et al.*, 2008). Such endocrine disrupting pesticides include 2,4-D, diuron, glyphosate (McKinlay *et al.*, 2008), dieldrin (Jorgenson, 2001), lindane (HCH) (Danzo, 1997), heptachlor and heptachlor epoxide (Reuber, 1987).

Some of the pesticides used in modern agriculture can reach groundwater through a variety of routes (**Figure 2.1**). Compounds may reach surface water through overland flow or direct application, or compounds may infiltrate and leach to groundwater. During the hydrological cycle all waters are cycled through the system and pesticides have the potential to be transferred throughout the system. Groundwater is used throughout the world as drinking water in various amounts. In Ireland approximately 26% of drinking water is supplied from groundwater (Lucey, 2009) while in Europe almost 70% of drinking water is derived from groundwater (Malaguerra *et al.*, 2012). Many studies have already

detected considerable amounts of pesticides in groundwaters (Broers and van der Grift, 2004; Silva *et al.*, 2006; Gonçalves *et al.*, 2007). Not only are pesticide active ingredients (a.i.) of concern in groundwater but also their transformation products (TPs). These are degradation products or metabolites of the parent compound used in a pesticide product formulation defined as “an intermediate or product resulting from the breakdown of a pesticide” (FOOTPRINT, 2006). TPs tend to be found more frequently in the environment than the parent compound and often in absence of the parent compound (Gonçalves *et al.*, 2007) with many deemed more toxic than the parent compound (Kolpin *et al.*, 1998b; Arias-Estévez *et al.*, 2008; Hildebrandt *et al.*, 2008). For example chlorothalonil-4-hydroxy, a TP of the fungicide chlorothalonil, is more toxic (Chaves *et al.*, 2007).

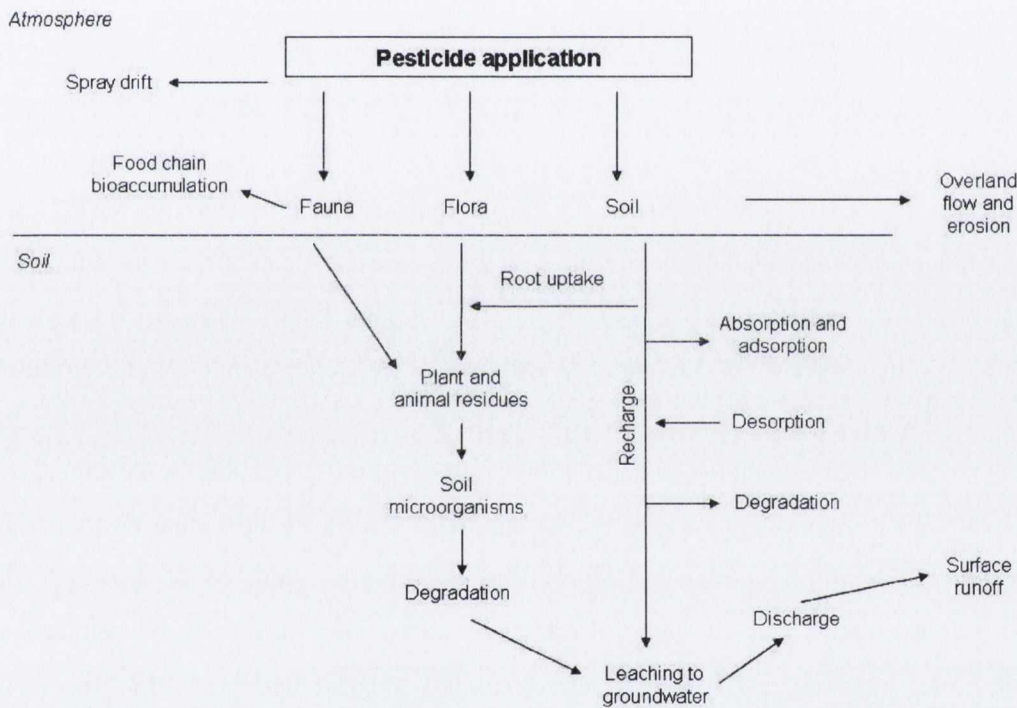


Figure 2.1 Possible pesticide pathways in the environment following land application (adapted from Rowell (1993)).

2.1.2 Legislation to control pesticide contamination in groundwater from pesticides

The original groundwater directive (GWD) was Council Directive 80/68/EEC of the 17th December 1979 on the protection of groundwater against pollution caused by certain dangerous substances. The purpose of Directive 80/68/EEC (European Communities, 1980) was to prevent the discharge of certain toxic, persistent, and bioaccumulating

substances into groundwater. Prohibited substances were included in List I and included organophosphorous compounds, which included pesticides. In List II the discharge of substances was limited and included toxic or persistent compounds, biocides, and their TPs which did not appear in List I. Groundwater directive 80/68/EEC will be fully superseded by the groundwater daughter directive 2006/118/EC in December 2013 which relates to the protection of groundwater against pollution and deterioration. Directive 2006/118/EC (European Parliament, 2006) highlights criteria for the assessment of good groundwater chemical status, criteria for the identification and reversal of significant and sustained upward trends, identify threshold values for pollutants, and adopt measures to prevent or limit inputs of pollutants into groundwater. Directive 2006/118/EC also requires the establishment of quality standards for PPP in line with provisions on the Marketing of PPP (Directive 91/414/EEC).

The original Drinking Water Directive 80/778/EEC (Council Directive, 1980) relates to the quality of water intended for human consumption and has since been superseded by Directive 98/83/EC (Council Directive, 1998) since 2003. Directive 98/83/EC aims to keep water clean and safe for consumption and not cause adverse affects to human health. The drinking water standards apply at the point of use, but the groundwater body standards from the groundwater directive (same in the case of pesticides) apply to the groundwater body. Drinking water standards specified in Directive 98/83/EC and groundwater quality standards specified in 2006/118/EC state that individual pesticides must adhere to the parametric value of 0.1 µg/L while total pesticides (sum of all individual pesticides found in any monitoring procedure) must adhere to the parametric value of 0.5 µg/L. Pesticides also includes their relevant TPs. In the literature TPs may also be referred to as metabolites, reaction products, derivatives, and degradates. In the case of the organochlorine compounds aldrin, dieldrin, heptachlor, and heptachlor epoxide, a lower parametric value of 0.03 µg/L has been set. Where no guideline value or standard is stated in Irish or EU legislation, the World Health Organisation (WHO) standards are used. The Irish Groundwater Regulations implement the Groundwater Directive in Ireland (Government of Ireland, 2010). The Irish Groundwater Regulations have specified groundwater threshold values under schedule 5. Some of these values relate to pesticides, and these are listed in **Table 2.1**. Threshold values are groundwater quality standards that are established by each EU member state to assess the chemical status of their groundwater bodies when undertaking trend assessments (Craig and Daly, 2010). The values

themselves can be national or on a local groundwater body scale. If a threshold value is exceeded it will prompt further investigation to determine if the GWB is at 'good' or 'poor' status however, they do not represent the boundary between 'good' or 'poor' status (Craig and Daly, 2010). The threshold value for pesticides in groundwater and drinking water is currently 0.1 µg/L. Both the national-scale and catchment-scale studies examined in this thesis will refer to the EU DWS(i) (Council Directive, 1998).

In December 2000 a water policy came into force across all member states called the Water Framework directive (WFD) 2000/60/EC (European Commission, 2000). It is a strategic framework for managing the water environment, protecting, and achieving the objectives once implemented. The WFD states that water is heritage which must be protected, defended, and treated as such. Objectives of the WFD and groundwater directive are to protect, enhance and restore all groundwater bodies as well as achieving and maintaining "good status" for chemicals. Groundwater is defined as all water below the surface of the ground in the saturation zone and in direct contact with the ground or subsoil. (European Commission, 2000).

The Groundwater Directive (2006/118/EC) (European Parliament, 2006) also specifies that quality standards for plant protection products (PPP) and biocides should be set as community criteria for the assessment of the chemical status of groundwater bodies and consistency should be ensured with Directive 91/414/EEC (Council Directive, 1991) of 15th July 1991 concerning the placing of PPP on the market and Council Directive 98/8/EC concerning the placing of biocidal products on the market. All PPP categorised as safe are placed in the Annex 1 list. Currently there are 250 products included on Annex 1 while 74% of PPP were removed from the market or failed to get EU approval (Cross *et al.*, 2011).

In November 2009 the EU released the Sustainable Use of Pesticides Directive (2009/128/EC) (European Parliament, 2009), the objectives of which are to reduce the risks and impacts of pesticide use on human health and the environment and promote the use of integrated pest management and of alternative approaches or techniques such as non-chemical alternatives to pesticides. The Department of Agriculture, Food and Marine (DAFM) Pesticide Control Service will report to the EU by 2018 their experience gained following implementation of this directive by 2018.

Table 2.1 Groundwater threshold values under S.I. No. 9 of 2010 taken from Ireland (Government of Ireland, 2010) and groundwater quality standards taken from Directive 98/83/EC.

Parameter	Assessment of the general quality of groundwater in a groundwater body in terms of whether its ability to support human uses has been significantly impaired by pollution	Overall threshold value range	Groundwater quality standard	Units
Electrical conductivity	-	800 – 1875	-	µS/cm
Ammonium	175	65 – 175	-	µg/L N
Nitrite	-	375	500	µg/L NO ₂
Nitrate	37.5	37.5	50	mg/L NO ₃
Chloride	-	24 – 87.5	-	mg/L Cl
Sodium	150	150	-	mg/L Na
Cadmium	3.75	3.75	5	µg/L Cd
Copper	1500	1500	50	µg/L Cu
MCPA	0.075	0.075	0.1	µg/L
lindane	0.075	0.075	0.1	µg/L
diuron	0.075	0.075	0.1	µg/L
dieldrin	0.075	0.075	0.03	µg/L
bentazone	0.075	0.075	0.1	µg/L
glyphosate	0.075	0.075	0.1	µg/L
mecoprop (MCP)	0.075	0.075	0.1	µg/L
2,4-dichlorophenoxyacetic acid (2,4-D)	0.075	0.075	0.1	µg/L
total pesticides	0.375	0.375	0.5	µg/L

2.1.3 International research on extent of the groundwater pesticide problem

A search on Web of Science in December 2012 using the key words of pesticide with either groundwater, surface water, soil, and air revealed that the most peer-reviewed scientific publications on pesticides are on soil (10,386 articles), followed by surface water (4,342), air (2,683), and finally groundwater with the fewest: 1,039. The reported extent of pesticide groundwater contamination varies between different countries and regions depending on the extent of awareness, monitoring, research, and pesticide usage. For example in America, atrazine is one of the most widely used pesticides, the most widely studied, and thus also the most frequently found in groundwater (Kolpin *et al.*, 2000; Barbash *et al.*, 2001). In Europe atrazine was banned in 1997 but was still detected in a karst spring in France by Baran *et al.* (2008) at concentrations between 0.025 – 5.8 µg/L along with its TP desethylatrazine at concentrations up to 5.8 µg/L. Atrazine was banned because of its persistence in the environment and because of its mode of action. Many studies are published each year on its presence in the environment, especially of its TPs (Kolpin *et al.*, 1997; Fava *et al.*, 2007; Iker *et al.*, 2010; Jablonowski *et al.*, 2011). Once atrazine is applied it creates a layer in the soil which prevents weeds from penetrating the barrier, and this layer acts as a source of atrazine for leaching. Other banned pesticides have been detected in groundwater in Europe. In an industrial area of Berlin concentrations of 65 µg/L for α -HCH were found (Frische *et al.*, 2010). The EU DWS(i) for α -HCH is 0.1 µg/L, the concentration recorded in Berlin was 650 times greater than statutory legislation (Council Directive 98/83/EC). Lindane is the generic term used for α -HCH which was banned in Ireland in 2001. A more recently banned compound in Ireland is dichlobenil. It was banned in 2010 and is a well known groundwater contaminant in Danish groundwater which was banned there in 1997 because it degrades to 2,6-dichlorobenzamide (BAM). BAM readily leaches into groundwater because of its mobility and it is highly persistent in comparison to dichlobenil (Clausen *et al.*, 2007). BAM has been found at concentrations frequently exceeding the EU drinking water standard (EU DWS(i)) in Italian groundwaters ranging from 0.148 – 3.11 µg/L (Porazzi *et al.*, 2005). In Ireland no published data currently exists for the presence of either dichlobenil or BAM in groundwater.

Pesticide concentrations found in groundwater from a New Zealand monitoring study (Gaw *et al.*, 2008) have been: alachlor at 34 µg/L, atrazine between 0.011 – 0.094 µg/L, bentazone between 0.1 – 0.16 µg/L, mecoprop at 0.2 µg/L, and terbutylazine (a TP of

atrazine) between 0.05 – 0.085 µg/L. In England Lapworth *et al.* (2006) found 22 different pesticides in shallow boreholes of a Triassic Sherwood Sandstone aquifer, 34% of detections exceeded the EU DWS(i) and mecoprop (MCP), bentazone, isoproturon, and atrazine were some of the most frequently detected compounds.

2.1.4 Pesticide monitoring and research in Ireland

Few studies have been carried out on pesticide occurrence in Ireland. Some of the earliest work published was for organochlorine pesticides monitored in Ireland between 1964 – 1971 by An Foras Talúntais (Eades, 1976). Lindane (all isomers), aldrin, endrin, heptachlor, heptachlor epoxide, DDT, DDE and TDE were analysed for in various foodstuffs and aquatic wildlife including milk, butter, kidney fat, pig meat, and human fat. Eades (1976) found low levels of organochlorines and their TPs to be widespread throughout the environment, with predatory birds containing the highest concentrations of organochlorines, owing to these compounds bioaccumulation potential. However, this study did not analyse pesticides in waters across Ireland, only in some aquatic wildlife and foodstuffs.

McGrath (1995) published a study on the organochlorine compounds lindane (α - and γ -HCH), DDT, and DDT's TPs (DDE and DDD) which were quantified in soils across Ireland from agriculture, urban amenity, town garden, suburban garden, and industrial areas (McGrath, 1995). Almost all agricultural soils contained organochlorines below the method detection limit (MDL). Only one farm, which grew soft fruits and would have used organochlorines in the past, contained >90 ng/g in soil. The same site was sampled two years later, and McGrath (1995) found lower concentrations of organochlorines in soil indicating that considerable degradation of DDT had occurred. DDT was also found near urban dwellings in greater quantities, attributed to delousing in dwellings. In 2008 a modeling simulation was carried out to include how soil and subsoil (Quaternary deposits) would affect pesticide occurrence in groundwater. Moe (2008) concluded that the thinner and more permeable the soil, the faster the breakthrough, and the higher the rate of pesticide loading and concentration would be in groundwater. The most recent pesticide study on Irish soils was carried out by Piwowarczyk and Holden (2012) using soil monoliths collected from tillage fields throughout Ireland. This batch equilibrium experiment focused on the fungicide chlorothalonil and its sorption and desorption through the soil. Results indicated that adsorption of chlorothalonil dominated compared to

desorption inferring that chlorothalonil leaching to groundwater would be slow especially in comparison to phenoxyacid herbicides which have lower K_{OC} values. The K_{OC} is the soil organic carbon and water partition coefficient and indicates the mobility of a compound. A low K_{OC} correlates to a more mobile compound while a high K_{OC} indicates a less mobile compound (see section 2.3.2.1).

Local authorities for each county within Ireland were requested to report to the EPA for compliance against the total pesticide EU DWS(t), individual EU DWS(i), and detections above the limit of detection (LOD). Between 2006 – 2007 Page *et al.* (2007) stated that 1,342 samples were analysed for pesticides in 880 water supply zones which were monitored. 1,152 had no detections greater than the LOD. Of the remaining 190 samples with detectable concentrations, two had concentrations exceeding the total pesticide EU DWS(t) (0.5 µg/L) and 11 exceeded the individual EU DWS(i) (0.1 µg/L). **Table 2.2** summarises the results. Drinking water quality was then investigated in a more recent report for samples collected between 2008 - 2009 (Feehan *et al.*, 2011). As with Page *et al.* (2007) 26 chemical parameters were measured in drinking water (which includes both surface water and drinking water) and of these, 99.9% of samples complied with the EU DWS. The EU DWS(t) is currently 0.5 µg/L although this parametric value may become obsolete in the future (Moody *Pers. Comm.* 2012). Drinking water samples are often collected post-treatment from taps in the distribution system (Moe, 2008) and for this reason many of the pesticide compounds may have been removed via treatment processes such as chlorination and UV light, should these treatment systems exist for the area reliant on that water source.

The first report on pesticide occurrence specifically in groundwater in the Irish environment came in 1994 from the STRIDE report (K.T. Cullen & Co. Ltd., 1994). Trace organics were sampled in groundwater to include the compounds atrazine, lindane, dieldrin, DDT, and aldrin. However, the report focused mainly on industrial trace organics and few data were collected or interpreted for pesticides. In 2008, Moe published a modelling study to try and bridge the gap between the lack of available pesticide data in Irish groundwater and the effects of land use, physical characteristics, and chemical characteristics of the organic compound on groundwater quality. The model predicted a range of variables which would affect pesticide leaching to groundwater but did not verify the predictions with actual field data. The results from the model indicate that simulated high concentrations at the groundwater table exceeded the EU DWS(i) for only X

(exposed), E (extreme), and some H (high) groundwater vulnerabilities (GSI, 2009) (see section 2.1.5). The most important chemical property was the degradation rate of the pesticide, with atrazine the only pesticide to show breakthrough. The model also found that thin and permeable soils and subsoils would result in increased pesticide loading and concentration in groundwater. Rainfall was the most important variable in controlling leachate breakthrough times and concentrations, and crop types influenced infiltration and percolation. Thick, clayey deposits of subsoil would reduce infiltration rates and reduce the potential for breakthrough. Moe (2008) also calculated dilution factors for four aquifer types in Ireland: Pl/Pu (bedrock which is generally unproductive except in local zones/bedrock which is generally unproductive), Ll (bedrock which is moderately productive except in local zones), Lm (bedrock which is generally moderately productive), and sand & gravel (see section 2.3.4). Karst aquifers were not assessed by the model. Results suggest that dilution would occur in sand & gravel aquifers the most, followed by Lm, then Ll, and lastly Pl/Pu aquifer types.

In Ireland the EPA is designated the responsible body for monitoring and reporting of water quality in Ireland. The groundwater monitoring network was established in 2006 as described by Daly (2009) as part of the implementation of the WFD. The Irish network was designed to be representative of the hydrogeology and pollution pressures on each groundwater body. One of the aims of the network is to obtain and analyse groundwater samples that can be used to characterise groundwater quality throughout the country. Many of the monitoring points (MPs) in the groundwater quality monitoring programme are actually public water supplies, because boreholes with high abstraction rates were targeted as providing a more representative sample of groundwater from groundwater bodies. The network focuses on monitoring the main pressures and pollutants identified in Article 5 risk characterisation (National Summary Report, 2005). This detailed report was prepared in December 2004 by the relevant local authorities covering each River Basin District. Samples taken as part of the national groundwater programme in the two year period 2007-2008 have been analysed, interpreted, and reported in Chapter 3 only for pesticides. The main pressures and pollutants identified in the National Summary Report (2005) are livestock farming, arable activities, intensive enterprises, septic tanks, agrochemical use in agriculture, urban and household products, contaminated land, effluents, and landfill sites.

Table 2.2 Summary of pesticides detected in Irish drinking water supplies in 2006 from Page *et al.* (2007).

Compound	No. samples with a detection	No. samples > EU DWS(i)
Atrazine	100	1
Simazine	86	1
Dichlobenil	29	0
Terbutylazine	19	0
MCPA	16	3
Mecoprop	15	0
2,4-D	10	0
Triclopyr	10	0
Methoxychlor	9	5
Tebuconazole	9	0
Trietazine	7	0
p,p-DDD	6	0
Diuron	6	0
Triadme fon	6	0
Isoproturon	4	0
Lindane	3	0
Chlorpropham	2	0
p,p-DDT	2	0
hexachlorobenzene	2	0
Malthion	2	1
Propazine	2	0
2,4-DB	1	0
Bromoxynil	1	0
Clopyralid	1	0
p,p-DDE	1	0
Dieldrin	1	0
parathion-ethyl	1	0

2.1.5 Groundwater vulnerability

Vulnerability has been defined by the Geological Survey of Ireland (GSI) as the intrinsic geological and hydrogeological characteristics that determine the ease with which groundwater may be contaminated by human activities (DELG/EPA/GSI, 1999).

Groundwater vulnerability depends on the time of travel of groundwater and contaminants, and on the contaminant attenuation capacity of the materials. The hydrological connection between the land surface and groundwater determines the vulnerability to contamination. Therefore groundwater which can receive recharging water and contaminants more effectively due to the connection between the overlying materials and groundwater will be more vulnerable to contamination than in a scenario where the overlying materials prevent the water to reach groundwater because of their nature e.g. deep, clayey subsoils (Daly and Warren, 1994). Janniche *et al.* (2011) found that a 1m thickness of soil would substantially increase the natural attenuation of three herbicides including mecoprop compared to a thickness of 30 cm. The same study also found mecoprop sorption to sandy aquifer samples very low (Janniche *et al.*, 2011). Groundwater vulnerability from the GSI has listed four categories which indicate how vulnerable groundwater in a particular location is to anthropogenic contaminants. The categories are extreme (E), high (H), moderate (M), and low (L) and within the extreme category the 'X' category refers to areas of bedrock within a 30 m radius of a point recharge area. To determine groundwater vulnerability, the subsoil permeability and thickness are used, with thin, high permeability subsoils being classed as for example extreme (E) vulnerability for bedrock aquifers (**Table 2.3**). Sand and gravel aquifers only use the depth of the unsaturated zone to categorise the groundwater vulnerability. High permeability subsoils are sandy subsoils, moderate permeability subsoils have sand and gravel, and low permeability subsoils are clayey subsoil or peat >10 m deep. The groundwater vulnerability assumes that contaminants are released 1-2 m below ground and delineated zones should be regarded as provisional and subject to change as information is updated.

Table 2.3 The matrix used to categorise groundwater vulnerability. Adapted from the DELG/EPA/GSI (1999).

Vulnerability category	Hydrogeological conditions				
	Subsoil permeability and thickness			Unsaturated zone	Karst radius
	High permeability	Moderate permeability	Low permeability	Sand and gravel aquifers	<30m radius
Extreme (E)	0-3 m	0-3 m	0-3 m	0-3 m	-
High (H)	> 3 m	3-10 m	3-5 m	>3 m	n/a
Moderate (M)	n/a	>10 m	5-10 m	n/a	n/a
Low (L)	n/a	n/a	>10 m	n/a	n/a

2.2 Sources of pesticides in the environment

2.2.1 Agricultural land use

Pesticide sales worldwide has increased from US\$850 million in 1960 to US\$31,191 million in 2005 (Zhang *et al.*, 2011). Alavanja (2009) state that approximately 5.6 billion pounds of pesticides are used worldwide. EuroStat keeps statistical records of EU countries' pesticide usage, rather than sales of products. Since 1999 a decline in the use of pesticides has occurred throughout the EU, thought to be because of more stringent reviews for placing PPP on the market, the withdrawal of some products, many of which were used at higher dosage levels, and their replacement with products used at lower dosage rates (Nadin, 2007). In the 25 countries of the EU a total of 219,771 tonnes of PPP were used in 2003. Five countries made up nearly 75% of this total: France at 28%, Spain and Italy at 14%, Germany at 11%, and the UK at 7%. Ireland represents 0.6% of the total and is ranked 17th for the total amount of PPP used across the EU. In Ireland PPP use in 2003 was dominated by 653 tonnes of herbicides, 537 tonnes of fungicides, 43 tonnes of growth regulators, and 6 tonnes of insecticides. A total of 1,239 tonnes of PPP was used in Ireland in 2003. The area surveyed by Nadin (2007) for EuroStat represents 27% of the 44,000,000 ha of Ireland's total usable agricultural area to include cereals, maize, oil seeds,

potatoes, sugar beet, vegetables, and fruit trees. The remaining 73% is permanent grassland.

The main agricultural crops to which PPPs are applied in Ireland are cereals, potatoes, and sugar beet. However, sugar beet production has declined considerably since 2003. The most widely used herbicides in 2003 were glyphosate, mecoprop-p, and MCPA. For fungicides chlorothalonil and fenpropimorph were the most commonly used. In 2003 a total area of 1,182,000 ha was cultivated for cereals in Ireland with 2.7 kg a.i./ha applied to cereal crops in 2003 (Nadin, 2007). The most commonly applied compounds to cereals in 2003 were: mecoprop-p with 131 tonnes of a.i., chlorothalonil with 68 tonnes of a.i., MCPA with 46 tonnes of a.i., and fenpropimorph with 44 tonnes of a.i..

Other agricultural sources are sheep dip products which use the a.i.s cypermethrin, amitraz, and diazinon in Ireland (Conroy *Pers. Comm.*, 2011). The chief concern relating to sheep dipping is appropriate waste disposal, rather than the application methods adopted, since inappropriate disposal can act as a point source of contamination.

2.2.2 Urban land use

In urban environments the main potential source of pesticides are weed killers which are applied to roads, paths, and railway lines. Atrazine and simazine, banned in 2007 and 2008 respectively, were historically used in road maintenance but these have since been replaced with glyphosate and diuron (Conroy *Pers. Comm.*, 2011). The National Roads Authority of Ireland released a report on techniques to control noxious weeds and non-native invasive species (National Roads Authority, 2010). These management techniques can also be applied to paths under the management of local authorities. The control of both noxious weeds and non-native invasive species can be broken into either physical methods or chemical treatment. Physical methods include cutting, digging, or excavating, hoeing, and pulling by hand. Chemical treatment may involve the application of herbicide either by targeted spot-spraying or direct application to the individual plant by wiping or direct injection. Examples of noxious weed control for spear thistle include spraying with a PPP containing the a.i. MCPA or 2,4-D between February and June. For the non-native invasive species Japanese Knotweed, spraying with glyphosate between September and October is recommended, although for small infestations 2,4-D can also be used. To eliminate all vegetation from railways, roads, airfields, and other paved areas a higher rate

of pesticide application is common in comparison to agricultural practices (Foster and Chilton, 1991).

2.2.3 Aquatic management

Up until 2010 water course maintenance in Ireland was dominated by use of the a.i. dichlobenil (2,6-dichlorobenzonitrile) which is present in the PPP Casoran G. Between 2000-2009 a total of 970.31 kg of Casoran G was used per year on 100-130 km of waterways (Grand Canal, Royal Canal, and Barrow Canal) in the Eastern region of Ireland before its exclusion from the market in 2010 (Horgan *Pers. Comm.*, 2011). One of the reasons for this ban was the widespread groundwater occurrence in Europe of its TP BAM (2,6-dichlorobenzamide) (Holtze *et al.*, 2008). Water course maintenance in Ireland has moved to mechanical weed control using weed cutting machines but glyphosate is still routinely used for terrestrial plants and invasive species near water courses as a replacement to glyphosate. Between 2003-2011, 508 L of Round-Up (a.i. glyphosate) was used on a total of 100-130 km of the waterways including the Grand Canal, Royal Canal, and Barrow Canal system, for the treatment of Giant Hogweed (Horgan *Pers. Comm.*, 2011).

2.2.4 Amenity uses

Amenity environments such as golf courses, leisure parks, and personally owned allotments may act as a source of pesticides in the environment.

Currently there are no pesticide usage data available for the 285 golf courses in Ireland. In the UK the three main PPP formulations used on golf courses are 2,4-D/dicamba, 2,4-D/mecoprop, and mecoprop-p/fluroxypyr (Garthwaite, 1998). Each PPP formulation contains two a.i. In France these a.i. are also used along with dichloroprop and MCPA (Blanchoud *et al.*, 2004). In the UK the average pesticide application rate is 0.5 kg/ha for total a.i. per application over the entire golf course. Assuming this application rate is used in Ireland, with an average of 60 hectares, Moe (2008) estimates that the total area of 4,600 ha could receive applications on an area basis and assuming from UK studies that approximately 41% of a.i. by weight consists of fungicides, 41% of herbicides, and the remaining 18% of insecticides, a total of approximately 3,500 kg a.i. of herbicides and

fungicides may be applied annually to Irish golf courses. This application only relates to high usage areas such as greens, fairways, and tees (Moe, 2008).

Local authorities will manage leisure areas such as parks and sports fields through spraying PPP at appropriate times. No data on pesticide usage in amenity areas such as these exist for Ireland but surveys in the UK by DEFRA (Department of the Environment and Rural Affairs) indicate that 92% of all pesticides applied are glyphosate, 2,4-D, mecoprop, MCPA, triclopyr, or dicamba (Moe, 2008). These are all herbicides used to kill weeds.

2.3 Processes affecting pesticide leaching to groundwater

The concept of groundwater vulnerability recognises that different soil and hydrogeological conditions will give rise to differing vulnerabilities and afford different degrees of protection to the underlying aquifer, which is the source of groundwater. Land use, soil type, climate, and aquifer properties in combination with intrinsic properties of the pesticide compound such as solubility and molecular branching will affect pesticide movement to groundwater (Worrall and Kolpin, 2004). The unsaturated zone is the medium through which pesticides move from soil to surface and groundwater, and is an important area to consider when predicting pesticide transport downwards. The term “leaching” is defined as the process whereby pollutants are flushed vertically through the soil profile by rain or irrigation water (Hornsby *et al.*, 1995). Polluting substances such as pesticides are subject to complex physical, chemical, and biological transformations on their journey through the unsaturated zone and their displacement depends on the transport properties of the water-air-porous medium system (Yaron, 1989) which complicates predictions. Following pesticide application a pesticide may attach (sorb) to soil particles or other surfaces and remain near the site of application, pesticides may sorb to soil particles and move with eroded soil in run off and wind, dissolve in water and be taken up by plants, move in run off as overland flow or leach, and some pesticides (depending on their chemical nature) may volatilize or erode from foliage or soil with wind and become airborne (Kerle *et al.*, 2007). The main processes which affect pesticide migration through soil, the unsaturated zone, and the aquifer are sorption to organic matter and organic carbon, clay mineral sorption, ion exchange, and microbial degradation (Estévez *et al.*, 2012). Each of these processes will be discussed in the following sections.

2.3.1 Agricultural management

Groundwater contamination from pesticides is common in agricultural areas and usually results from routine applications to cropped fields, rather than from spills or other point sources (Rodvang and Simpkins, 2001) although spills, inadequate storage, and poor handling can contribute to elevated pesticide concentrations in groundwater (Gregoire *et al.* 2009). Pesticide applications across arable fields have a non-point or diffuse nature, and routine, annual applications will contribute pesticides to the land. Through personal communication with land managers, land owners, and advisors, many farmers will not apply the full recommended dosage to their crops because of fear of weed and pest resistance to the pesticide compound and concern over the PPP's removal from the market yet not being replaced.

Certain practices that influence pesticide leaching include; the amount of pesticide applied, the timing of applications relative to seasonal rainfall, crop coverage, and the temperature of the environment. The method of application such as spot spraying or using a boom may affect pesticide leaching; cultivation practices such as applying a herbicide (e.g. glyphosate) several days before harvest to harden and desiccate the husk in a spring barley crop. Other land management practices such as riparian buffer strips, set aside, rotational cropping systems, cover crops, constructed wetlands, irrigation, vegetated agricultural drainage ditches, or artificial subsurface drains can also play a role indirectly on pesticide leaching to groundwater. For example by distributing pesticides to surface water, pesticides may be added and subsequently bound to alluvial sediments and these over time may leach to groundwater should favourable conditions occur e.g. losing streams. A study by Moore *et al.* (2011) found that vegetated agricultural drainage ditches decreased chlorpyrifos concentrations in ditch outflow by 20% from an alfalfa field. Moore *et al.* (2011) acknowledges the benefits of vegetated drainage ditches compared to constructed wetlands as an edge of field management practice for agricultural runoff but realises that removing land from production to include a constructed wetland is not always viable, especially as production needs to be efficient to cope with today's demand for food products.

Herbicides are some of the most commonly detected pesticides in groundwater in the UK (Foster and Chilton, 1991) and herbicide application timing may play a role in these detections since they are applied to bare soil pre-weed emergence. Land managers will avoid applying pesticides during or in anticipation of rainfall events because this may

cause the compounds to leach or move in overland flow, decreasing pesticide efficacy. Good land management also involves applying pesticides in the evening when solar radiation is less strong. Many pesticides if applied to crops during sunshine may damage the crop, volatilize or photodegrade (Rowell, 1993). Photodegradation can take place in the environment directly or indirectly as a natural phenomenon. Direct photodegradation occurs when a pesticide absorbs photons and as a result undergoes degradation, indirect photodegradation involves other photo-sensitive compounds present alongside the pesticide in the water such as nitrates and humic substances which themselves become energised in the water and instigate degradation of the pesticide (Gatidou and Iatrou, 2011).

2.3.2 Soil type

The soil has a strong influence on pesticide transport to groundwater. It protects groundwater by “filtering” contaminants out of recharging water but the capacity for soils to degrade potential contaminants is limited and dependent on numerous other factors. Diffusion and mass flow are the mechanisms by which contaminants move from the surface to groundwater (Hornsby *et al.*, 1995). Diffusion and mass flow are affected by the contaminant’s properties and the soil’s properties. This pathway is complicated by many factors such as soil saturation, the fraction of sand, silt and clay, the presence of clay minerals, organic matter, microbial population density and diversity, hydraulic properties, oxygen status, and pH for example. All of these factors are made more complicated to predict since individual pesticides have contrasting affinities for different soils and their constituents. In addition to the mass flow and diffusion properties of soil, the pesticide’s persistence and sorption will affect its leachability. Persistence is the residence time of a chemical subjected to degradation or physical removal in a defined environmental compartment (Stephenson *et al.* 2006). The majority of pesticides degrade and become inactive over time as a result of reactions within the soil (Hornsby *et al.*, 1995). Persistence can be expressed as half-life, which is defined as the amount of time for 50% of the original amount applied to become biologically inactive or broken down to half its value (Buttler *et al.*, 2003; Stephenson *et al.*, 2006). Also half-life can be defined as the amount of applied pesticide completely degraded and released as CO₂ and H₂O (Hornsby *et al.*, 1995).

2.3.2.1 Sorption and desorption

Sorption may be permanent where it is referred to as adsorption or may be less permanent through absorption. Persistence and sorption are probably the two most important properties influencing a pesticide's ability to leach to groundwater (Hornsby *et al.*, 1995; Buttler *et al.*, 2003). When a pesticide enters the soil environment, it may attach itself to soil particles such as organic matter or clay minerals depending on the pesticide's chemical nature. Strongly sorbed pesticides with a high K_{OC} will be less likely to reach groundwater (Buttler *et al.*, 2003). The K_{OC} is the soil organic carbon-water partition coefficient relative to the organic carbon content of soil and is a useful predictor for pesticide mobility. The K_{OC} is defined as the ratio of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium concentration in soil (Farenhorst *et al.* 2010). Statistical analyses of detection frequencies in groundwater for different sets of pesticides indicate positive correlations with degradation half lives in aerobic soils and negative correlations with sorption coefficients on organic carbon (Böhlke, 2002). The sorption coefficient of a pesticide is a value which has been normalized to the organic carbon (OC) content of the soil and can be used as an indicator to the binding capacity of the chemical on soil organic matter (OM) (Ahmad *et al.*, 2009). The sorption coefficient allows comparisons to be made between different pesticide compounds. Many pesticides are adsorbed by OM which reduces their rate of downward movement. Some pesticides, depending on their chemical characteristics, may dissolve in the soil-water between soil particles and as more recharge enters the soil environment, these pesticide molecules will leach downwards towards groundwater and desorb from soil particles (Hornsby *et al.*, 1995). This is a dynamic process controlled by a compounds solubility and ability to sorb to the soil constituents. The solubility of a pesticide compound will ultimately determine its ability to leach within recharging water. The higher the compound's water solubility value, the more likely that it will leach with recharge. Should a pesticide compound be soluble in soil solution and where the soils sorption capacity has already been decreased with other pesticides taking up sorption sites, the compound will more readily leach to groundwater.

The ability of a pesticide to adsorb to clay minerals and organic matter can be expressed by the compound's partition co-efficient, this is normally only available for non-polar adsorption on organic carbon (K_{oc}) (Foster and Chilton, 1991) and will vary amongst different soil types depending on the soil contents (Burkart *et al.*, 2001; Jacobsen *et al.*,

2008; Alister *et al.*, 2011). For example a pesticide exposed to a sandy soil will behave differently to the same pesticide exposed to a clayey soil. The clay sized fraction of soils ($<2\ \mu\text{m}$) together with the OM fraction, largely controls the physical and chemical properties of a soil (Rowell, 1993). The mineral components in the clay-sized fraction are primarily clay minerals, sesquioxides, and amorphous minerals in association with humus. Their small particle size and electrical charge mean they can be described as colloidal (Rowell, 1993). Clay minerals are crystalline hydroxyl silicates containing aluminium, iron, and magnesium. A study by Wang and Keller (2009) found atrazine and diuron sorb more efficiently to clay fractions compared to bulk soils, silt, and sand fractions because of the higher amount of OC. The principal soil properties that affected adsorption of the herbicides MCPA, simazine, diuron, and terbutylazine was the soil OC content, especially the fulvic acid-humus fraction (Alister *et al.*, 2011). OC was also found (Hiller *et al.*, 2006) to be the most important property affecting MCPA sorption to surface soils and sediments.

Soil pH affects sorption, with kinetic studies showing that bentazone and 2,4-D are weakly sorbed by a variety of soils following application (Boivin *et al.*, 2004), but that this sorption is greatly affected by soil pH (Clausen and Fabricius, 2002). pH affecting sorption can be attributed to pH's ability to affect ionic strength thus affecting other properties such as electric charge (Clausen and Fabricius, 2002). Fredslund *et al.* (2008) found MCPA sorption to show a strong positive correlation with soil OC content and negatively correlate with soil pH. To complicate pesticide leaching to groundwater further, pesticides may desorb from soil under certain favourable conditions such as pH and may be rendered mobile in soil solution. Currently desorption is less researched than sorption with even fewer studies existing on TP desorption.

2.3.2.2 Preferential flow

Preferential flow in soils occurs in the unsaturated or vadose zone and is a term loosely used to describe any phenomenon in soils or rocks whereby water moves in a heterogeneous pattern along certain pathways whilst bypassing volume fractions of media through which it is flowing (Kramers *et al.*, 2009). Factors influencing preferential flow include soil structure (Akhtar *et al.*, 2011), water repellence (Hangena *et al.*, 2005), macropore tortuosity and continuity (Vervoort *et al.*, 2003), recharge, and land management practices (Kramers, 2009). Soils with a fine texture are more prone to

preferential flow (Rodvang and Simpkins, 2001; Reichenberger *et al.*, 2007). As a consequence of preferential flow, water will move at an accelerated pace through the unsaturated zone, leaving little time for pesticide attenuation, which means that the transport of pesticides to groundwater is likely to be different to that of Darcian theory. Sorption retardation during transport through such preferential porous fractures is weaker than in the bulk soil, due to their small surface areas and significant kinetic effects, especially in larger macropores (Jarvis, 2007). Preferential flow accelerating pesticide movement to groundwater has been widely reported in the literature (e.g. Elliott *et al.*, 2000; Roulier and Jarvis, 2003).

2.3.2.3 Artificial subsurface pathways

Soil permeability is the rate of diffusion of a fluid under pressure through soil. In low permeability soils, permeability is often low resulting in overland flow. These soils can become waterlogged and anaerobic which does not favour successful crop production. Land managers thus install artificial subsurface drains to let excess water escape and lower the water table; however, these drains can transport pesticides from the point of application and contribute significantly to contamination of surface waters (Brown and van Beinum, 2009). In accelerating water movement to surface waters, groundwater recharge is reduced (Rodvang and Simpkins, 2001). In Ireland approximately 2% of land has been artificially drained as a proportion of the total agricultural land area in Ireland (Brown and van Beinum, 2009). Artificial subsurface drains act as pathways and can allow pesticides to rapidly travel in drainflow (Bottcher *et al.*, 1981; Kladivko *et al.*, 1991) remaining relatively unaltered. Preferential flow through structural and biological voids accentuates transport to subsurface drains (Harris *et al.*, 1994; Brown *et al.*, 1995), with preferential flow pathways common in heavier clay soils which will also be more likely to contain subsurface drains to ease waterlogging.

2.3.2.4 Colloidally bound transport

Some strongly adsorbed compounds can be mobile in fissured or coarsely grained formations in the sorbed phase when attached to colloidal particles (Foster and Chilton, 1991). Colloidal particles have diameters $<10\ \mu\text{m}$ and may consist of organic and inorganic materials in groundwater inducing macromolecular components of “dissolved”

organic carbon such as humic substances, “biocolloids” such as microorganisms, microemulsions of non-aqueous phase liquids, mineral precipitates and weathering products, precipitates of transuranic elements, and rock and mineral fragments (McCarthy and Zachara, 1989). The nature of the colloid and the pesticide compound will influence the ability of colloids to transport pesticides to and within groundwater. Some pesticides will have a greater affinity to particular colloidal components in groundwater than others just like some pesticides have contrasting affinities to sorb to particular soil materials (see section 2.3.2.1). Colloids can be produced after drilling boreholes. The disturbance of material introduces sediment into the borehole and also provides a conduit for air to reach groundwater. The introduction of oxygen will assist the production of colloids, especially Fe(III)-oxides (McCarthy and Zachara, 1989). Wang and Keller (2009) observed a clear relationship between soil OC contents in clay particle sized fractions and sorption of atrazine and diuron onto this fraction. This highlights the need to better understand pesticide sorption to the smallest colloids, the water dispersible fraction, which can be potentially mobilised under field conditions, leading to widespread contamination. In addition Goody *et al.* (2007) found significantly higher pesticide concentrations with the $< 0.45 \mu\text{m}$ and $< 1.0 \mu\text{m}$ colloidal fractions than the unfiltered soil solution samples.

2.3.2.5 Pesticide Degradation

Pesticide degradation plays an important role controlling pesticide residue levels in soil. Degradation is governed by biotic and abiotic factors and may involve many complex pathways along which a variety of interactions occur with the pesticide, soil microorganisms, and soil constituents (Arias-Estévez *et al.*, 2008). Biodegradation is defined as any biologically induced structural transformation in the parent compound that changes molecular integrity and may be oxidative, reductive, hydrolytic, or conjugative (Yaron, 1989). Biodegradation can be affected by soil type, pH, moisture, and temperature. OM can also affect biodegradation, soils with higher OM contents tend to have more microbial activity, but at the same time pesticides tend to sorb strongly in these soils, and this may protect the pesticide from degradation (Yaron, 1989). Chemical degradation may also occur within the soil as the solute in the aqueous phase or solute adsorbed on solid phase surfaces. Hydrolysis as a chemical reaction in soil is one of the most important reactions that pesticides can undergo in the soil media. The reactions of hydrolysis and oxidation can metabolise parent compounds in the soil environment to

create TPs. Pesticides tend to degrade much more quickly in the liquid phase than in the sorbed phase, so adsorption decreases degradation (Rodvang and Simpkins, 2001).

The degradation of pesticides in aquifer sediment is less well studied (Janniche *et al.*, 2010b) and in the aquifer microbial communities will differ since the environment is unlike soil, through differences such as the pH and OC contents (Janniche *et al.*, 2010a) which will affect the K_{OC} . With depth, pesticide degradation is said to decrease however, degradation can be faster in the subsoil than in the topsoil (Janniche *et al.*, 2011). Janniche *et al.* (2010b) found that sorption of the pesticide a.i. acetochlor was weak in limestone and aerobic sandy aquifers and strong in topsoil, with reduced redox conditions causing increased sorption of this pesticide to aquifer sediment. Janniche *et al.* (2010b) attribute this to redox conditions changing the nature of the functional groups on OC which will influence their K_{OC} sorption. Janniche *et al.* (2011) found that the degradation capacity of the aquifer was higher when the aquifer had already been exposed to phenoxyacid herbicides in comparison to a pristine aquifer which had no legacy of phenoxyacid pollution. In 2012 the same author (Janniche *et al.* 2012) found that long term diffuse pollution from agriculture may facilitate the mineralization of pesticide compounds in groundwater as over time the microbial communities are altered.

The awareness and study of TPs in the environment is a relatively new phenomenon. Their study in surface water and groundwater is an important topic because of their frequency of occurrence, possible herbicidal activity, and elevated concentrations (Thurman and Meyer, 1996). Many TPs are also unknown regarding their persistence and toxicity, TPs are still being found, and many of the reactions which occur in the soil environment between components of the soil and TPs and with TPs and pesticides with each other are still unknown. Halogenated TPs of parent compounds often have herbicidal activity and the possibility exists for toxic effects to aquatic life (Thurman and Meyer, 1996). Halogenation requires a reaction with one of five different halogens (fluorine, chlorine, bromine, iodine, and astatine). The degradation process of herbicides generally increases the water solubility and polarity of the compound (Scribner *et al.*, 2005). Chemical degradation can occur through oxidation-reduction reactions, biological degradation occurs through the action of environmental microorganisms (Souza *et al.*, 2010), and photodegradation or photolysis is degradation by sunlight which would be more common in surface waters than groundwaters.

Some TPs can be less toxic than the parent, some have equal toxicity, and others exhibit higher toxicities (Kolpin *et al.*, 1998b). For example aminomethylphosphonic acid (AMPA) is a TP of glyphosate and has been commonly found in surface waters and at higher concentrations than its parent (Skark *et al.*, 1998). However, studies by Reding *et al.* (2011) indicate its source is more than likely detergent additives and sequestering agents rather than as a degradation product of the herbicide glyphosate, particularly in urban environments. Other examples of degradation products include dichlobenil and its TP 3,5-dichlorobenzamide (BAM) (Clausen *et al.*, 2004) and MCPA and 4-chloro-2-methylphenol (4C2MP) (Craig, 2010).

2.3.3 Quaternary deposit type

Quaternary deposits or subsoil is defined in the Irish literature (DELG/EPA/GSI, 1999) as glacial, fluvial, and glacio-fluvial sediments, which cover most of the country's bedrock aquifers (Missteart *et al.*, 2009). Subsoils were laid down during the Quaternary period, and in Ireland they typically range in depth from greater than 15 m in the East while in Western areas thickness's are commonly less than 5 m. Some surficial deposits of sand and gravel in extensive areas can serve as aquifers with transmissivities of up to 500m²/day and specific yields between 10% and 28% (Missteart and Daly, 2008). These aquifers are termed regionally important sand/gravel aquifers (Rg) or locally important sand/gravel aquifers (Lg) in Ireland (GSI, 1999). These gravel aquifers have intergranular flow. They are composed of discrete grains of sand and gravel in which groundwater flows tortuously through the pores.

Subsoils can influence groundwater quality since they can have a large impact on the potential attenuation of pollutants. Quaternary deposits may often reduce the vulnerability of an underlying aquifer to pollution by both increasing the travel time for pollutants to reach the water table, allowing additional time for degradation, and retardation through sorption onto clay minerals or other organic material (Griffiths *et al.*, 2011). Quaternary deposits include tills which will naturally contain more OC, iron oxides, and clay minerals (Rodvang and Simpkins, 2001) than Rg and Lg aquifers which are also composed of Quaternary deposits. The presence of certain constituents in tills such as OC sampled by Allen-King *et al.* (1997) showed higher sorption due to the lipophilic nature of soil OC. Overall the presence of Quaternary deposits above aquifers can protect the underlying

water resource to varying degrees from potential sources of contamination (Daly and Warren, 1998).

2.3.4 Aquifer type

Pesticide compounds leached from the soil and Quaternary deposits enter an aquifer which generally has a smaller proportion of organic matter, clay minerals, and microbes (Foster and Chilton, 1991). It is postulated that once pesticides reach the aquifer they are less likely to sorb to materials and are free to travel within the aquifer system because there is less sorptive material. However, the transport of any substance, including pesticides, undergoes certain phenomena:

- (1) Diffusion: both ionic and molecular species dissolved in water move from areas of higher concentration to areas of lower concentration (Yaron, 1989). Diffusion of a solute through water is described by Fick's Laws (Fetter, 2001).
- (2) Advection: groundwater carries with it dissolved solutes. This rate of flowing groundwater can be determined by Darcy's Law (in aquifers where this is applicable), where contaminants that are advecting are travelling at the same rate as the average linear velocity of the groundwater (Fetter, 2001).
- (3) Mechanical dispersion: As solutes are carried through porous media, dispersion acts to dilute the solute and lower its concentration. During mechanical dispersion as the contaminated liquid moves through a porous medium, it will mix with non-contaminated water to result in dilution of the contaminant. Mechanical dispersion can be affected by how it moves among pores, the length of its pathway, and if the flow path splits and branches out to the side. Flow in large pores is faster than in small pores, and faster in the centre of the pore than near its periphery (Yaron, 1989).

Molecular diffusion and mechanical dispersion cannot be separated in flowing groundwater, instead the co-efficient of hydrodynamic dispersion is introduced which considers mechanical mixing and diffusion. The concentration of a solute will decrease with distance from the source because of hydrodynamic dispersion (Fetter, 2001), although for diffuse agricultural sources with annual inputs of pesticides the source is continuous and widespread. This continuous source will create a plume of pesticide in the groundwater, should it reach that far. The greatest risk to aquifers from pesticides has been

found to be where the aquifer is of low porosity and dilution is small (Chilton *et al.*, 1998). In low porosity environments the pore space for groundwater to travel in aquifers is small and as a result when pesticides are present in this environment, groundwater is not abundant enough to dilute pesticides.

Chemical and physical processes can cause retardation of solute movement so that they may not move as fast as the advection rate would indicate (Fetter, 2001). These solutes may be conservative or reactive. Conservative tracers such as chloride do not react with the soil. Reactive solutes, such as pesticides, will react with other components in the subsurface. Pesticides as reactive solutes have a wide-range of solute specific distribution coefficients, similar to those mentioned for soil (see section 2.3.2.1). Cations are more often strongly adsorbed than anions, and divalent cations will be adsorbed more readily than those of a monovalent species. The relative tendency for an organic compound to remain dissolved in water rather than to be adsorbed onto OC is related to the octanol-water partition co-efficient (Fetter, 2001).

In the Republic of Ireland the majority of bedrock is of Carboniferous age or older (>290 million years) with only fissure permeability. Fissure permeability has reasonably fast flow pathways and in the case of karst limestones such pathways may be particularly rapid due to solutional widening within the bedrock (Richards *et al.*, 2005). While bedrock permeabilities vary depending on lithology, tectonic history and in the case of limestones, the degree of solution, all bedrock types are regarded as having a certain degree of permeability and consequently can to varying degrees yield water for supply. Ireland has gravel aquifers, fissured aquifers, and karstified aquifers. The majority of Irish bedrock aquifers have fissure flow only (Fitzsimons *et al.*, 2005). Gravel aquifers have intergranular flow, they are composed of discrete grains of sand and gravel materials in which groundwater flows tortuously through the pores between the grains. Groundwater can flow in fissures such as joints, fractures, and bedding planes and the number of these fissures will determine whether the aquifer is productive or unproductive. In Ireland aquifers have been categorised based on their hydrogeological characteristics and on the value of the groundwater resource (GSI, 2008a). There are ten aquifer categories in existence which are displayed below.

1. Rk – regionally productive karstified bedrock
2. Rkc – regionally productive karstified bedrock conduit in nature

3. Rkd – regionally productive karstified bedrock diffuse in nature
4. Rf – regionally productive fissured bedrock
5. Rg – regionally productive extensive sand/gravel
6. Lm – bedrock which is generally moderately productive
7. Ll – bedrock which is generally moderately productive only in local zones
8. Lg – locally productive extensive sand/gravel
9. Pl – bedrock which is generally unproductive except for local zones
10. Pu – bedrock which is generally unproductive

The GSI (1999) have created a table of each aquifers characteristics which has been summarised in **Table 2.4**.

Across the World 12% of the terrain is karst, with 25% of the World's population receiving water from karst aquifers (Mudarra and Andreo, 2011). In Ireland the percentage of the population who obtain water from karst aquifers varies depending on location. In Co. Roscommon for example 75% of drinking water can be obtained from karst aquifers (Lucey, 2009). Up to 50% of the Republic of Ireland is underlain by Carboniferous limestone, much of which is pure enough to be classed as karstified (Aldwell *et al.*, 1988; Drew, 2008). In the glaciated karst landscape of Ireland the depth to bedrock is often shallow, and the landscape contains geological features such as swallow holes, springs, enclosed depression (dolines), caves, sinking streams, and turloughs (Mellander *et al.*, 2012). Solution features such as swallow holes and caves are created over time through dissolution. These sites can serve as points of focused groundwater recharge, and allow water to rapidly enter the underlying carbonate aquifer (Lindsey *et al.*, 2010). Should this water contain pesticides, they can be input into the aquifer system with little time for natural attenuation or biogeochemical processes, and may be flushed through.

The nature of karst is complicated because of uncertainties in the porosity and permeability which can be dual or triple in karst aquifers and often in the matrix or intergranular voids and always in fractures and solutional conduits (Daly *et al.*, 2002). Within these carbonate aquifers water can move rapidly through fissures widened by dissolution and water can enter groundwater directly through sinking streams (Daly *et al.*, 2002). However,

pesticides may remain in the karst system for several years. A study by Morvan *et al.* (2006) found atrazine and its TP desethylatrazine in a spring draining a 250 ha catchment in France five years following the last application of atrazine. Two explanations for these compounds occurrence were, (1) that there were long transfer times in the unsaturated or saturated zone, and (2) there was a progressive leaching of the stock of atrazine and desethylatrazine which owing to their persistence allowed them to accumulate in the soil and the vadose zone (Morvan *et al.*, 2006).

Table 2.4 Each aquifer categories characteristics. Taken from GSI (1999).

Aquifer category	Transmissivity values (m²/day)	Borehole yields	Large springs	Lithology type	Annual fluctuations in water levels
Rf	Most >50. Several >500.	Excellent	Potentially	Thin bedded sandstones, limestones, volcanics.	Generally <10m
Rkd	Variable. A few >500.	Excellent	Potentially	Pure or dolomitic limestones	Generally <15m
Rkc	Variable. A few >500.	Extremely variable	Potentially	Pure limestones	Often >15m
Lm	Some >50. A few >500.	Excellent	Potentially	Pure limestones, thin-bedded sandstones, volcanic	No criteria
Lk	As for Rkc or Rkd.	As for Rkc and Rkd	No	As for Rkc or Rkd	As for Rkc or Rkd
Ll	Some >50. A few >500.	Some excellent	Perhaps but unusual	Impure limestones, sandstones, shales, others	No criteria
Pl	Most <50. One or two >500.	Excellent yields very rare	No	Impure limestones, sandstones, shales, others	No criteria
Pu	<50.	Good yields rare if any.	No	Impure limestones, sandstones, shales, others	No criteria

2.3.5 Weather and climate

Many experiments have demonstrated that higher rainfall intensities increase the leaching of surface-applied solutes (Jarvis, 2007). Rainfall ultimately influences recharge, with higher amounts of rainfall generally causing more leaching or at least the capacity to leach will rise. Total rainfall data gathered at a site minus the evapotranspiration will equal the potential rainfall amount which may enter groundwater however, this does not consider lost potential rainfall amounts to overland flow nor does it consider the recharge capacity of the aquifer. A recharge coefficient can be determined for this from Missstear *et al.* (2009). Potential recharge may all not reach the groundwater since the geological material it passes through will influence how much can travel through (Missstear *et al.*, 2009). For example a soil with a high soil moisture deficit on a day of high evapotranspiration will not allow much water to replenish groundwater below as opposed to a saturated soil with a high groundwater table. This does not take into consideration preferential flow which may occur in dry soils (Kramers *et al.*, 2009). Using total rainfall, minimum temperatures, maximum temperatures, wind speed, and radiation the soil moisture deficit can be calculated to generate effective rainfall data (Schulte *et al.*, 2005) providing the location, soil drainage, and altitude of the site are known. Ireland has a temperate maritime climate with mild winters and mild summers. In the west of Ireland more precipitation is common while in the east and south east more sunshine hours and drier conditions occur in comparison to the west and north west.

Weather can also affect leaching through the type of pesticide required, the intensity of the pest problem caused by unfavourable weather conditions and the consequent disease or insect control required, and temperatures and sunlight can affect pesticide occurrence by influencing degradation. In warmer climates such as Spain and Italy more pesticides are used in comparison to Ireland (Nadin, 2007), and also in areas of higher humidity more compounds are applied. In Ireland some of the most unfavourable conditions for crops are moist and warm conditions, especially for potatoes where the risk of blight to the crop increases. At these times land managers will spray additional PPP to combat the risk. In the case of potatoes in Ireland this is commonly the fungicide a.i. chlorothalonil. PPP are preferably applied in the evening when the strength of sunlight is reduced because the pesticide may volatilise and be rendered less effective. There is also the risk of the crop being burnt if the PPP remains on the leaves and then reacts with sunlight damaging the leaf. Land managers also will not apply during rainfall since the compound will leach

through the soil and not be effective as it does not remain at the point of application (leaves and root zone).

2.4 Chapter 2 conclusions

Pesticides are used around the World for numerous applications and are indispensable in modern agriculture. However, their use has environmental consequences which were highlighted by Carson (1962). Many of the compounds mentioned by Carson (1962) have since been removed from the market owing to their persistence and toxicity such as heptachlor and DDT. They have been replaced with more modern compounds with higher solubilities (phenoxyacid and phenyl urea herbicides) and compounds which are more specialised in affecting their target. However, even modern pesticides can be dangerous. For example 2,4-D has been classed as an endocrine disruptor (McKinlay *et al.*, 2008). The risks associated with pesticide use are controlled by several pieces of legislation such as the Sustainable Use of Pesticides Directive (2009/128/EC) and regarding pesticide risk to groundwater, the Drinking Water Directive (98/83/EC) and the WFD (2000/60/EC). However, pesticides are still being detected in groundwater across the World, or at least in those with established monitoring for a wide range of substances. In Ireland very little monitoring and research has been undertaken on pesticide occurrence in Irish groundwaters. This thesis aims to target agricultural areas which are under the influence of diffuse pressures, taking into consideration the many complex processes affecting pesticide leaching to groundwater. In order for pesticides to enter groundwater they are subject to many processes from their original site of application. Pesticides are greatly influenced by the soil type especially its organic and clay mineral content, which will affect how a pesticide can sorb to the soil. However, this sorption varies among each pesticide and among each particular soil type which complicates pesticide leachability and makes it very specific for each location and pesticide. Pesticides can also sorb to material in the Quaternary deposits and within the aquifer such as humic acids. Pesticides may also sorb to colloidal material in the soil and Quaternary deposits. These colloids can rapidly get transferred in the aquifer and through preferential flow pathways and artificial drainage networks. Preferential flow pathways and drainage ditches are particularly common in fine grained, heavy soils. The complex nature of pesticide leaching from applications at the ground surface to groundwater means that assessing areas more susceptible to pesticide contamination must take into consideration all the processes which may occur.

CHAPTER 3

ANALYSIS OF NATIONAL – SCALE GROUNDWATER PESTICIDE OCCURRENCE[‡]

3.1 Introduction

This chapter aims to compare the attributes of a monitoring points (MPs) zone of contribution (ZOC) to pesticide occurrences in groundwater sampled at one of 158 MPs across Ireland sampled up to seven times during a two-year monitoring campaign by the Environmental Protection Agency (EPA). As of yet no one has used ZOC characteristics to help predict pesticide presence in groundwater to highlight areas prone to pesticide contamination. This study aims to add a new dimension to characterising pesticide leaching to groundwater by identifying the ZOC physical attributes that are most associated with groundwater pesticide occurrence. This chapter aims to determine which physical site characteristics are most associated with detections of active ingredients (a.i.s) in a range of groundwater sampling points across the Republic of Ireland using available data from the EPA groundwater monitoring program. Physical site characteristics were taken from available national datasets and used in conjunction with ZOC boundaries, instead of the arbitrary and potentially misleading use of a buffer zone around a MP. Those characteristics least associated with detections in groundwater are also stated. A summary of the EPA 2007-2008 groundwater monitoring programme for a.i.s is also given in relation to the most frequently detected a.i.s and the proportion of MPs with detections. The combination of national datasets and ZOCs may help inform decision making to protect groundwater bodies used for drinking water in other countries with similar datasets. This chapter aims to contribute to fulfilling objective 4 and 5 in Chapter 1.

[‡] This chapter is the basis for a paper submitted for publication in the Journal of Environmental Monitoring and Assessment in March 2013 as: Sarah-Louise McManus, Karl G. Richards, Jim Grant, Anthony Mannix, and Catherine E. Coxon 'Pesticide occurrence in Ground Water and the factors contributing to these detections in Ireland'.

3.2 Materials and methods

3.2.1 EPA network summary and sample analysis

The EPA is the designated body responsible for monitoring and reporting groundwater quality and levels in Ireland. The EPA national groundwater monitoring network was established in 2006 as part of the implementation of the WFD 2000/60/EC (European Parliament, 2000) as described by the EPA (2006) and Daly (2009). The network was designed to be representative of the variation in hydrogeology and pressures across a groundwater body or group of groundwater bodies (Craig *et al.*, 2005). The network was used to obtain groundwater samples that can be used to characterise groundwater quality nationally and to determine trends and groundwater body status. Many of the MPs in the monitoring network are public or private drinking water supplies with relatively large abstraction rates, or springs with relatively large discharges. These were targeted because the water quality from their relatively large ZOC is less likely to be impacted by localised pressures (Craig *et al.*, 2005). It may be noted that no Irish groundwater supplies have been withdrawn because of pesticide exceedances; therefore the use of water supplies at MPs should not introduce a bias into the dataset.

Monitoring began in 2007 with samples taken as part of the national groundwater programme in the two year period 2007-2008 used. 158 MPs were sampled between one and nine times during the campaign (arithmetic mean 5.4; median 6). Representative samples were collected using standard methods. Samples were kept at 4°C and transported to an ISO 17025:2005 accredited external laboratory where 13 pesticide a.i.s were analysed within seven days. For solid phase extraction (SPE) 2.5L of groundwater was loaded at 2 ml/min through a Biotage C18 (Uppsala, Sweden) SPE cartridge conditioned using 5 mls of liquid chromatography (LC) grade dichloromethane, left to dry for 10 mins, and then further conditioned using 2 x 5 mls aliquots of LC grade methanol. Compounds were eluted from the cartridge using 10 mls of dichloromethane and blown down under Argon at 30°C. Quantification was carried out using an Agilent gas chromatogram mass spectrometer (GC-MS) in electron ionization (EI) mode. Total GC-MS run time per sample was 45 mins. Calibration ranged from 0 – 0.2 µg/L with eight points across the calibration and used the internal standards acenaphthene D-10 and chrysens D-12. The 13 pesticides analysed are detailed in **Table 3.1** along with their current registration status in Ireland in 2007.

3.2.2 Zones of Contribution (ZOCs)

Each MP was given a ZOC, defined as the catchment area that contributes water to the MP (Misstear *et al.*, 2009) which supports an abstraction from long-term groundwater recharge. Each MP used for EPA monitoring had a ZOC delineated around it in a previous study (Kelly, 2010), and these ZOCs were utilised for spatial analysis in the present study. ZOC delineation was beyond the scope of this doctoral study and was not carried out as part of this work. ZOC delineation for each MP allows examination of the land use pressures, and geological and hydrogeological characteristics that influence the concentration of dissolved substances in groundwater. There are various methods for determining a ZOC, ranging from an arbitrary fixed radius to numerical modelling. Hydrogeologically mapped ZOCs are preferred over arbitrary radii around a MP, since the latter generally do not adequately characterise the pressures and pathways contributing to the concentrations measured at a MP (Franzetti and Guadagnini, 1996; Lim *et al.*, 2010), especially in heterogeneous environments.

ZOC delineation around MPs by Kelly (2010) was based on the principles developed for Irish groundwater source protection zones (DELG/EPA/GSI, 1999). For some EPA MPs, detailed hydrogeological mapping was undertaken to delineate ZOCs. For the majority of MPs, however, a simpler and more rapid, generally 'desk-based' approach was used to delineate ZOCs, with advisory input, and field investigations for certain groundwater abstraction points where necessary (Fitzsimons *et al.*, 2005). ZOCs were drawn in GIS with a tool developed by the Irish EPA (Kelly, 2010), using datasets of recharge (Hunter-Williams *et al.*, 2011) and abstraction. The default ZOC shape is a typical well head protection area 'bullet' shape. Examples of ZOCs used in the study are given in **Figure 3.1**. In the majority of Irish aquifers, groundwater is unconfined and the water table is generally a subdued reflection of topography (Fitzsimons *et al.*, 2005). Therefore, the ZOC is automatically aligned with the topographic gradient (Kelly, 2010). A rapid water balance calculation for the ZOC was determined interactively within the GIS tool using the groundwater recharge and abstraction rate data. The water balance compares the annual volume of water recharging the aquifer over the area of the ZOC with the annual abstraction volume (Kelly, 2010). For the ZOC delineated around a MP to represent the catchment that sustains long-term abstraction, the values should be similar. To determine the area of the ZOC needed to sustain the MP abstraction, the abstraction rate (m^3/day) is divided by the average daily recharge rate

Table 3.1 Pesticides quantified during monitoring, their registration status in Ireland in 2007 and use. CAS = Chemical Abstracts Service.

Name	CAS name	CAS number	Registration status	Use
2,4-D	(2,4-dichlorophenoxy)acetic acid	94-75-7	active	Herbicide
Atrazine	6-chloro- <i>N</i> -ethyl- <i>N'</i> -(1-methylethyl)-1,3,5-triazine-2,4-diamine	1912-24-9	banned 2007	Herbicide
Bentazone	3-(1-methylethyl)-1 <i>H</i> -2,1,3-benzothiadiazin-4(3 <i>H</i>)-one 2,2-dioxide	25057-89-0	active	Herbicide
Chlorotoluron	<i>N'</i> -(3-chloro-4-methylphenyl)- <i>N,N</i> -dimethylurea	15545-48-9	banned 2006	Herbicide
Cypermethrin	cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	52315-07-8	active	Insecticide, veterinary treatment
DDT	1,1'-(2,2,2-trichloroethyldiene)bis[4-chlorobenzene]	50-29-3	banned 1981	Insecticide
Dieldrin	(1 <i>aR</i> ,2 <i>R</i> ,2 <i>aS</i> ,3 <i>S</i> ,6 <i>R</i> ,6 <i>aR</i> ,7 <i>S</i> ,7 <i>aS</i>)-rel-3,4,5,6,9-hexachloro-1 <i>a</i> ,2,2 <i>a</i> ,3,6,6 <i>a</i> ,7,7 <i>a</i> -octahydro-2,7:3,6-dimethanonaphth[2,3- <i>b</i>]oxirene	60-57-1	banned 1981	Insecticide
Diuron	<i>N'</i> -(3,4-dichlorophenyl)- <i>N,N</i> -dimethylurea	330-54-1	banned 2009	Herbicide, biocide
Glyphosate	<i>N</i> -(phosphonomethyl)glycine	1071-83-6	active	Herbicide
Isoproturon	<i>N,N</i> -dimethyl- <i>N'</i> -[4-(1-methylethyl)phenyl]urea	34123-59-6	active	Herbicide
Lindane	(1 <i>α</i> ,2 <i>α</i> ,3 <i>β</i> ,4 <i>α</i> ,5 <i>α</i> ,6 <i>β</i>)-1,2,3,4,5,6-hexachlorocyclohexane	58-89-9	banned 2001	Insecticide, acaricide
MCPA	(4-chloro-2-methylphenoxy)acetic acid	94-74-6	active	Herbicide
Mecoprop	2-(4-chloro-2-methylphenoxy)propanoic acid	7085-19-0	active	Herbicide

(m/yr/365). To determine the optimal ZOC with the GIS tool, the ZOC polygon requires manual alignment - to honour hydrogeological controls on the orientation, and scaling - to match abstraction with recharge. As such, the ZOCs represent a relatively robust, but rapidly derived, spatial estimate of the region contributing groundwater flow to a MP (Kelly, 2010).

3.2.3 Dataset assembly for statistical analysis with corresponding zones of contribution

The dataset was categorised into three levels based on the detected pesticide concentration found at each MP. This approach was required because of the extremely high level of censoring in the data set due to analytical limits of detection (LOD). Kayhanian *et al.* (2002), Helsel (1987; 1990; 2006) all note that data sets with non-detects should not have non-detect values substituted by another numerical value as it may lead to errors in the statistical conclusions.

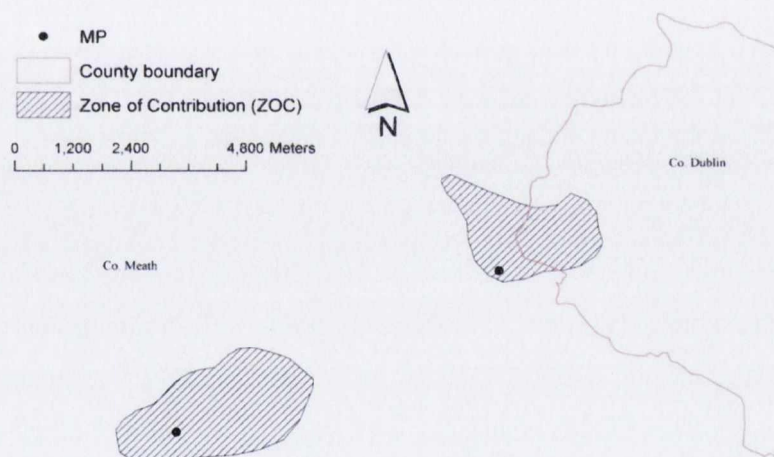


Figure 3.1 Examples of zone of contribution (ZOC) boundaries for two monitoring points (MPs) in Co. Meath.

Such an un-recommended approach was adopted by Finizio *et al.* (2011) and Worrall *et al.* (2002) where samples with concentrations below the LOD were given a concentration value of half the LOD or given a value of zero, respectively. In our study, non-detects were treated as such and because of this, standard statistical methods for continuous data could not be applied. The concentration category levels were chosen with reference to the EU DWS(i). For every compound the LOD was 0.01 µg/L and this was unadjusted for all

data analysis. Unadjusted detection frequencies maximize the ability to track the movement and fate of individual pesticides in groundwater because every detection is included with no loss of information (Kolpin *et al.*, 1998b).

The concentration category levels that MPs were grouped into were:

1. MPs which never had a detection greater than or equal to the LOD of 0.01 µg/L during the two year monitoring period.
2. MPs with at least one detection greater than the LOD but less than the EU DWS(i)
3. MPs with at least one detection greater than or equal to the EU DWS(i).

The concentration level detected at each MP explained above, and the most widespread category for each physical characteristic in the MP's ZOC (explained below) was then collated to produce a combined dataset. This was used to generate count tables for statistical analysis in SAS (2004).

3.2.4 Physical characteristic national data set summary

The most prevalent ZOC physical characteristics for each MP were assigned using all available national datasets (**Table 3.2**). The datasets used were MP type (unpublished data from the EPA), for land use Corine Land Cover 2006 (European Environment Agency, 2011), soil association (Gardiner and Radford, 1980), soil drainage class (Bulfin *et al.*, 2002), Quaternary deposits (subsoil) (Fealy *et al.*, 2009), subsoil permeability (GSI, 2011), bedrock geology (GSI, 2008b), aquifer type (GSI, 2008a), and groundwater vulnerability (GSI, 2009).

MP type was taken from unpublished EPA groundwater monitoring data (2007 – 2008). The MPs were classified by the EPA as springs (Sp(s)), drilled boreholes (BHs), and wells. (Wells include sites known to be dug wells and sites where the well construction method is unknown).

Land use was taken from the Corine land cover dataset in 2006 (European Environment Agency, 2011) and categories within the entire Corine land cover dataset were amalgamated into a fewer number of categories (**Table 3.2**) so (1) there were enough observations for statistical analysis and (2) there were fewer categories to assist logistic regression.

Two national soil datasets are currently available and both were examined. These were the 1980 General soil map of Ireland in digitized GIS format which was used for the dominant soil type within each association given by Gardiner and Radford (1980). Soil association is not a soil classification category but rather a cartographic unit consisting of two or more soils, derived from the same parent material, which are associated on the landscape in a particular pattern. The dominant soil association in each ZOC was found and the principal soil type in that association was recorded. These nine amalgamated categories are listed in **Table 3.2**. The second soil national dataset used was the Irish Forest Soils project national map of IFS soil type for Ireland (Bulfin *et al.*, 2002) which shall hereafter be referred to as soil drainage class. The soil drainage class (IFS soil type) description combines several soil types to create a class based on the soils' drainage class with the nine amalgamated categories listed in **Table 3.2**.

Subsoils play a particularly important role in protecting underlying fractured bedrock aquifers in Ireland (Daly and Warren., 1998); subsoil is defined in the Irish hydrogeological literature as superficial unconsolidated deposits of Quaternary age, such as glacial, fluvial, and glacio-fluvial sediments, which cover most of the country's bedrock aquifers (Misstear *et al.*, 2009). Quaternary deposit type was subdivided using two methods, the first according to the type (genesis) and the second (subsoil acid/base) based on its reaction with 10% v/v hydrochloric acid to determine the calcium carbonate (CaCO_3) content. Both classifications are detailed by Fealy *et al.* (2009). Subsoil permeability was determined by the Geological Survey of Ireland (GSI, 2011) using the British Standards Institution BS 5930 system (1981) (Swartz *et al.*, 2003). Textural descriptions were made of each subsoil using plasticity, dilatency, density, compactness, and the presence of discontinuities (Misstear and Brown, 2008).

Bedrock geology was obtained from the GSI (1999) and contains bedrock units created by grouping bedrock formations and members based on their hydrogeological properties and other factors. Examples of Irish bedrock geologies are given in **Table 3.2**. The simplified bedrock geology map was also the foundation for the national aquifer type map which was generated through a desk study and analysis of field data following a system of bedrock aquifer classification (GSI, 2008a). This produced 11 aquifer types across Ireland of which two groupings were used for statistical analysis (**Table 3.2**). The grouping termed 'GSI aquifer importance' is a classification by the GSI of aquifers according to their importance at providing a source of water using a surrogate of transmissivity e.g. poor

aquifers, while the grouping termed 'WFD aquifer flow regime' is a classification of Irish aquifers for the WFD based on their flow regime e.g. intergranular aquifers.

Groundwater vulnerability in Ireland is determined primarily according to the thickness and permeability of the subsoil. The GSI also use recharge type (whether point or diffuse) and the thickness of the unsaturated zone in the case of intergranular aquifers (Daly and Warren, 1998). In karstic areas recharge type is also considered since point recharge from solution features (e.g. swallow holes) are associated with extreme groundwater vulnerability (Misstear *et al.*, 2009). Categories are listed in **Table 3.2** in order of decreasing vulnerability. More detail can be found in section 2.1.5.

3.2.5 Statistical methods

For each MP the most prevalent category for each physical characteristic within its ZOC was recorded to generate count tables for input into SAS (2004). These tables of observational data were analysed using the categorical data analysis procedures of SAS (2004). Tables were generated using the three concentration level categories listed above with an emphasis on answering a priori questions. All statistical results have been given with 95% confidence intervals ($p \leq 0.05$).

Fisher's Exact Test (Agresti, 2002), a non-parametric test, was used for the analysis of the summary data tables as the low counts caused by non-detects in a large proportion of the cells made a chi-square test unreliable. The analysis was carried out using the Proc Freq procedure in SAS (2004) using the Monte-Carlo approximation for larger tables.

Physical characteristics were deemed to be significantly associated with pesticide occurrence if the Fisher's Exact Test p value was < 0.05 . These significant associations were then further tested using logistic regression (Agresti, 2002) to determine which categories within the physical characteristic differed and which had the greatest likelihood of a pesticide detection to enable comparisons. Worrall and Kolpin (2004) and Malaguerra *et al.* (2012) state that logistic regression is the most appropriate technique for predicting a binary outcome from continuous explanatory variables. In order for logistic regression to perform stably and accurately, large numbers of individual categories within each physical characteristic with an association from Fisher's Exact Test had to be collapsed into a smaller number of categories. To avoid numerical problems in the regressions, logistic regression was carried out on a dichotomised form of the tables with only two

Table 3.2 National datasets for physical characteristics selected for the prediction of groundwater pesticide occurrence and categories for each characteristics subsequent associations within each category.

MP type	Corine Land Cover 2006 ¹		Soil Type		Quaternary deposits (subsoil)			Bedrock geology ⁶	Aquifer type ⁵		Groundwater vulnerability ⁵
	Land use II	Land use III	Soil type ^{2†} (soil association)	Soil drainage class ^{3‡} (IFS soil type II)	subsoil genesis ⁴	subsoil acid/base ⁴	subsoil permeability ⁵		GSI aquifer importance	WFD flow regime	
spring	1. Agriculture (non-irrigated arable land and pasture)	1. arable (non-irrigated arable land)	acid brown earth	Deep well drained mineral	Alluvium	Acidic	High	e.g. limestone and calcareous shale	poor aquifers	poorly productive fissured bedrock	Exposed (X)
drilled borehole	2. forestry (broad leaved forest, coniferous forest, mixed forest, and transitional woodland scrub)	2. non-arable (pasture)	blanket peat	Shallow well drained mineral	Peat	Alkaline	Low	e.g. granite	locally important aquifers	karstic	Extreme (E)
well	3. Other land use (natural vegetation, urban land use, bare rocks, mineral extraction sites, and peat bogs)	3. forestry (broad leaved forest, coniferous forest, mixed forest, and transitional woodland scrub)	brown podzolic	Deep poorly drained mineral	Gravels		Low-high	e.g. upper basalt information	regionally important aquifers	productive fissured bedrock	High (H)
		4. Other land use (natural vegetation, urban land use, bare rocks, mineral extraction sites, and peat bogs)	degraded brown podzolic	Shallow poorly drained mineral	Irish sea tills		Low-low	e.g. pale-grey massive limestone		intergranular	High-low (H-L)*
			gley	Poorly drained mineral soils with peaty topsoil	Karstified rock		Medium	e.g. rhyolite			Moderate (M)
			grey brown podzolic	Shallow, lithosolic or podzolic type soils potentially with peaty topsoil	Tills		Medium-high				Low (L)
			minimal grey brown podzolic	Alluvium			Medium-low				
			rendzina and outcropping rock	Peats			M/L*				
			shallow brown earth	Miscellaneous							

¹ European Environment Agency (2011)² Gardiner and Radford (1980)³ Bulfin *et al.* (2002)⁴ Fealy *et al.* (2009) and GSI (2011)⁵ GSI (2011)⁶ GSI (1999)

† Dominant soil type for each association in each ZOC

‡ Amalgamation of categories listed by Bulfin *et al.* (2002) into a fewer number for input into statistical analyses

* Where incomplete vulnerability or permeability was assigned an 'interim' classification

concentration level categories: detections and non-detections. Proc Logistic in SAS (2004) was used for the analysis, and where quasi-complete separation occurred in the model-fitting process, Firth bias correction (Firth, 1993) or exact logistic regression was used. The estimate of the odds ratio has also been stated and the 95% Wald confidence intervals estimate of this odds ratio. The odds ratio shows the strength of association between the predictor and the response while the Wald confidence intervals give a range of likely outcomes for future observations. Statistical tests of various sub-groupings of the data set are intended to be interpreted in an exploratory sense and are not adjusted for the multiplicity of tests carried out. The sequence of method steps for identification of physical characteristics most associated with pesticide detections in groundwater is summarised in **Figure 3.2**.

3.3 Results

3.3.1 Frequency of occurrence in groundwater

Of the 845 samples analysed, 73% had no detection of any pesticide, 24% had detections greater than the LOD but less than the EU DWS(i), and 3% of samples had at least one detection greater than or equal to the EU DWS(i). The percentage frequency of occurrence from the national groundwater pesticide dataset (**Figure 3.3**) shows the most common pesticides detected during monitoring in 2007 and 2008, with the number of detections for each pesticide expressed as a percentage of the total number of samples analysed for that particular pesticide. Nationally, MCPA and mecoprop were the most frequently observed pesticides in groundwater samples, being found in 9.5% and 9.1% of samples, respectively. The EU DWS(i) was exceeded for MCPA and mecoprop in 0.71% and 0.83% of samples, respectively. All bentazone detections (0.47% of samples, or four detections) exceeded the EU DWS(i), even though the analytical detection limit was 0.01 µg/L. Three priority substances: atrazine, isoproturon, and diuron (European Parliament, 2008) were analysed for during monitoring. Atrazine and isoproturon were present in 1.3% and 0.12% of all samples, respectively but were under the EU DWS(i). Diuron was detected in 0.47% of samples, with one detection (0.12%) being greater than the EU DWS(i). Lindane, glyphosate, and 2,4-D were also included for analysis and were found in detectable concentrations with only glyphosate and 2,4-D having detections greater than or equal to the EU DWS(i). Lindane was present in detectable quantities in 3.67% of all samples, glyphosate was found in 1.78% of all samples with four detections exceeding the EU DWS(i) (0.47% of all samples). 2,4-D was in 0.95% of all samples with three detections

exceeding the EU DWS(i) (0.36% of all samples). Samples were analyzed for chlorotoluron, dieldrin, DDT, and cypermethrin but no detections greater than the LOD were observed for these four compounds.

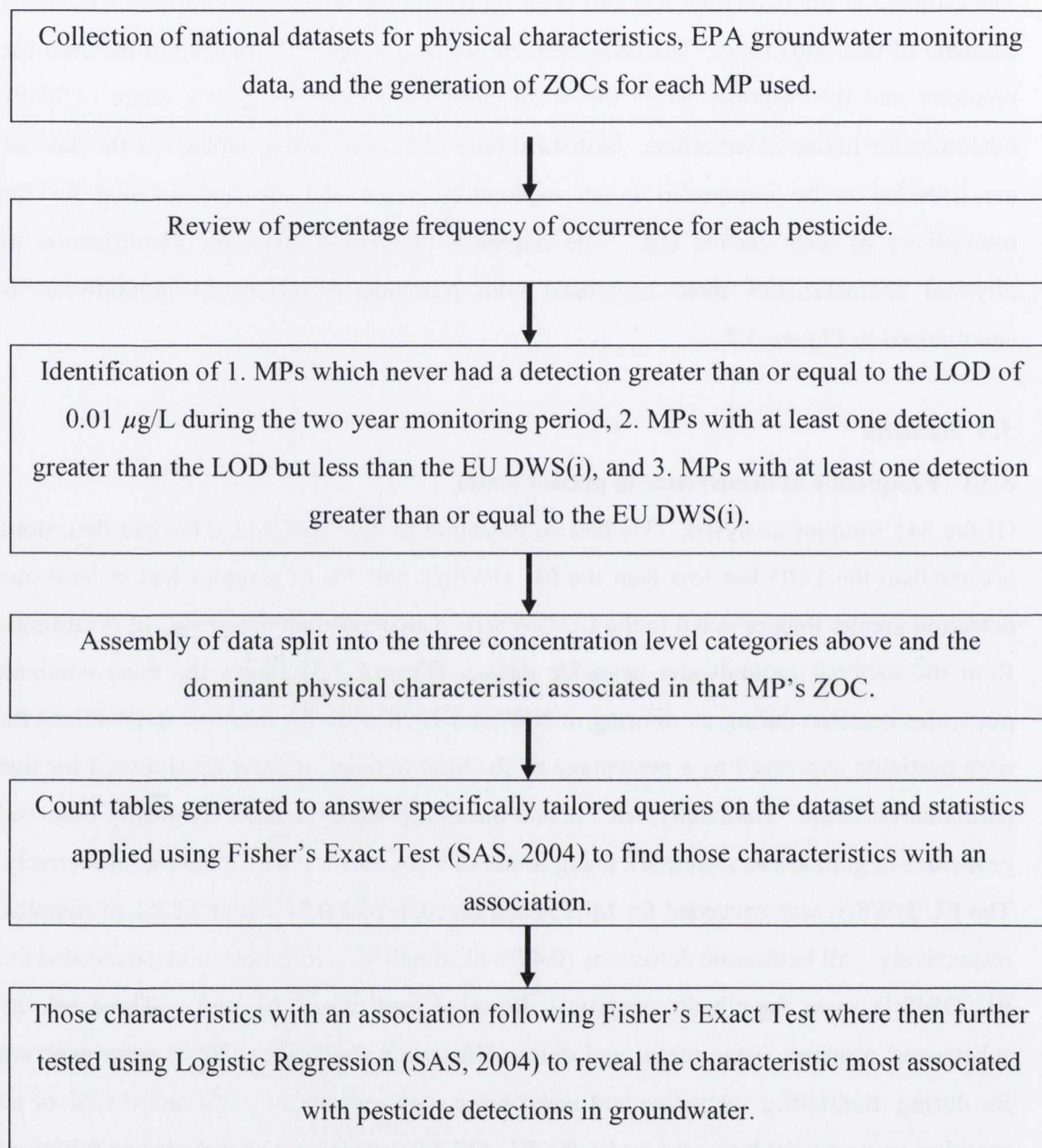


Figure 3.2 Sequence of work undertaken to allow for the assessment of ZOC physical characteristics and pesticide detections in groundwater.

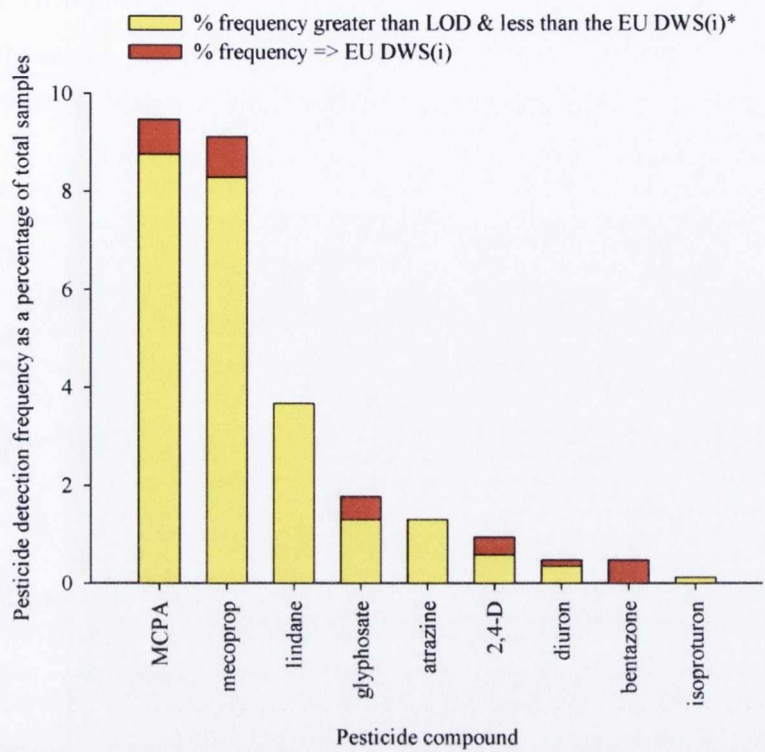


Figure 3.3 Frequency of pesticide detections as a percentage of the total number of samples analysed for a particular pesticide compound from the 2007 – 2008 EPA groundwater monitoring dataset: n = 845. Values are adjusted to each compound’s limit of detection (LOD) of 0.01 µg/L. The Council Directive 98/83/EC drinking water standard (EU DWS(i)*) is 0.1 µg/L.

When positive detections were expressed as a function of the total number of MPs sampled during the campaign, 47.5% of MPs had no detection, 40.5% of MPs had one or more detections greater than the LOD but less than the EU DWS(i), and 12% of MPs had a detection greater than or equal to the EU DWS(i) on at least one sampling occasion. No samples processed during the monitoring campaign exceeded the 0.5 µg/L EU DWS(t) limit set for total pesticides in any one sample. **Figure 3.4** indicates MPs which did not have a pesticide detection throughout the course of monitoring during 2007 – 2008, MPs that had a pesticide detection greater than or equal to the EU DWS(i), or MPs that had a detection greater than the LOD but less the EU DWS(i). **Figure 3.5** shows the geographical spread of the four most commonly detected individual pesticides. MCPA and mecoprop were the most commonly encountered pesticides at MPs with 39% and 36 % of MPs having at least one detection of these compounds, respectively. Lindane was present

in 17% of MPs and glyphosate at 8%. The percentage of MPs with detections for each of the other individual compounds which are not shown in **Figure 3.5** was 6% for atrazine, 4% for 2,4-D, 3% for bentazone and diuron, and 0.6% for isoproturon.

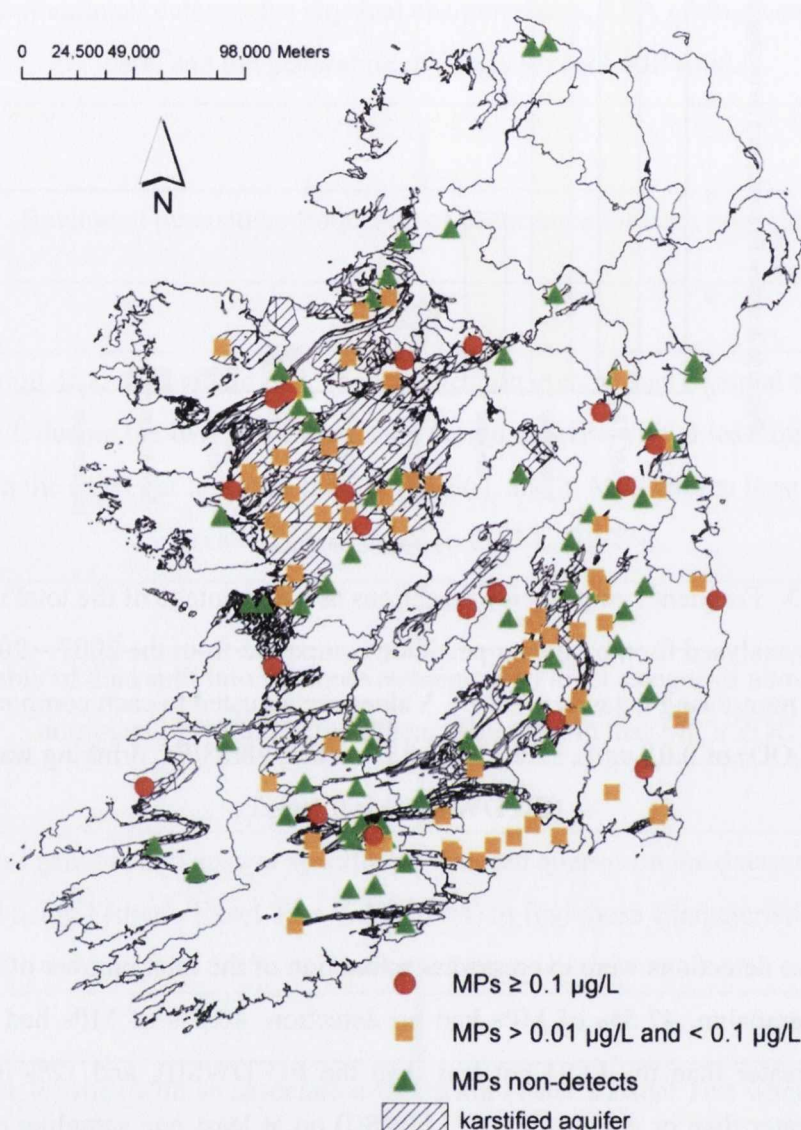


Figure 3.4 Monitoring points (MPs) with detections exceeding the European Union Drinking Water Standard for individual compounds (EU DWS(i)), MPs with detectable detections of pesticides, and MPs which never had a pesticide detection throughout the two year monitoring campaign.

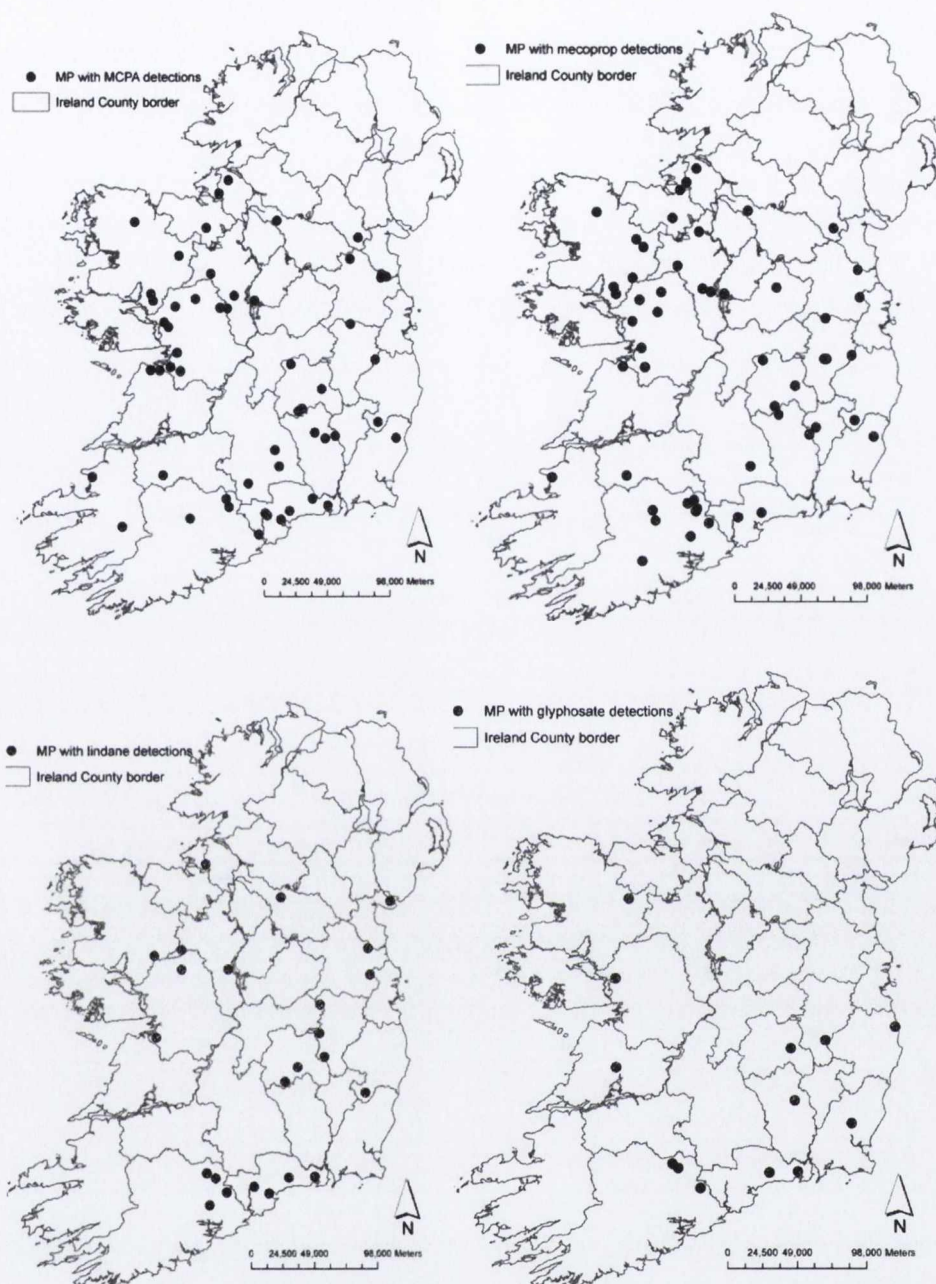


Figure 3.5 Monitoring points (MPs) with detections greater than the limit of detection for MCPA, mecoprop, lindane, and glyphosate on at least one occasion.

3.3.2 Statistical analysis of occurrence with zone of contribution properties

This EPA data set is a sample of convenience. Since it was not truly random there is the possibility that there is some unquantifiable bias associated with it. However, given the large size and wide coverage of the data set, it is the authors' opinion that it is informative

and can be used effectively to examine relationships in a purely exploratory manner. Formal inferences using Fisher's Exact Test and logistic regression can be regarded as indicative of relationships for future investigations.

Fisher's Exact Test

Pesticide detections in groundwater were found to be significantly related to five of the physical characteristics present in each MP's ZOC (**Table 3.3**). Some of the original physical characteristic national datasets were further amalgamated into a fewer number of categories (**Table 3.2**). 13 datasets and their variations showed no significant relationship with pesticide detections in groundwater while pesticide detections were significantly associated with aquifer type (all 11 aquifer types) ($p=0.0001$), MP type ($p=0.0080$), subsoil acid/base ($p=0.0101$), soil drainage class ($p=0.0116$), and subsoil type (Quaternary deposits **Table 3.2**) ($p=0.0260$).

Logistic regression

Following Fisher's Exact Test, the five physical characteristics with a significant degree of association were tested using logistic regression. The results indicate that springs are more likely to have a pesticide detection followed by wells, and then closely followed by BHs ($p=0.0028$) (**Figure 3.6**). Odds ratio comparisons indicate that a pesticide detection in a Sp. MP, compared to a BH, is 3.6 times more likely (significant, 95% confidence interval is 1.72 – 7.69). With a detection in a Sp. compared to a well 3.2 times more likely (significant, 95% confidence interval is 1.11 – 9.24).

With aquifer types split according to their GSI classification based on aquifer importance, the output revealed (**Figure 3.6**) that there is a greater likelihood of a detection in a regionally important aquifer compared to a locally important aquifer or a poor aquifer ($p=0.0007$). Odds ratio comparisons indicate that a pesticide detection in a regionally important aquifer compared to a locally important aquifer is 4.33 times more likely (significant, 95% confidence interval is 1.92 – 10). Further odds ratio comparisons indicate that a pesticide detection in a regionally important aquifer compared to a poor aquifer is 4.09 times more likely (significant, 95% confidence interval is 1.3 – 12.5).

The 11 aquifer types were also classified using the Irish system of flow regime used for the WFD (**Table 3.2**; **Figure 3.6**). In descending order of probability of a pesticide detection in groundwater were karstic aquifers > intergranular > productive fissured bedrock >

poorly productive fissured bedrock aquifer types ($p=0.0002$). Odds ratio comparisons indicate that a detection in a karstic aquifer compared to a poorly productive fissured aquifer is 5.62 times more likely (significant, 95% confidence interval is 2.63 – 11.1). Further odds ratio comparisons indicate that a detection in an intergranular aquifer compared to a poorly productive fissured aquifer is 3.35 times more likely (significant, 95% confidence interval is 1.99 – 0.84).

An association was found between subsoil type and groundwater pesticide detections using Fisher's Exact Test ($p=0.0260$) using the 69 subsoil types according to Fealy *et al.* (2009). The suite of subsoil types had to be amalgamated into a fewer number of categories to assist logistic regression and these new categories input into Fisher's Exact Test prior to logistic regression. Splitting subsoil type into six categories (subsoil genesis; **Table 3.2**) revealed no association ($p=0.1820$) using Fisher's Exact Test thus no further logistic regression was performed. However, there was a significant ($p=0.0101$) association between subsoil chemistry (subsoil acid/base) (Fealy *et al.*, 2009) and groundwater pesticide detections using Fisher's Exact Test. Logistic regression on this subsoil classification revealed that there was a significantly ($p=0.0048$) greater chance of a pesticide detection in an alkaline subsoil type compared to an acid subsoil (**Figure 3.6**). The odds ratio estimate indicated that a pesticide detection is 2.47 times more likely with an alkaline subsoil type than an acidic (significant, 95% confidence interval is 1.31 – 4.54). The greater potential for pesticide detection in alkaline subsoils relates to the correlation between alkaline subsoils and karst aquifers. When karst aquifer types were removed from the dataset, Fisher's Exact Test found no association between detections in groundwater and whether the subsoil was alkaline or acidic ($p=0.3074$).

Although Fisher's Exact Test indicated an association between pesticide detections in groundwater and soil drainage type II (IFS soil type II) using Fisher's Exact Test ($p=0.0095$), logistic regression on this classification indicated that there was no further statistically significant relationship within the nine categories listed in **Table 3.2** ($p=0.1069$).

Table 3.3 Statistical analysis p values for Fisher's Exact Test and Logistic Regression. $p \leq 0.05$ infers there is an association between pesticide detections in groundwater and the physical characteristic or amalgamated category (in *italics*).

Physical characteristic	p value
Fisher's Exact Test	
<i>Aquifer type</i> [†]	0.0001
<i>GSI aquifer importance excluding karst aquifer types</i>	0.0013
<i>Monitoring point type</i> [†]	0.0080
<i>Soil drainage class II (IFS soil type II)</i> [†]	0.0095
<i>Subsoil acid/base</i> [†]	0.0101
<i>Soil drainage class (IFS soil type)</i>	0.0116
<i>Subsoil type</i> [†]	0.0260
Soil association (soil type) [†]	0.1061
Land use III excluding karst aquifers	0.1173
Bedrock geology [†]	0.1203
Land use II	0.1331
Subsoil genesis [†]	0.1820
Land use III excluding springs as MPs	0.2689
Groundwater vulnerability only for karst aquifers	0.2766
Land use III	0.2822
Subsoil type excluding karst aquifers	0.3074
Groundwater vulnerability [†]	0.4214
Subsoil permeability [†]	0.4634
Land use [†]	0.5489
Logistic Regression	
<i>WFD flow regime aquifer type</i>	0.0002
<i>GSI aquifer importance aquifer type</i>	0.0007
<i>GSI aquifer importance aquifer type excluding karst</i>	0.0030
<i>Subsoil (Quaternary deposits) acid/base</i> [†]	0.0048
<i>Monitoring point type</i> [†]	0.0080
Soil drainage class II	0.1069

[†]Fisher's Exact Test results for original physical characteristic datasets which were not amalgamated into a fewer number of categories.



Figure 3.6 Results from logistic regression based on (a) the type of monitoring point ($p=0.0028$), (b) aquifer type classified using the GSI classification system based on aquifer importance ($p=0.0007$), (c) aquifer type classified using the Irish system of flow regime adopted for the WFD ($p=0.0002$), and (d) acid versus basic subsoil as identified by their reaction with 10 v/v hydrochloric acid ($p=0.0048$).

3.4 Discussion

3.4.1 Frequency of occurrence in groundwater

MCPA and mecoprop were the most frequently detected pesticides in groundwater (**Figure 3.3**) with 9.5% and 9.1% of total samples containing these compounds. MCPA and mecoprop were also the most frequent pesticides to exceed the EU DWS(i) with 0.71% and 0.83% exceeding the EU DWS(i), respectively. MCPA and mecoprop are extensively used across Ireland in varying land uses (**Table 3.4**). Based on MCPA's low sorption and relatively high water solubility the herbicide is potentially mobile, especially in soils with low OC contents (Hiller *et al.*, 2006; Fredslund *et al.*, 2008). MCPA is not attenuated in deeper soil layers which renders it a threat to groundwater quality (Sørensen *et al.*, 2006) should it reach that far. Isoproturon never exceeded the EU DWS(i) during monitoring while bentazone was detected in 0.47% of all samples with all detections greater than or equal to the EU DWS(i). The LOD for both isoproturon and bentazone was 0.01 µg/L. It is interesting that so little bentazone was applied in comparison to isoproturon yet all four detections of bentazone (0.47% of samples) exceeded the EU DWS(i) (**Table 3.4**). Bentazone was also found by Loos *et al.* (2010) with 4% of samples exceeding the EU DWS(i) and 32% of samples having detections. Isoproturon had approximately 191 times the amount applied in Ireland in comparison to bentazone (**Table 3.4**), yet only one MP had a detection which was not above the EU DWS(i). Baran *et al.* (2008) also observed very few detections of isoproturon in France, even though isoproturon was the most widely applied pesticide: application timing may have been a contributing factor. Bentazone is more soluble in water at 25°C at 570 mg/L than isoproturon at 70 mg/L, and also more mobile with a partition coefficient (K_{OC}) of 51 L/kg compared to 122 L/kg for isoproturon (Coppola *et al.*, 2011). Both compounds are quite mobile but bentazone's higher solubility may be one of the reasons why it has been detected in more samples than isoproturon and at higher concentration levels.

Present day pesticide usage can not be the only contributing factor to pesticide occurrence in groundwater, with banned compounds also detected. Lindane, banned in 2001 (**Table 3.1**), was the third most frequently detected pesticide in groundwater. In contrast isoproturon, the fourth most commonly applied pesticide, was the least frequently detected (**Table 3.4** and **Figure 3.3**). Three compounds (atrazine, lindane, and diuron), banned between 2000 and 2008 (**Table 3.1**), were detected in groundwater during monitoring.

Neither chlorotoluron, cypermethrin, dieldrin nor DDT were detected in groundwater during EPA monitoring between 2007 and 2008. Lindane was removed from the Irish market for the longest amount of time prior to the start of monitoring but was the most frequently detected of the banned compounds. Previous studies found lindane to be ubiquitous in environmental waters such as in Portugal where 53% of groundwater samples analysed contained lindane (Gonçalves *et al.*, 2007), which was attributed to lindanes moderate to high persistence with a half-life ($t_{1/2}$) of 191 days and a water solubility of 7.3 mg/L. Lindane was also detected in a study by Batista *et al.* (2002) with 5% of groundwater samples from two agricultural areas monitored in Portugal having detections greater than the EU DWS(i) and a maximum observed concentration of 1.1 µg/L. The maximum concentration of lindane observed in this sampling campaign was lower at 0.03 µg/L with no detections exceeding the EU DWS(i).

Table 3.4 Total amounts of active ingredient applied to arable, and grassland & fodder crops in Ireland.

Pesticide (a.i.)	Grassland and fodder crops, 2003 (Pesticide Control Service, 2006)	Arable crops, 2004 (Pesticide Control Service, 2007b)	Total (kgs a.i.)
MCPA	221,883	10,012	231,895
glyphosate	93,056	116,731	209,787
mecoprop-p	74,598	112,058	186,656
isoproturon	349	107,852	108,201
mecoprop	21,761	8,992	30,753
atrazine	24,152	0	24,152
2,4-D	23,458	0	23,458
cypermethrin	73	2,274	2,347
bentazone	566	0	566
TOTAL	459,896	357,919	817,815

Atrazine and simazine, which were banned in 2007 and 2008 respectively, were historically used in road maintenance but have now been replaced with glyphosate and diuron in Ireland (Conroy *Pers. Comm.* 2011). In agriculture atrazine was solely used on maize with 24,152kgs applied in 2003. In non-agricultural situations atrazine was used

along with simazine for weed control in amenity areas, footpaths, road verges, and industrial areas. Atrazine was the fifth overall most frequently detected pesticide with 1.3% of all samples containing atrazine (**Figure 3.3**). Atrazine was banned in Ireland in 2007, coinciding with the commencement of the EPA groundwater pesticide monitoring programme. Atrazine's maximum observed concentration was 0.07 µg/L and no detections exceeded the EU DWS(i). Atrazine has also been frequently detected in other European groundwater studies (Croll, 1991; Batista *et al.*, 2002; Cerejeira *et al.*, 2003; Gonçalves *et al.*, 2007; Loos *et al.*, 2010). Most other monitoring programmes analyse for atrazine's TPs which tend to be found more frequently than the parent compound and often in absence of the parent compound (Spliid and Køppen, 1998; Gonçalves *et al.*, 2007). TPs should be considered for future monitoring campaigns not just in Ireland but across the world, to help further understand their fate, transport, and persistence in the environment. Several of the phenoxyacid herbicide TPs have been classed as hazardous compounds in a report by Craig (2010) including 2,4,5-trichlorophenol (TCP), 4-chloro-2-methylphenol (4C2MP), and 2,6-dichlorophenol (DCP). These compounds have been classed as hazardous based on their toxicity to aquatic organisms, bioaccumulation potential, and persistence in the environment. Diuron banned in 2009 (**Table 3.1**) was extensively used in amenity, industrial areas, and non-crop areas in Ireland. Blanchoud *et al.* (2004) observed diuron in surface waters from French urban catchments and attribute its widespread presence due to impervious surfaces and private users unaware of appropriate application rates. Whether pesticides are used or not is a contributing factor to pesticide detections in groundwater although it is not the sole reason for detections since the frequency of detection (**Figure 3.3**) does not correspond with active or the time compounds were banned (**Table 3.1**). If pesticide use was the sole contributing factor then compounds such as isoproturon should have been detected more frequently than banned compounds such as lindane; yet the opposite is true. Kolpin *et al.* (1998b) stated that intensive pesticide use was necessary for pesticide detections in groundwater but was not the main cause. Other contributing factors such as physical characteristics the pesticide is subject to following application will affect its ability to maneuver to groundwater.

A wider range of pesticide compounds were observed in Irish surface waters compared to groundwater but as with groundwater, mecoprop, atrazine, and glyphosate were some of the most frequently detected compounds (McGarrigle *et al.*, 2010). In descending order of frequency of detection over the three years of surface water monitoring in Ireland the

following pesticide compounds were detected, with the approximate percentage of total samples with detections in brackets: simazine (35%), mecoprop (23%), atrazine (18%), glyphosate (15%), 2,4-D (7%), isoproturon (5%), and diuron (5%). The surface water monitoring programme did not analyze for MCPA or lindane, the more ubiquitous pesticides found in groundwater during this study.

3.4.2 Frequency of detections at monitoring points

Of the 158 MPs sampled during 2007-2008, 47.5% never had a pesticide detection greater than the analytical detection limit of 0.01 µg/L, while 40.5% of MPs had a detection greater than the LOD and less than the EU DWS(i), and 12% of MPs exceeded or equaled the EU DWS(i) on at least one occasion. Kolpin *et al.* (1998a) observed pesticides in 54.4% of 1,034 groundwater sites sampled across the United States, a similar percentage of detections observed in Ireland (52.5%). A detailed study in Iowa observed pesticides, above the analytical detection limit of 0.05 µg/L in 70% of wells sampled (Kolpin *et al.*, 1997). In Portugal, Batista *et al.* (2002) found 72% of the 79 sites studied had pesticide residues detected in groundwater. Within the positive detections, 40% of these sites had levels less than 0.1 µg/L, and 32% of sites had detections greater than 0.1 µg/L. In Ireland 40.5% of MPs had a detection less than 0.1 µg/L, and 12% of MPs had detections greater than the EU DWS(i). **Figure 3.4** displays the MPs which had either a detection greater than or equal to the EU DWS, a detectable detection, or never had a detection throughout monitoring. The cluster of detections in the West of Ireland corresponds to an area dominated by karst geology, alkaline subsoils, and where many of the MPs are springs – also highlighted during statistical analysis (**Figure 3.6**). For the four most frequently detected compounds their detections, as with **Figure 3.5**, centre in karst areas in the West and South. MCPA and mecoprop are much more widespread than the other pesticides.

3.4.3 Physical characteristics and detections

Aquifer type

Pesticide detections at MPs were tested in relation to aquifer transmissivity, using aquifer importance as a surrogate (GSI aquifer importance, **Table 3.2**). Regionally important aquifers were more likely to have a pesticide detection in groundwater than poor- or locally important- aquifer types ($p=0.0007$, **Figure 3.6**). From the GSI aquifer importance

category, karst aquifer types were removed from the count tables and re-analysed. Following this change there was still an association with pesticide detections in groundwater using Fisher's Exact Test ($p=0.0013$) (**Table 3.3**). Further logistic regression on this category revealed that regionally important aquifer types were still more associated with pesticide detections in groundwater, even with karst aquifer types removed. **Figure 3.7** shows the SAS output for logistic regression. Odds ratio comparisons indicate that a pesticide in a regionally important aquifer compared to a locally important aquifer is 5.78 times more likely (significant, 95% confidence interval is 2.04 – 16.39). Further odds ratio comparisons indicate that a pesticide detection in a regionally important aquifer compared to a poor aquifer is 4.38 times more likely (significant, 95% confidence interval is 1.23 – 15.62). Regionally important aquifers are capable of yielding water on a regional scale having a greater number, size, and connectivity of fractures and fissures within their lithology compared to locally important- and poor- aquifers (DELG/EPA/GSI, 1999). Regionally important aquifers have a transmissivity of approximately 200 m²/day and locally important aquifers approximately 20 m²/day (Fitzsimons *et al.*, 2005). In lower transmissivity aquifers, recharge may be filtered in the aquifer material more than in higher transmissivity aquifers. There may also be a higher chance of contact and longer contact with clay material in lower transmissivity aquifers. As a result, pesticides present in locally important and poor aquifers may be under the influence of more filtration and attenuation mechanisms, such as sorption, chemical reactions, and microbial degradation (Zipper *et al.*, 1998). These factors could contribute to lower groundwater pesticide concentrations in these aquifer types.

Within the WFD aquifer flow regime classification, karstic aquifers had the highest probability of having a pesticide detection ($p=0.0002$). These aquifers have rapid response times and long pathways with very high transmissivities of approximately 1,000 m²/day (Fitzsimons *et al.*, 2005), which could aid pesticide transport to groundwater with little time for attenuation or transformation. Karst systems are very heterogeneous with many having solution features that can act as easy access points for water containing pesticides to enter the groundwater below. Sinking streams, closed depressions, and limestone pavement (exposed limestone bedrock surfaces with little to no soil cover (Williams, 1966)) all allow direct access into the groundwater beneath, where water flows quickly through with little attenuation to outlets or springs (Lindsey *et al.*, 2010; Coxon, 2011). Irish Carboniferous limestone aquifers have negligible primary permeability so

groundwater flow is via solutionally widened fractures and cave conduits (Drew, 2008). Karst aquifers in which groundwater is transmitted through conduits (Rkc) can generally accept a significant quantity of recharge, because transmissivities are very high which can input more pesticides into the aquifer system as a result. Karst aquifers are mainly found in the West and North West of Ireland. Productive fissured aquifers are regionally important aquifers with flow through fissures which act as fluid pathways carrying with it diluted pesticides. The fractures are larger and more connected than those present in poorly productive fissured aquifers potentially allowing more movement of pesticides carried within in productive fissured aquifers. Intergranular flow aquifers, which in Ireland are generally composed of fluvioglacial sands and gravels, ranked second in their association with pesticide occurrence in groundwater (**Figure 3.6**). In a German study Milde *et al.* (1988) found that sand aquifers were very sensitive to groundwater contamination by pesticides but not to the same degree as karst areas, the same finding was also found through this study using physical characteristics within ZOCs. A confirmation that the method adapted works to reflect ‘real-life’ situations.

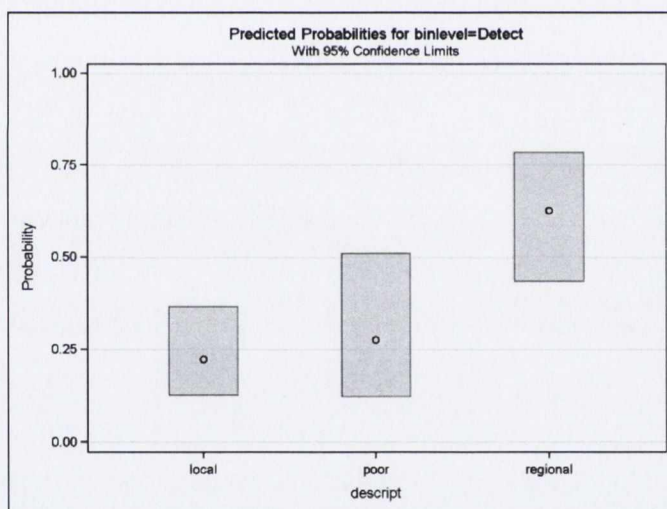


Figure 3.7 Results from logistic regression for GSI aquifer importance aquifer types with karst aquifer types removed from the count tables ($p=0.0030$).

Monitoring point type

Monitoring point type was associated ($p=0.008$) with groundwater pesticide detections, and springs used as sampling points were the most likely MP to have a pesticide detection followed by wells and finally BHs (**Figure 3.6**). A similar finding was found by Morris (2005) who identified springs draining fracture-flow aquifers as the most susceptible to *Cryptosporidium* contamination. In Ireland, 81% of Sp.s used as MPs during this

campaign had ZOCs dominated by karst aquifers composed of Carboniferous limestone. As explained above, point recharge present in karst systems, combined with conduit flow through the karst aquifer, does not allow much time for natural attenuation which may otherwise occur in non-karst systems. In Ireland, such karst Sp.s frequently serve as potable water sources. Wells as opposed to drilled BHs were found to be more associated with pesticide detections in groundwater (**Figure 3.6a**). Through a monitoring study by Melo *et al.* (2012) in Northern Portugal, more fungicides and insecticides above the limit of quantification (LOQ) were detected in dug wells compared to drilled wells.

Subsoil type

It is assumed the thicker the layer of subsoil, the less likely the pollutant will be able to travel to groundwater beneath. It was also anticipated that the matrix grain size will affect pesticide leaching based on its permeability. However, subsoil permeability tested using Fisher's Exact Test revealed no association with groundwater pesticide detections ($p=0.4634$). An association was found for subsoil type using Fisher's Exact Test ($p=0.0260$) but when these 69 subsoil types were grouped according to their genesis (six classes detailed by Fealy *et al.* (2009)) in **Table 3.3** no association was found ($p=0.1820$). Subsoil -type, -permeability, and -thickness were combined in the Irish groundwater vulnerability classification, and a relationship between pesticide occurrence and groundwater vulnerability class was anticipated, but no significant association was found ($p=0.4214$) (**Table 3.3**). Further groupings were made to the subsoil dataset with subsoils split according to their reaction with CaCO_3 (subsoil acid/base, **Table 3.2**). Pesticide detections were significantly related to alkaline subsoils using logistic regression ($p=0.0048$, **Figure 3.6**). However, karst areas have alkaline subsoils because the majority of limestone is overlain by glacial till derived from limestone and these areas tend to be more vulnerable such as through thinner overburdens. When karst aquifers were removed from the dataset and re-tested statistically no association was observed between alkaline subsoils and pesticide detections using Fisher's Exact Test (**Table 3.3**; $p=0.3074$).

Soil type and soil drainage class

Surprisingly no association was found when the original, ungrouped dataset of soil association ($p=0.1061$) was tested for pesticide detections in groundwater (**Table 3.3**). However, the other original soil physical characteristic dataset used, called soil drainage class (Bulfin *et al.*, 2002), did have an association ($p=0.0116$) using Fisher's Exact Test. This soil drainage class was amalgamated into soil drainage type II (**Table 3.2**; IFS soil

type II) and Fisher's Exact Test revealed an association (**Table 3.3**; $p=0.0095$). Further statistical analysis using logistic regression on soil drainage type II (IFS soil type II, **Table 3.2**) gave no significant association using Fisher's Exact Test ($p=0.1069$). The reason logistic regression was not able to uncover a relationship was due to low sample sizes between the two categories (detections Vs. non-detections among the categories listed in **Table 3.2** for soil drainage class). The majority of MPs were located on well drained soils with 32.3% of these MPs having a detection less than the EU DWS(i). 28.5% of MPs were on well drained soils which had no detection and 12% of well drained MPs had a detection greater than the EU DWS(i). The other 27.2% of MPs were located on varying soil drainage classes. Well drained soils were more likely to have a detection but this finding can not be confirmed statistically. An expected finding from the dataset was with peat soils. 6.7% of MPs were located on peat soils with only one MP having a detection, which was less than the EU DWS(i) inferring that peat soils in Ireland are not widely associated with pesticide detections in groundwater. Peat soils in Ireland would not be subject to routine pesticide application and tend to solely be managed for fuel (peat cutting) which requires negligible pesticide applications. Previous studies (Lapworth *et al.*, 2006) indicated that soil type was influential on pesticide transport to groundwater. Our results indicate that soil drainage class is more influential than soil type (amalgamation of soil associations in **Table 3.2**) when using large robust datasets in an exploratory manner to predict the physical characteristics which affect pesticide leaching to groundwater in a MP's particular ZOC.

The available soil association map used is crude and needs a further increase in resolution to include such soil characterisation parameters as soil texture, cation exchange capacity, OM, pH, and clay minerals. This may partly explain why soil association was not statistically significant. Adsorption of MCPA varies between soils and correlates with pH and the cation exchange capacity (Alister *et al.*, 2011). The lack of a statistically significant relationship between soil type derived from soil associations and groundwater pesticide occurrence may be due to the contrasting properties of the 13 pesticide compounds tested, with differences in their solubility and adsorption properties. Variation of soil and pesticide properties plus their interactions are complicated, as some pesticides are more likely to sorb to certain soils than others. The two most frequently detected pesticides in Irish groundwater in this study (MCPA and mecoprop) are both polar, negatively charged, anionic compounds with a high solubility in water. Because of their

negative charge they are less likely to be retained in the soil following application and can be transported with recharge to groundwater. The sorption and leaching potential of these herbicides varies considerably depending on soil type (e.g. OC content) and the amount of small pores (Celis *et al.*, 2005).

3.5 Chapter 3 conclusions

Pesticides were detected in 27% of samples, with MCPA, mecoprop, and lindane being the most frequently detected products. The EU DWS(i) was breached in 3% of samples. Pesticide compounds detected in groundwater were both banned and currently used, MCPA and mecoprop are widely used across Ireland and were detected in 9.5% and 9.1% of all samples, respectively. However, frequently used compounds such as isoproturon were detected less frequently than the banned compound lindane (banned six years prior to monitoring), suggesting that its not solely pesticide use and application controlling pesticide movement to groundwater. Other factors play a role and this study statistically determined aquifer type, MP type, and Quaternary deposit (subsoil) acid/base (as the physical characteristics, identified in each MP's unique ZOC) to be associated with pesticide detections in groundwater. Upon further analysis within each characteristic, Sp.s as MPs, alkaline Quaternary deposits (subsoils) in existence with karst aquifers, regionally important aquifers, and aquifers with a karstic flow regime were more associated with pesticide detections in groundwater. Methods used here should help guide policy makers to make decisions on the placing of pesticides on the market and highlight geographical areas susceptible to contamination. Banned compounds such as lindane and atrazine, which have a ubiquitous nature, should be monitored along with their TPs to record their depletion in the environment. This study improves conceptual understanding and assists in the assessment of groundwater chemistry through the interpretation of groundwater quality data: a fundamental requirement of the WFD and can be used in other countries with similar datasets to help differentiate the areas more prone to groundwater pesticide occurrences. The study of the characteristics of ZOC areas could help further indicate which areas are most susceptible to groundwater contamination.

CHAPTER 4

SITE SELECTION AND INTRODUCTION TO SITES

4.1 Introduction

4.1.1 Context

Once a pesticide is applied to an agricultural system, the compound has opportunity to reach unintended targets, which has been conceptually illustrated in **Figure 2.1**. Pesticides are formulated to be persistent for the duration of time it takes for them to cause a desired effect on their intended target, whether that is plant leaves, roots, or invertebrates in the soil. Their presence on the land surface following application is a source of pesticides in the environment, and a diffuse source of pesticides when they are applied to agricultural fields e.g. spring barley. The ultimate objective of this project is to indicate the characteristics of agricultural areas which have a source of diffuse pesticide application and which are more associated with pesticide detections in groundwater. To achieve this objective, sites had to be selected to 1) represent the physical characteristics in existence within Ireland (e.g. common soil types) and 2) have a range of contrasting characteristics which may affect groundwater pesticide occurrence. Worrall *et al.* (2002) indicate that the role physical properties play on the site of pesticide application is a contributing factor in controlling the mobility of pesticides through soils to groundwater, and this contribution is essential in the risk assessment of their environmental fate. Combining results from the UK and US, Worrall *et al.* (2002) concluded that chemical and site factors both have a statistically significant influence on groundwater pollution; site factors such as land use, soil type, and aquifer type on their own explained a greater proportion of data variance than chemical factors alone. Taking this into consideration it was important to acknowledge all physical characteristics (**Table 4.1**) which may affect pesticide leaching to groundwater and also include chemical characteristics to supplement and achieve the objective of determining characteristics which are more associated with pesticide occurrence in groundwater than others.

4.1.2 Conceptual model

To aid understanding of how pesticides from diffuse agricultural sources can leach to groundwater a conceptual model was compiled using the source, pathway, and receptor model. The main source of pesticide pollution from diffuse agricultural sources would be pesticide application on arable land (e.g. spring barley) (see section 2.2.1). Some of the pathways involved from the source to the receptor include the physical characteristics a pesticide is exposed to following application (**Table 4.1**) and the hydrochemical variables which may influence pesticide attenuation. The receptor is groundwater which can be used as drinking water, contamination of which would be detrimental to human health following both acute and chronic exposure. Groundwater may discharge to surface waters so pesticides reaching groundwaters may also reach surface waters by this pathway (as well as by surface and near-surface pathways). **Figure 4.1** shows the conceptual model adopted during this project. Potential MPs are shown in **Figure 4.1** although not all these may be present at a chosen site (e.g. artificial subsurface drains and streams). This study is concerned with groundwater either sampled through BH installations or Sp.s. No Sp.s are shown on the conceptual model.

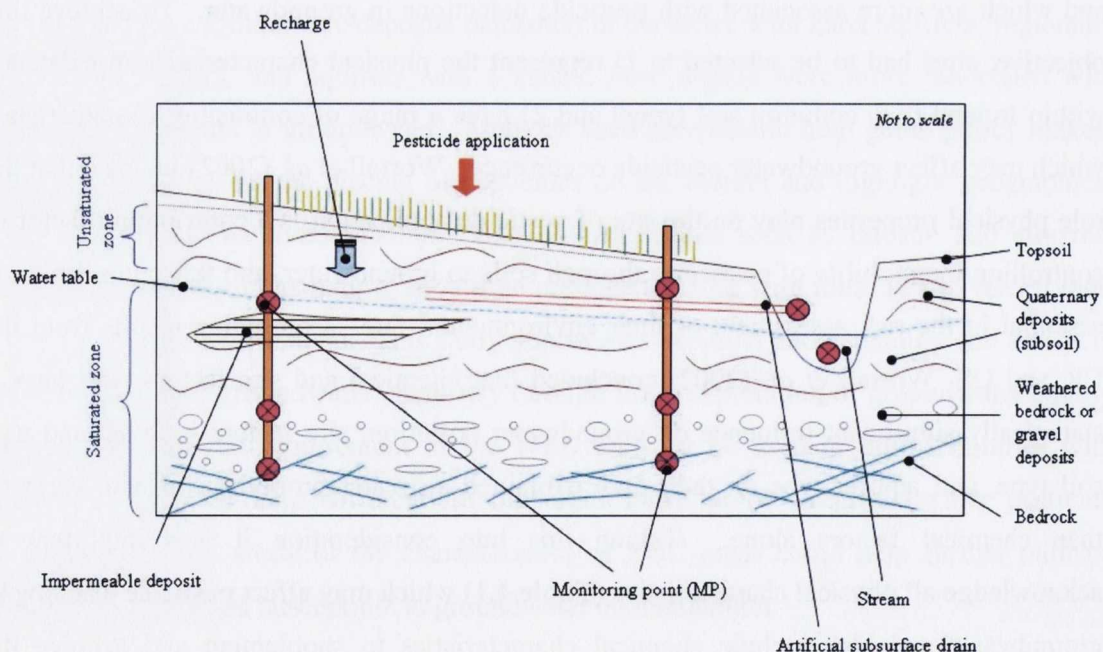


Figure 4.1 Hydrological conceptual model and potential sampling locations.

Table 4.1 Some physical characteristics which may affect pesticide leaching to groundwater and corresponding national datasets available in Ireland and their source used to assist in selecting suitable sites.

Physical characteristic	Nationally available dataset (source)
Land use	Corine Land Cover 2006 (European Environment Agency, 2011)
Soil type	General soil map 1980 of Ireland (Gardiner and Radford, 1980)
Quaternary deposit (subsoil) type	National subsoil type (Fealy <i>et al.</i> , 2009)
Subsoil permeability	Intrinsic subsoil permeability (GSI, 2011)
Aquifer type	National bedrock aquifer map 1:100,000 (GSI, 2008a)
Bedrock geology	National generalised bedrock map 1:100,000 (GSI, 2008b)
Groundwater vulnerability	National vulnerability map 1:50,000 (GSI, 2009)
Depth to bedrock	Borehole logs from the GSI and the national vulnerability map for exposed areas (GSI, 2009)

4.2 Methods used to select sites across Ireland

Initially national datasets listed in **Table 4.1** were acquired and the CORINE land cover (CLC) dataset for 2006 from the European Environment Agency (2011) was used to highlight arable land use across Ireland. Arable land is shown in **Figure 4.2** with arable land in Ireland dominated by the category; non-irrigated arable land e.g. spring barley, with a smaller fraction of land categorised as complex cultivation patterns e.g. orchard. Data collected in 2003 and 2004 by the Pesticide Control Service (PCS) indicates that arable cereal (e.g. spring barley) had the highest amount of a.i. applied at 1,049 tonnes a.i./yr with arable other second highest at 471 tonnes a.i./yr (PCS, 2007). For this reason the current project has focused mainly on arable land as the source of pesticide in agricultural areas. The main arable crop type in Ireland is spring barley with an average of 1,621,000 hectares sown between 2008 – 2010 (Central Statistics Office, 2011). In Ireland 17% of the total land area is under spring barley. A total of 398 tonnes/a.i. was applied to spring barley in 2004 (Pesticide Control Service, 2007a) and of this the main a.i. applied was mecoprop-p at 82 tonnes/a.i. Using ArcGIS 9.3 arable land was extracted from CLC 2006 and displayed as a separate GIS shapefile layer.

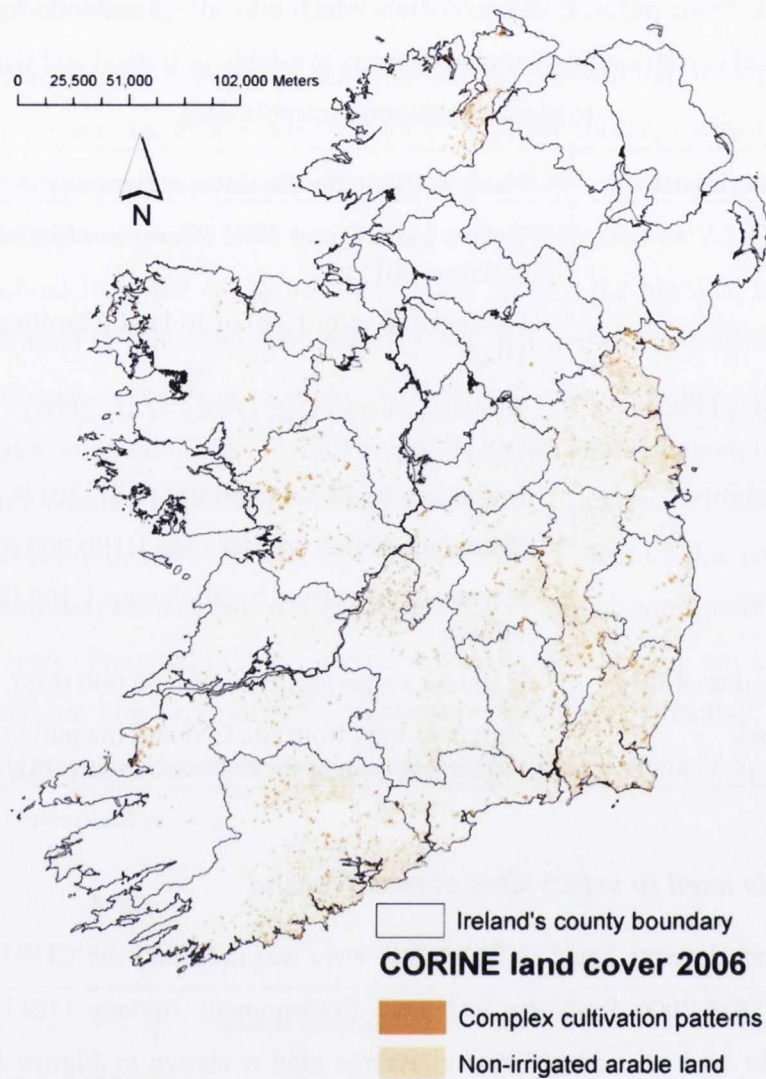


Figure 4.2 Arable land (non-irrigated arable and complex cultivation patterns) in Ireland from the CORINE Land Cover dataset in 2006 (European Environment Agency, 2011).

To extract only arable land from all land uses in the CLC 2006 shapefile, attributes for non-irrigated arable land and complex cultivation patterns were selected from the attribute table and these selected records exported to a new attribute table. Once arable land was located (**Figure 4.2**), other physical characteristics from the National datasets listed in **Table 4.1** which control pesticide movement to groundwater were loaded into ArcGIS 9.3. The general soil association map of Ireland 1980 (Gardiner and Radford, 1980) details principal soil types within mapped soil associations. The principal soil type, hereafter referred to as soil type, within the association was unionised together with the CLC 2006 layer for arable land and clipped to create a map with only soils displayed where arable

land use was present. Quaternary deposit, or subsoil, types were also unionised with arable land and clipped together to create a layer file which had all the subsoil types spatially projected together and excluded those subsoils which were not geologically located with arable land. The national bedrock aquifer map was then unionised and clipped with arable land use and the most common aquifer types associated with arable land recorded. Finally bedrock geology and groundwater vulnerability were unionised and clipped with arable land use in Ireland.

4.3 Site selection results

4.3.1 National physical characteristics results

The most common soil types associated with arable land use were acid brown earths, gleys, and grey brown podzolics (**Table 4.2**). In descending order of the most commonly found subsoil types associated with arable land were: gravels derived from limestones > gravels derived from lower Palaeozoic sandstones and shales > till derived from limestones > till derived from sandstones > Irish Sea tills. The most common aquifer type associated with arable land was regionally important fissured aquifers. **Table 4.3** details the areas the other aquifer types represent. The bedrock geologies most commonly associated with arable land were 1) granites and other igneous intrusive rocks, 2) Dinantian bedded limestones and 3) Dinantian lower impure limestones. All of the bedrocks found with arable land are mentioned in **Table 4.4** with their areas in Ireland represented where arable land exists. Groundwater vulnerability classes most associated with arable land were exposed followed by extreme and thirdly moderate vulnerability (**Table 4.5**). However, the groundwater vulnerability dataset was only available as an interim study at the time of writing so this order of importance may change as the dataset is updated.

Table 4.2 The principal soil types which are associated with arable land use and the area they represent in Ireland.

Soil association	Area (km²)
Acid brown earth	1,430.76
Gley	1,190.43
Grey brown podzolics	1,098.62
Shallow brown earth	184.55
Lithosol	10.04
Podzol	7.96
Rendzina	7.81

Table 4.3 The aquifer types which are associated with arable land use and the area they represent in Ireland.

Aquifer category	Aquifer category description	Area (km²)
Rf	Regionally important aquifer – fissured bedrock	136,255
Pl	Poor aquifer – bedrock which is moderately productive only in local zones	75,504
Rkd	Regionally important bedrock – karstified diffuse	42,855
Lm	Locally important aquifer – bedrock which is moderately productive only in local zones	10,251
Rg	Gravel aquifer – regionally important	9,721
Pu	Poor aquifer – bedrock which is generally unproductive	9,193
Lk	Locally important aquifer – karstified	4,023
Rkc	Regionally important bedrock – karstified conduit	2,687
Rk	Regionally important bedrock – karstified	149
Lg	Gravel aquifer – locally important	0

Table 4.4 The bedrock geology types which are associated with arable land use and the area they represent in Ireland.

Bedrock geology	Area (km²)
Granites and other igneous intrusive rocks	28,478
Dinantian pure bedded limestones	14,879
Dinantian lower impure limestones	12,513
Dinantian pure unbedded limestones	9,237
Dinantian upper impure limestones	8,858
Dinantian (early) sandstones, shales and limestones	8,355
Ordovician metasediments	7,103
Devonian old red sandstones	6,924
Ordovician volcanic	6,503
Dinantian mudstones and sandstones (Cork group)	4,322
Silurian metasediments and volcanics	4,153
Dinantian dolomitised limestones	3,000
Namurian undifferentiated	2,613
Cambrian metasediments	2,520
Dinantian mixed sandstones, shales and limestones	2,165
Precambrian quartzites, gneisses and schists	1,676
Namurian sandstones	1,202
Devonian kiltorcan-type sandstones	1,183
Namurian shales	939
Precambrian marbles	851
Dinantian sandstones	623
Permo-Triassic sandstones	255
Basalts and other volcanic rocks	216
Dinantian shales and limestones	177
Westphalian shales	82
Westphalian sandstones	50

Table 4.5 The groundwater vulnerability types which are associated with arable land use and the area they represent in Ireland using data sources from 2009. These areas will be subject to change as the GSI groundwater vulnerability map is updated.

Groundwater vulnerability	Area (km²)
Exposed (X)	882,097
Extreme	309,275
Moderate	137,062
High	102,341
Low	29,840
High-Low	5,763

In Chapter 3 the EPA's dataset of national scale groundwater pesticide occurrence was used to identify physical characteristics in each MP's ZOC which were more frequently associated with pesticide detections in groundwater. The outcome highlighted catchment characteristics that were statistically related to national pesticide occurrence in groundwater. These characteristics were springs used as sampling points ($p=0.0028$), regionally important aquifer types ($p=0.0007$), aquifers with karstic flow regimes ($p=0.0002$), and alkaline subsoils when present with karst aquifer types ($p=0.0101$). Since karst aquifers and springs were found to be important for national groundwater pesticide occurrence, sites were selected to include these characteristics which did not necessarily have arable land. The decision was made to include two sites with springs and karst flow regime aquifers as their characteristics, with one which had grassland and the other with arable land use.

4.3.2 Potential candidate results

It was important to incorporate the findings in Chapter 3 with the most common characteristics in existence in Ireland to (1) have a range of contrasting sites and (2) include those areas which may be more susceptible to pesticide contamination in groundwater. In order to fully benefit the project through hydrological understanding it

was also important to collaborate on sites were possible and try not to pick sites which had never been studied before. Access issues, the motivation of farmers and the distance from base (Johnstown Castle) were also considered. Twelve candidates (**Table 4.6**) were selected based on their physical properties using the most common properties associated with arable land use as detailed in section 4.3.1. Additional more site specific information on each area highlighted from GIS mapping was then sought to gain further insight into the site. The additional site specific characteristics investigated were boreholes nearby and their logs to obtain the depth to bedrock, if any EPA MPs were nearby and if site information about the MP had been gathered by the EPA. Visiting the potential site was also done on potential candidates already highlighted through GIS work. The candidates were then grouped into their theoretical risk category which is based on theories about how their characteristics would behave as regards pesticide leaching using the conceptual model (**Figure 4.1**). For example it was anticipated that a free-draining soil would allow rapid water movement through its matrix and potentially allow for a rapid transfer of pesticides to groundwater further below.

Table 4.6 The candidates selected and their main physical characteristics. The theoretical risk category is given in brackets (M)=moderate, (L)=low and (H)=high.

Site name (risk category)	Land use	Soil type	Subsoil type	Aquifer type	Bedrock	Depth to bedrock (m)	Collaboration	Existing site specific info.
Laois 1 (M)	Spring barley	Podzolic	Till derived from limestones	Rkd	Dinantian pure bedded limestones	unknown	none	none
Wexford 1 (M)	Spring barley	Acid brown earth	Till derived from lower Palaeozoic sandstones & shales	Ll	Ordovician metasediments	10	ACP	none
Wexford 2 (H)	Spring barley	Acid brown earth	Bedrock at or near surface	Rf	Ordovician volcanics	1-4	ACP	none
Cork 1 (M)	Maize	Acid brown earth	Till derived from Devonian sandstones	Rkd	Dinantian pure unbedded limestones	unknown	none	none
Mayo 1 (H)	Grassland	Rendzina	Bedrock at or near surface	Rkc	Dinantian pure bedded limestones	1-4	ACP	(Coxon and Drew, 1986)
Louth 1 (L)	Winter wheat & potatoes	Gley	Till derived from Devonian sandstones	Pl	Silurian metasediments and volcanics	13	ACP	none
Wexford 3 (L)	Spring barley	Gley	Irish sea till	Rf	Ordovician volcanics	12	ACP	none
Kilkenny 1 (H)	Spring barley	Podzolic	Bedrock at or near surface	Rkd	Dinantian pure bedded limestones	1-4	Pathways project	(Cawley, 1990)
Carlow 1 (H)	Spring barley	Podzolic	Gravels derived from limestones	Rkd & Rg	Dinantian dolomitised limestones	7	Teagasc	(Premrov, 2011)
Kilkenny 2 (H)	Spring barley	Podzolic	Bedrock at or near surface	Rkd	Dinantian pure bedded limestones	1-4	none	none
Waterford 1(M)	Maize	Acid brown earth	Till derived from Devonian sandstones	Rkd	Dinantian pure unbedded limestones	unknown	none	none
Wexford 4 (M)	Spring barley	Acid brown earth	Till derived from limestones	Rf	Ordovician volcanics	unknown	none	none

ACP = Agricultural Catchments Programme. Funded by the Department of Agriculture, Food and the Marine and run by Teagasc.

4.4 *Selected sites*

Of the 12 sites to choose from, only two represented a low risk to groundwater and these were Louth 1 and Wexford 3. After visiting Wexford 3 it was realised that within the 12 km² catchment existed Wexford 2 which had characteristics similar to the Wexford 4 site but which had the added benefit of collaboration with the Agricultural Catchments Programme (ACP). Louth 1 and Wexford 4 were thus dropped after this realisation on the basis of (1) the ACP collaboration and (2) because Louth 1 was located a six hour return drive away from base. Louth 1 also had a different arable land use to the majority of the other sites, with winter wheat and potatoes, making comparisons more difficult since a.i. usage would not be consistent with spring barley land use. Differences in the type of a.i. used would also require separate analytical techniques e.g. organophosphorous herbicides and phenylurea herbicides. Although it would have been interesting and fulfilling for the project to include a.i. such as chlorothalonil, one of the most commonly used fungicides in Ireland and a popular a.i. on potatoes, it was beyond the scope and resources of this project to monitor for this compound, as well as the phenoxyacid herbicides which are widely used on spring barley and grassland.

Karst aquifers are present across 12 – 25% of the World and supply approximately one quarter of the world's population with freshwater (Van Brahana, 2008). Since nearly 50% of Ireland is underlain by Carboniferous limestone which has the capacity to be karstified (Drew, 2008), it was important for the project to include these sites especially those with springs, since springs as MPs were highlighted in Chapter 3 as having an association with pesticide detections in groundwater. Several karst sites were investigated and it was decided to choose sites with collaborations and existing data since karst groundwater is difficult to explore regarding groundwater direction, flow paths, and lag time. Two karst sites with springs as MPs were chosen at Mayo 1 and Kilkenny 1 with the aim of comparing two karst systems with different land uses. Mayo 1 with grassland and Kilkenny 1 with arable. Carlow 1 was also picked because it has both a gravel and karst diffuse aquifer plus the site referred to locally as the Sawmills field, has been intensively studied as regards its hydrology and nutrient pathways (Hooker, 2005; Premrov, 2011; Jahangir, 2012).

A moderate risk site was also chosen and again it was decided to collaborate with the ACP. Wexford 1 was chosen as six boreholes (BHs) were going to be installed with funding

outside of this project and there was an unusual field situation in that two replicates (regarding physical characteristics) within the same catchment were present, the only difference in physical characteristics being that one transect had slightly more clay present in its Clonroche series soil (acid brown earth). The funding to install these BHs came from the ACP, Teagasc.

Site names were generated to help introduce each site regarding its physical characteristics for the seven sites chosen (**Figure 7.4**) and for confidentiality with the land owners and managers at each site. The first part of the site name refers to the sites dominant aquifer, the second part refers to the unsaturated zone deposits and their drainage, and the last part of the name in subscript refers to the land use. For example the I/KWDa site has two aquifers present: the intergranular flow aquifer above the karst aquifer hence why 'I' is before 'K'. The other sites for aquifer type indicate the flow regime of the aquifer (e.g. karst or fractured/fissured) and the second lower case letter refers to the bedrock geology (e.g. metasediments). For Karst no lower case letter for geology has been provided since all the karst sites are Carboniferous. **Table 4.7** details the new site names for the chosen sites and their acronym.

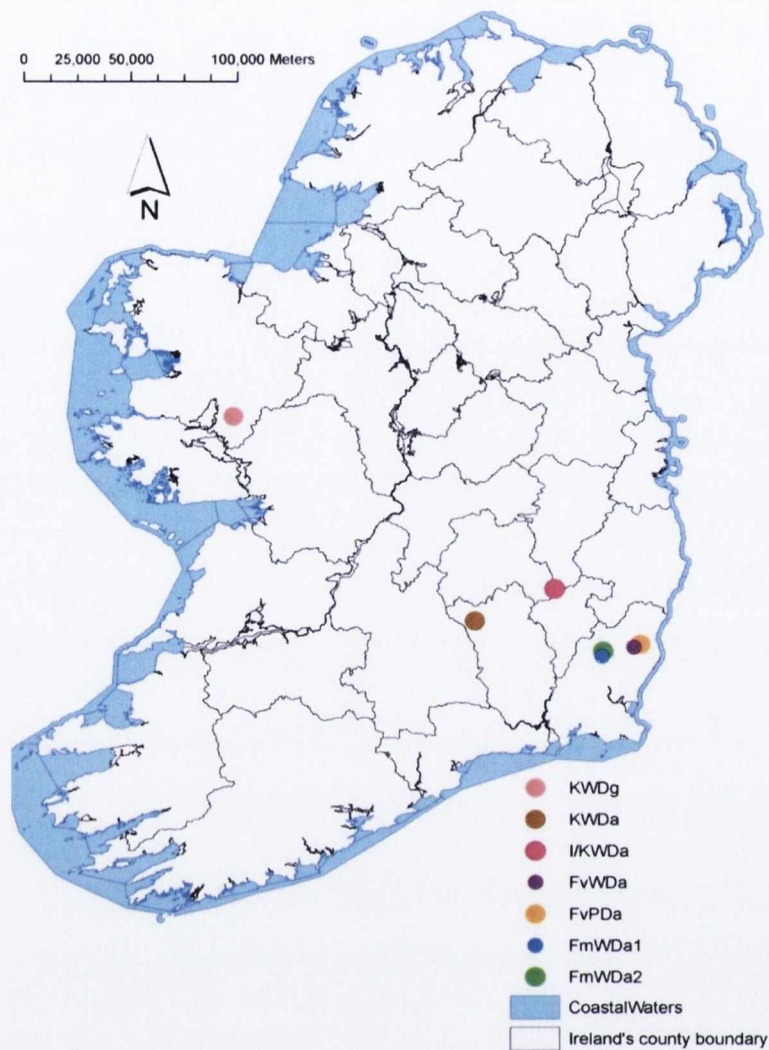


Figure 4.3 Location of monitoring sites across Ireland used for collecting monthly data.

Table 4.7 Site names.

Description of site name	Acronym
Karst well-drained grassland	KWDg
Karst well-drained arable	KWDa
Intergranular/karst well-drained arable	I/KWDa
Fractured-volcanics well-drained arable	FvWDa
Fractured-volcanics poorly-drained arable	FvPDa
Fractured-metasediments well-drained arable site 1	FmWDa ₁
Fractured-metasediments well-drained arable site 2	FmWDa ₂

4.5 Characteristics of the chosen sites

Section 4.5 details the information already known and available for each of the seven sites selected for monitoring throughout this project. Knowledge gained on each site throughout the duration of this doctoral study has been included in Chapter 5.

4.5.1 Karst well-drained grassland (KWDg)

4.5.1.1 Introduction

The catchment of KWDg is approximately 46 km², located on Carboniferous limestone with associated karst features such as springs, turloughs, swallow holes, rock outcrops, and shallow rendzina soils (**Figure 4.4**) (Mellander *et al.*, 2012). The catchment is based around a number of undrained turloughs but the catchment boundary was not fully known in 2009 when sites were selected because of the complex nature of the conduits underground. The current catchment boundary in **Figure 4.4** is provisional and was delineated by the ACP using tracer studies already carried out in the area. In Chapter 5 the catchment boundary is amended based on additional tracer studies and water balance. The spring at Grid Reference 122697; 263556 is thought to represent the bulk of outflow from the catchment and was the spring sampled throughout this project. However, there are four other springs nestled around this spring: the area collectively termed “Cregduff Risings” (IAH, 2011). At the particular spring selected for monitoring (122697; 263556), there is an active group water scheme (GWS) which abstracts approximately 7,000 m³/d with the spring discharging an average of 10,829 m³/day (IAH, 2011). Discharge from the Risings Springs was measured using a Thermo-Fisher time-of-flight area velocity meter, by the EPA. Nutrients in the discharging water were collected, analysed, and recorded by the ACP for phosphorus and nitrate. The land surface is undulating, with ground elevations ranging from 10-130 mAOD (metres above ordnance datum) and sloping gently south west. The area has a cool maritime climate with an annual mean air temperature of 12.6°C, the annual rainfall is 1,140 mm (1961-1990 mean, Met Éireann, Irish Meteorological Service), and the mean annual evapotranspiration is estimated as 400-500mm (Mellander *et al.*, 2012).

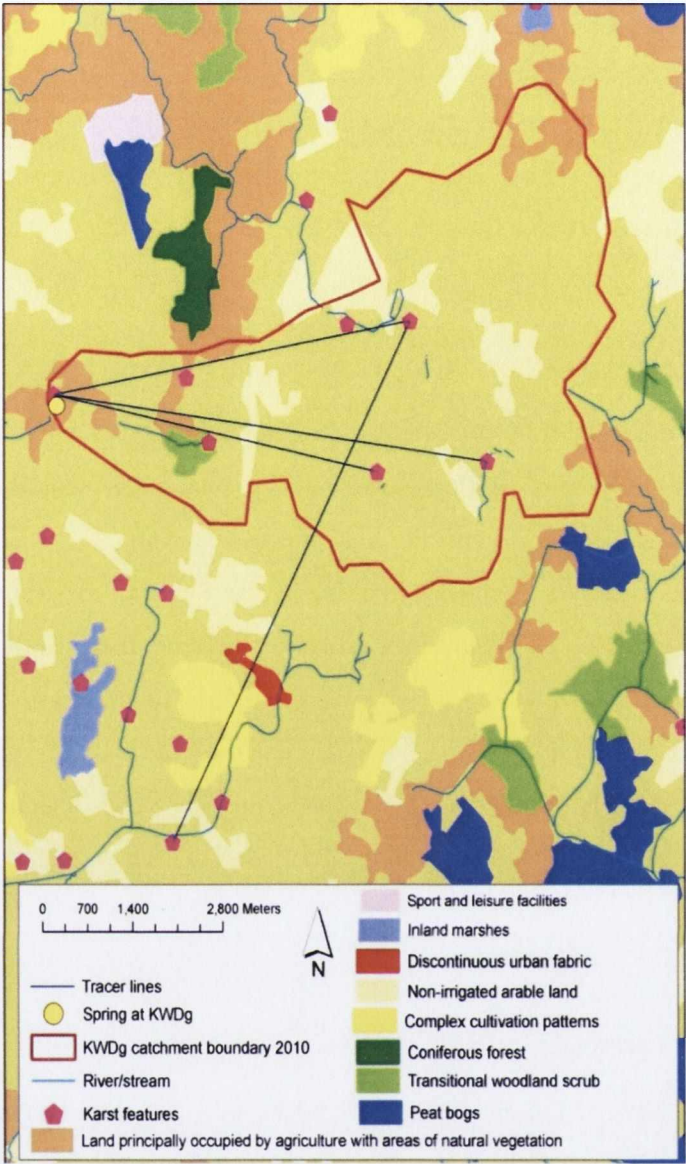


Figure 4.4 The catchment of monitoring point (MP) karst well-drained grassland (KWDg). Map indicates the spring sampled, karst features known by the GSI in the area, tracer lines from studies carried out by Coxon and Drew (1986), and the catchment boundary estimated by the ACP which is finalised in Chapter 5 using water balance and additional tracer studies carried out by the ACP. Land cover from Corine 2006 is also shown.

4.5.1.2 Land use

There are approximately 90 farmers with holdings in the catchment area and a number of other farmers renting land. The farming is predominately suckler cows, beef, and sheep

with some pockets of intense dairying and a few fields of tillage, mainly maize for dairy herds with land grazed for 7-8 months (Mellander *et al.*, 2012). Arable land occupies approximately 2 km² of the entire catchment. Over winter animals are housed and manure is stored in slurry tanks. The average farm size is 0.3 km², characterised by the dispersed nature of the holdings.

4.5.1.3 Pesticide applications

The catchment is dominated by grassland with approximately 41 km² of the catchment in permanent pasture from CLC 2006. Grassland as a land use would expect to receive applications of MCPA, dicamba, fluroxypyr, and mecoprop-p as these are the four most common a.i. present in PPP permitted for use in the Republic of Ireland on established grassland (**Appendix 1**). The small proportion of the catchment (approximately 2 km²) dedicated to forage maize would receive applications of fluroxypyr, mesotrione, and pendimethalin (**Appendix 1**). No pesticide application records were gathered for the 46 km² catchment of KWDg but under advice from the ACP advisor, land managers would use standard pesticide applications available through Teagasc which would include those a.i. listed above.

4.5.1.4 Physical characteristics

The soils in over 90% of the catchment at KWDg are classified by Gardiner & Radford (1980) as an association of shallow brown earth and rendzinas (60%), grey brown podzolic (25%), gley (10%), and peat (5%). Rendzinas often occur in association with bedrock outcrops, of which there are many in the area. Rendzinas are the simplest of soil types consisting of just two horizons: an A horizon which is the soil and a C horizon the bedrock. According to the Irish Forest Soils (IFS) project soil drainage class, at KWDg greater than 90% of the catchment has deep well drained mineral soils derived mainly from calcareous parent materials however, where the spring is located the soil drainage class is shallow well drained mineral soils derived mainly from calcareous parent materials (Fealy *et al.*, 2009). At KWDg the bedrock is pure bedded Dinantian (Lower Carboniferous) limestone with a high degree of karstification, rendering this aquifer regionally important and dominated by conduit flow (Rkc). Parts of the area are underlain by silty till, with smaller proportions of cutover raised peat, and karstified bedrock at or near the surface (Mellander

et al., 2012). These glacial deposits are thickest (1-5 m) towards the east of the catchment and thin out to the west where exposed patches of limestone pavement become more frequent (Coxon and Drew, 1986) and where the spring is located. Karstic features are widespread with dolines the most common (Mellander *et al.*, 2012). Dolines are sinkholes caused by a depression in the topography of karst environments. Karst conduit groundwater can flow across the surface water divides in the KWDg catchment, proven by Coxon and Drew (1986) with a positive tracer test linking a turlough to the east of KWDg Sp. to Fountainhill Sp. to the south of the catchment (**Figure 4.4**). Both point and diffuse recharge occurs in the area. Diffuse recharge occurs by rainfall percolating through permeable subsoil and rock outcrops, while point recharge occurs through swallow holes, collapsed features, and dolines. Groundwater flow at KWDg is through fissures, faults, joints, and bedding planes. Karstification within the limestone will greatly enhance the permeability of the rock which may allow several underground flow paths to travel several kilometres. Coxon (1986) found travel times of between 10 and 123 m/h to exist within the karst conduits at KWDg. The movement of groundwater is generally east to west (Drew and Daly, 1993). Due to the complex network of conduits underground and the random assortment of karst features acting as point sources, it will be very difficult to pin point the source of contamination at the spring (see section 5.6.1).

4.5.2 Karst well-drained arable (KWDa)

4.5.2.1 Introduction

The MP at KWDa is a karst spring termed locally as the 'Boiling Spring'. It is located 4.5 km west of Freshford village in Co. Kilkenny (Grid. Ref.: 235663; 163412) and lies within a larger 21 km² catchment which was delineated by the EPA Pathways Project team (**Figure 4.5**). The ZOC of the Boiling Spring was unknown at the start of the project, but will be discussed in Chapter 5. Within the catchment the topography ranges from 120 mAOD along the river valley in the south rising to 160 mAOD in the north with undulating topography in local areas and many dry valleys. The average annual rainfall in the catchment (1961-1990) is 967 mm and average annual potential evapotranspiration is 527 mm (Cawley, 1990).

4.5.2.2 Land use

Land use in the catchment is generally farmland with mixed tillage and grassland use. 73% of the 21 km² catchment is pasture (sheep and dairy) while 19% is dedicated to arable cereals (**Figure 4.5**). In the vicinity of the Boiling Spring there is permanent pasture but further North and up gradient there is winter wheat and spring barley, then further North of this in the highest altitude areas (160 mAOD) sheep farming dominates the landscape with scrub vegetation. There are a number of private dwellings within the catchment in addition to some derelict buildings, and in the vicinity of the Boiling Spring there are two houses. There is a population of approximately 600 in the catchment which are serviced by private wells, septic tank systems, and four group water schemes (Archbold and Deakin *Pers. Comm.*, 2011).

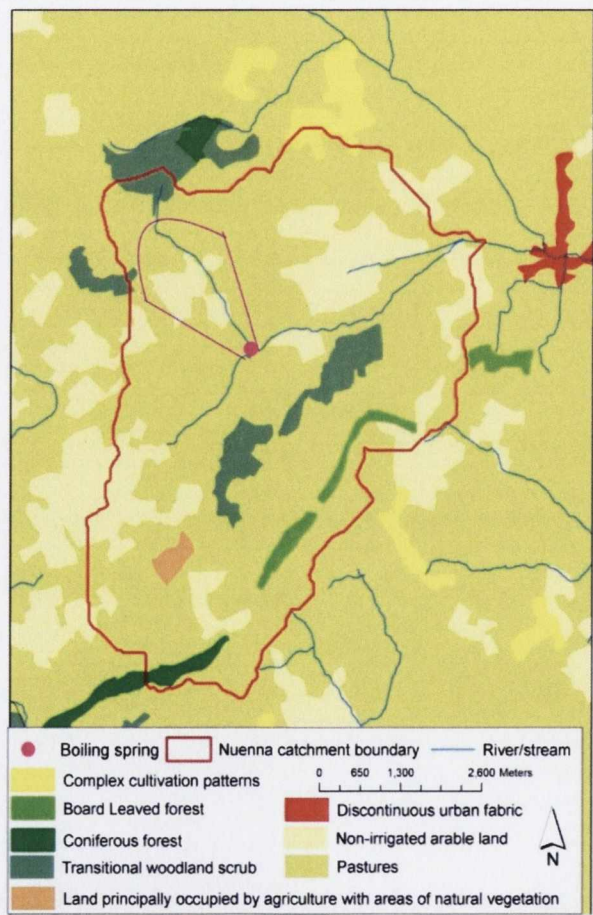


Figure 4.5 Land use at karst well-drained arable (KWDa) in Co. Kilkenny. The purple boundary North West of the Boiling Spring shows an estimation of the Boiling Springs ZOC. Land cover from Corine 2006 is also shown.

4.5.2.3 Pesticide applications

Detailed farmer records from the catchment were unavailable at the time as regards the PPP applied but since the catchment has grassland, forage maize, and spring barley the following a.i. would be commonly applied (**Appendix 1**): MCPA, dicamba, fluroxypyr, mecoprop-p, epoxiconazole, and 2,4-D. The EPA Pathways Project stated they would carry out questionnaires among the catchment farmers which included the pesticide applications they applied to land they managed. In the estimated ZOC of the Boiling Spring (**Figure 4.5**) the pesticides applied have been listed in **Appendix 2**.

4.5.2.4 Physical characteristics

The geology is described by the Geological Survey of Ireland (GSI, 2008b) and consists of Lower Carboniferous (Dinantian) pure bedded limestones mapped as the Ballyadams formation which comprise of crinoidal wackestone/packstone, and is classed as a regionally important karstified aquifer dominated by diffuse flow (Rkd) (GSI, 2008a). At higher altitude in the catchment the geology is Clogrenan limestone formation and the Killeslin formation which comprises of the relatively impermeable Namurian shales (Cawley, 1990). Above the Dinantian pure bedded limestones are over 5 m of Quaternary deposits consisting of gravelly clay and sandy gravels, with gravels becoming coarser and more chaotic towards the River Nuenna and in the vicinity of the River Nuenna the depth of these fluvio-glacial deposits can reach 20 m (Cawley, 1990). The principal soil association of the area as classed by Gardiner and Radford (1980) are minimal grey brown podzolics. Soils closest to the river have higher permeability than soils which overly the Namurian bedrock being poorly drained (Archbold and Deakin *Pers. Comm.*, 2011). Fealy *et al.* (2009) states the soil drainage class immediately north of the Boiling Springs ZOC as deep well drained mineral soil derived mainly from calcareous parent materials. This soil is present in approximately 85% of the estimated ZOC for the Boiling Spring (**Figure 4.5**). At the most north western point of the estimated ZOC for the spring, smaller fractions of deep well drained mineral and deep poorly drained mineral soils derived from mainly non-calcareous parent materials, reflecting the non-calcareous Namurian bedrock. There is also a small fraction of shallow well drained mineral soils derived from calcareous parent materials. Geophysical surveys carried out by the EPA in 2009 revealed that to the north of the River Nuenna and north of the Boiling Spring in its estimated ZOC is a karstified conduit with a depth-to-bedrock varying between 2-5 m thick. A fissure exists along this

conduit as revealed through 2D resistivity profiles (**Appendix 5**). Flow velocities established from underground water tracing work carried out by another researcher during the time period of this research project indicated a relatively poorly developed conduit system, with the Boiling Spring exhibiting hydrochemistry of springs dominated by diffuse recharge and flow (Walsh, 2011); this is discussed further in section 5.6.2.

4.5.3 Intergranular/karst well-drained arable (I/KWDa)

4.5.3.1 Introduction

At I/KWDa the field sampled was the Sawmills field. It is situated in the River Barrow catchment and managed by the National Centre for Arable Crops Research (a Teagasc Research Centre) which occupies 225 ha of research farmland. The Sawmills field is 10.7 ha (272733; 179118) (**Figure 4.6**). The land is relatively flat, sloping approximately 2° from north to south. The elevation is 56 mAOD and groundwater flow beneath the site is in a south-west direction, towards the R. Barrow approximately 500 m away (Premrov *et al.*, 2009b). At I/KWDa BHs were installed to target shallow, interface, and deep groundwater. These installations are detailed in section 5.3.1 (**Appendix 3**). South west of the Sawmills Field exists a redundant sugar mill which has been out of operation since 2007.

4.5.3.2 Land use

The Sawmills field has a long history of arable land use spanning over ten years with the dominant crop over this time being spring barley. In the Sawmills Field a cover crop of mustard or regenerated spring barley has been used since 2006 to reduce nitrate leaching during winter where the land is bare and exposed (Premrov *et al.*, 2009a). Surrounding the Sawmills Field and up gradient there is also arable land use, with several different field trials and experiments ongoing for winter wheat, oilseed rape, miscanthus, and barley.

4.5.3.3 Pesticide applications

Records of pesticide applications to the Sawmills Field only date back to 2003/04 when wild oats was the crop grown at Oak Park. **Appendix 2** details the PPP applied to the Sawmills Field along with the a.i., the application date, and rate. The most commonly used

pesticides were propiconazole, chlorothalonil, fenpropimorph, mecoprop-p, metsulfuron-methyl, and tribenuron-methyl. Pesticide records were sought for the other arable fields up gradient and surrounding the Sawmills Field but were not made available to this project.



Figure 4.6 The Sawmills Field at intergranular/karst well-drained arable (I/KWDa), Co. Carlow. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland. The red line indicates the boundary of the Sawmills Field.

4.5.3.4 Physical characteristics

The soil here is free draining, lightly textured and loamy. 65% or more of the topsoil is sand and 90% is sand and gravel (Conry and Ryan, 1967). The soil is from the Athy Complex which is described as a sandy to gravelly sandy loam (Hooker, 2005). The soil is

a brown earth. These are mature well drained mineral soils of medium texture, often acidic, and generally extensively cultivated (Conry and Ryan, 1967).

The FAO international classification of these soils is Cambisols and according to the IFS soil drainage classification these are shallow well drained mineral soils derived mainly from calcareous parent materials (Fealy *et al.*, 2009). The subsoil is fluvioglacial dominated by sand and gravel deposits (Conry and Ryan, 1967). In 2002 Minerex (Kildare, Ireland) carried out BH excavations and found that most of the south eastern part of I/KWDa is underlain by a highly- to extremely- vulnerable shallow sand and gravel aquifer (Unpublished report by Minerex, 2002 cited by Premrov, 2011). These shallow fluvioglacial sand and gravel deposits are very vulnerable to leaching (Conry and Ryan, 1967) and can act as rapid transfer pathways for water containing within it pesticides. The deposits below the site are part of a fluvioglacial sand and gravel aquifer with interbedded sands and clays which extend along the Barrow Valley (Daly, 1981). The GSI (2008a) have classified the site as having two aquifer types present: a regionally important sand and gravel aquifer with intergranular flow (Rg) and a regionally important karstified aquifer dominated by diffuse flow (Rkd) beneath. Clay lenses are present across the site which impede permeability but they are not continuous rendering overall permeability high except in localised spots (Premrov, 2011). The bedrock geology is Dinantian dolomitised limestones, a common bedrock geology type in Ireland associated with arable land (**Table 4.4**).

4.5.4 Fractured-volcanic well-drained arable (FvWDa)

4.5.4.1 Introduction

The FvWDa site is located in the south west of the Ballycanew catchment (309830; 150502) (**Figure 4.7**); this catchment is also the location of the fractured-volcanic poorly-drained arable (FvPDa) site (see **Figure 4.9**). The MPs at FvWDa are located on the periphery of the catchment boundary and span the steep slope present here. At the Upper Spring, the elevation is 136 mAOD and at the Lower BH, the lowest sampling point at the site, the elevation is 88 mAOD.

4.5.4.2 Land use

Since 2004 the field with the BHs and the field above this (red boundary lines shown in **Figure 4.7**) used for monitoring have been growing spring barley and prior to this some sugar beet and winter wheat. In 2011 mustard was sown to help prevent excessive nitrate loss to surrounding waters as part of management introduced by the ACP. An additional MP outside of these fields has been included for monitoring called the House Spring as it has a significant discharge year round (approximately 11 L/min).

4.5.4.3 Pesticide applications

Between 2003 to 2008 the fields within the red boundary shown in **Figure 4.7** received 24 different a.i. The top five most commonly applied a.i. were chlormequat, azoxystrobin, epoxiconazole, chlorothalonil, and CMPP. **Appendix 2** lists the products applied to FvWDa.

4.5.4.4 Physical characteristics

The soil here is an acid brown earth classified with the soil series of Clonroche. The IFS soil drainage type is deep well drained mineral derived from mainly non-calcareous parent materials (Fealy *et al.*, 2009). This soil is very light, crumbly, and as a consequence free-draining. The site is classified by the GSI (2009) as having an unsaturated zone of approximately 1m or less before contact with bedrock beneath. From walking the field there are many exposed bedrock outcrops and large angular stones. Locals call the field 'Plunders' because these outcrops have ruined several pieces of machinery during harvesting. The bedrock geology of the site is Ordovician volcanics (GSI, 2008b). The GSI have classified this bedrock as a regionally important fissured aquifer (Rf) which is capable of generating high yields of water. Several springs are present across the site and three were monitored as part of this study.

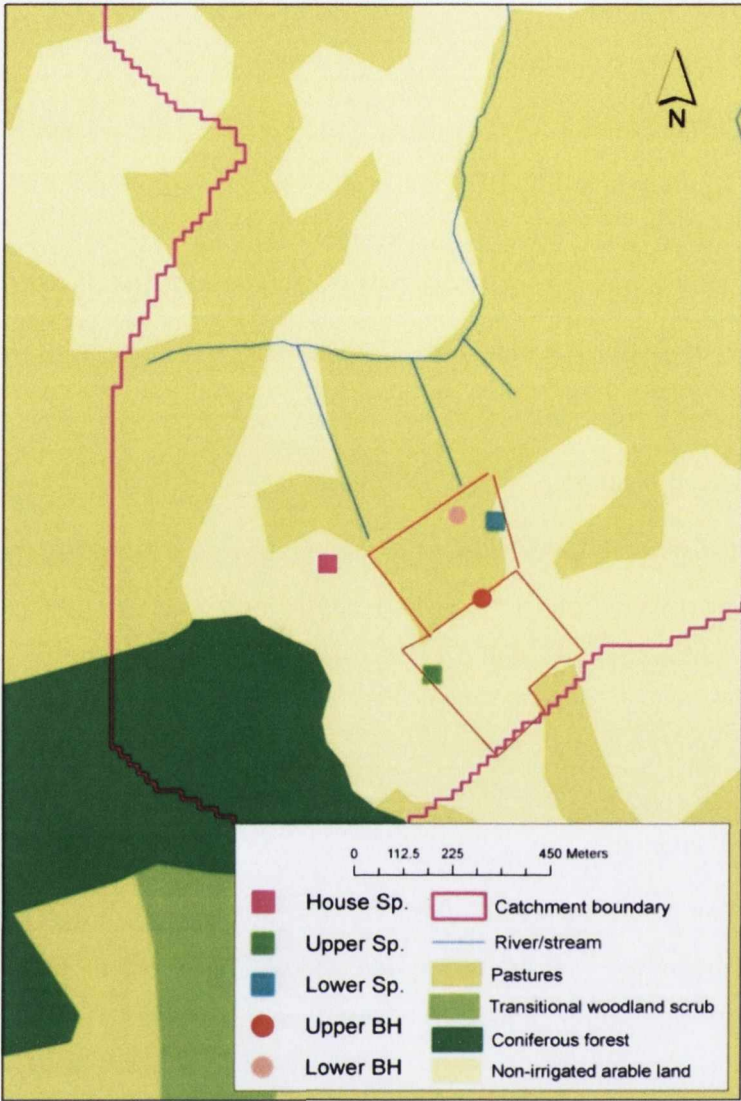


Figure 4.7 Fractured-volcanic well-drained arable (FvWDa) site situated in the catchment of Ballycanew showing the five monitoring points (MPs) sampled with the red boundary showing the location of the fields housing the MPs. Land cover from Corine 2006 is also shown.

4.5.5 Fractured-volcanic poorly-drained arable (FvPDa)

4.5.5.1 Introduction

The second site in the Ballycanew catchment is FvPDa (**Figure 4.8**) and is located 3.2 km from FvWDa. The total catchment size is 11 km² (**Figure 4.9**). This site was chosen because it contrasts with the FvWDa site in its soil, Quaternary deposits, and depth-to-bedrock. The FvWDa site has a heavy-textured clay-rich gley soil (Gardiner and Radford,

1980) with Quaternary deposits of Irish Sea Till and a soil drainage class of deep poorly drained mineral soils derived mainly from calcareous parent materials (Fealy *et al.*, 2009). **Figure 4.8** shows the location of the MPs at FvPDa with circles representing piezometers installed using a Gidding’s Rig, squares to indicate boreholes installed using air rotary drilling, triangles to indicate drains, and pentagon’s to indicate the location of streams sampled. Further details on construction of these MPs can be found in Chapter 5.

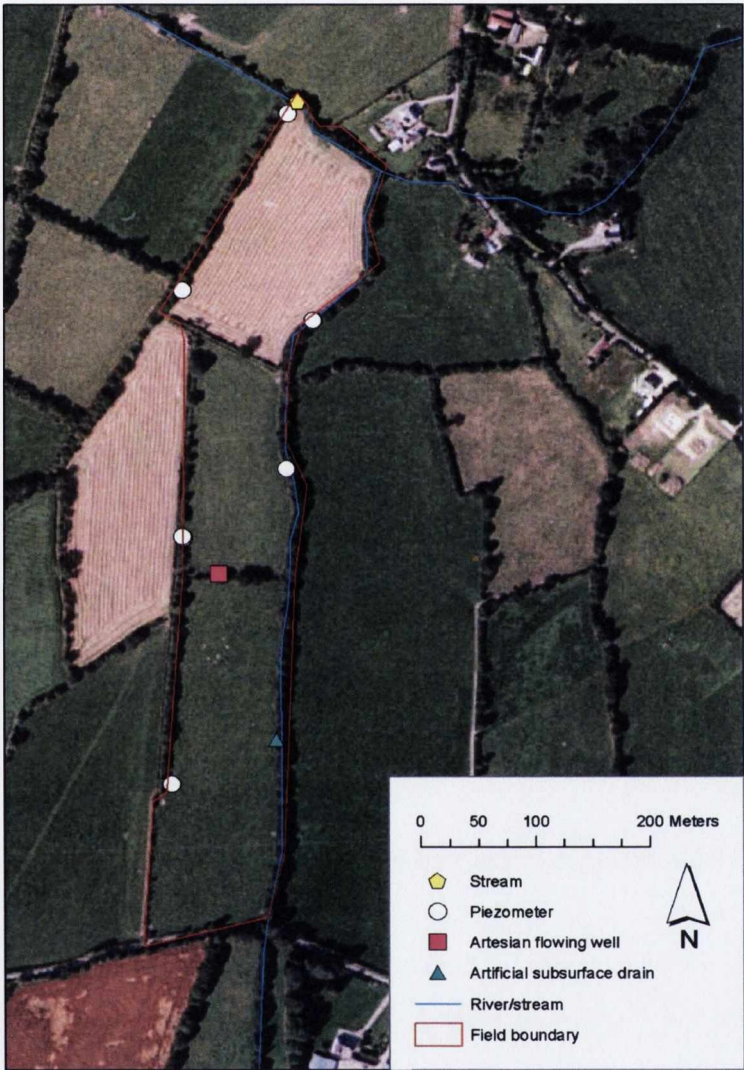


Figure 4.8 The Fractured-volcanic poorly-drained arable (FvPDa) site and approximate field boundaries (red line) situated in the catchment of Ballycanew. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

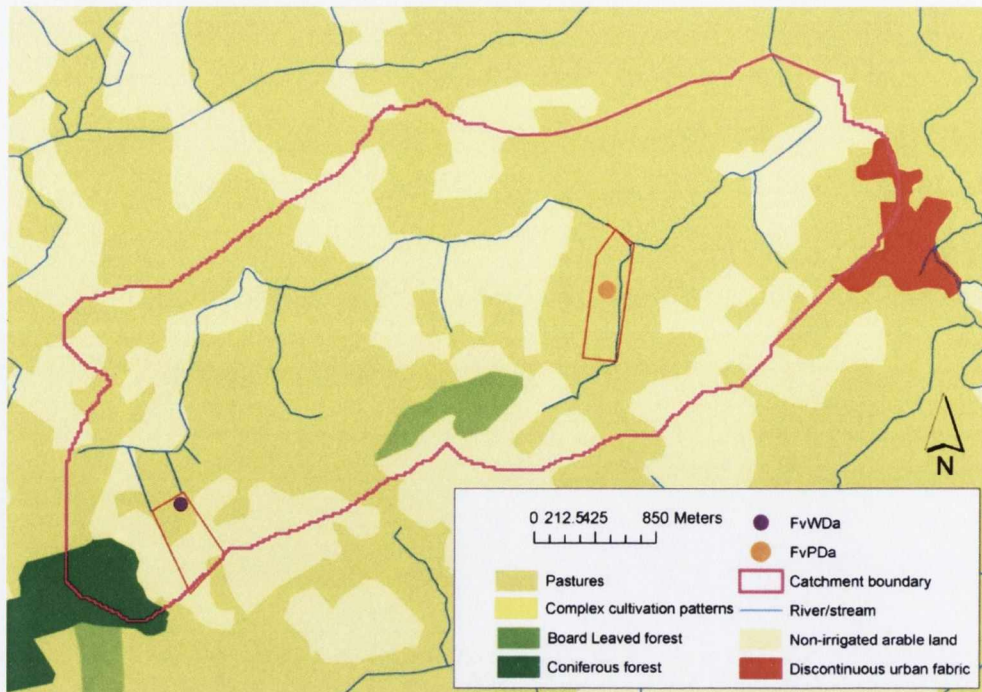


Figure 4.9 The 11 km² catchment showing the relative locations of the fractured-volcanic well-drained arable (FvWDa) site in the south west and the fractured-volcanic poorly-drained arable (FvPDa) site in the centre-east, each with their approximate field boundaries shown in red. Land use is taken from the CORINE land cover dataset from 2006 (European Environment Agency, 2011). Approximately 77% of the catchment is in grassland and 20% in arable.

4.5.5.2 Land use

Since 2006 the fields outlined in red in **Figure 4.8** were sown in spring barley. Prior to this they were grassland. The lower fields closest to the stream were in winter wheat and spring barley but the land manager changed fields for arable land use in 2006 because the lower fields were too difficult to manage in wet conditions because of the soil's heavy nature causing waterlogging.

4.5.5.3 Pesticide applications

Pesticide records for the area included in the red boundary in **Figure 4.8** were only available for 2009 because the land owner hires a contractor to manage his arable land

since the land owner only has a small proportion of his farm dedicated to arable crop production. Pesticide applications are presented in **Appendix 2**.

4.5.5.4 Physical characteristics

The soil here is water-logged, relatively impermeable, with properties nearly opposite to that of a Clonroche soil present at site FvWDa. The IFS soil drainage class classifies the soil as deep poorly drained mineral derived from mainly calcareous parent materials (Fealy *et al.*, 2009). The soil here is very similar to that of a Macamore soil series which are notoriously heavily-textured soils which are hard to manage however, the soil can not be classed as a Macamore because the soil here is derived from calcareous material, and a true Macamore soil would not be (Creamer *Pers. Comm.*, 2011). The Quaternary deposit is Irish Sea Till with a low permeability, and the bedrock geology is the Campile formation of Ordovician age. These rocks consist of rhyolitic volcanic and grey and black slates. Felsic volcanics may also be present in the area and these rocks can be highly weathered in places (GSI, 2008b). Ordovician volcanic rocks are high water yielding and as such the GSI have classified the aquifer as regionally important with fissure flow (Rf) (GSI, 2008a). Both sites FvWDa and FvPDa exist above the same regionally important productive fissured aquifer (GSI, 2008a) and the same bedrock geology: Ordovician volcanics (GSI, 2008b). However, the material above each of these sites contrasts greatly.

4.5.6 Fractured-metasediments well-drained arable site 1 and 2 (FmWDa_{1/2})

4.5.6.1 Introduction

FmWDa is an 11 km² catchment in Co. Wexford (295339; 148539) which is also being studied by the ACP for nutrient losses. Within the catchment two sites were picked, site 1 and site 2, which are approximately 2 km from each other. Both catchments have the same physical characteristics such as aquifer type and land use. Groundwater was sampled from piezometers located in three BHs at each site, a total of six BHs, details of which are given in Chapter 5 section 5.3.1. **Figure 4.10** shows the catchment and the two sites each with three BHs, nine piezometers, and a stream each.

4.5.6.2 Land use

The catchment has 54% arable land and approximately 39% grassland. Both sites in the catchment grew spring barley for the duration of monitoring and the sites have a legacy of arable land use, dominated by spring barley production.

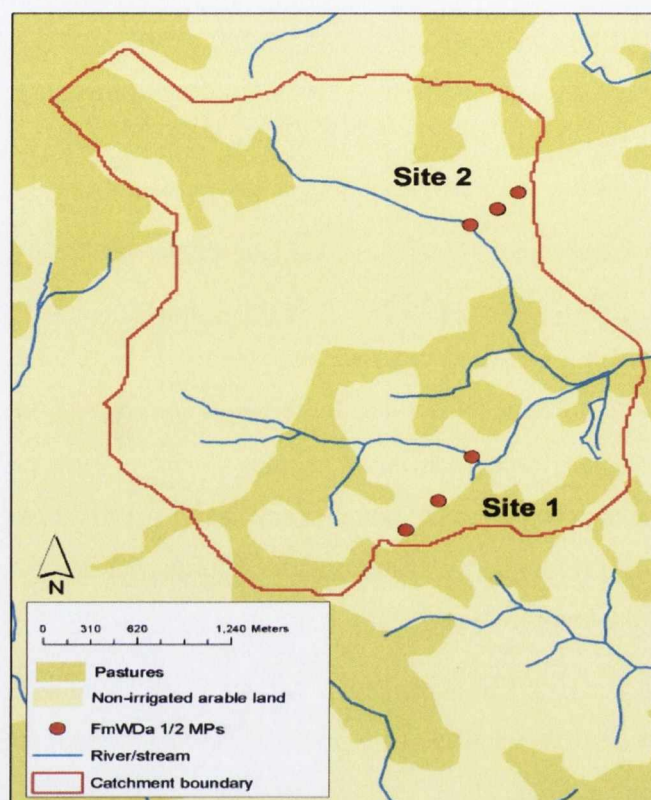


Figure 4.10 The fractured-metasediments well-drained arable (FmWDa) catchment showing the location of each site and the monitoring locations within. Land cover from Corine 2006.

4.5.6.3 Pesticide applications

Appendix 2 details the pesticide applications in the fields housing MPs at both sites. Site 1 received a total of 24 separate a.i.s between 2008 – 2012 while site 2 only received 18. The most commonly applied compounds at site 1 were azoxystrobin, chlorothalonil, and prothioconazole. At site 2 the most commonly applied compounds were prothioconazole, mecoprop-p, chlorothalonil, and cypermethrin.

4.5.6.4 Physical characteristics

Both sites at FmWDa have a Clonroche series acid brown earth soil (Gardiner and Radford, 1980) with the IFS classifying the area a deep well drained mineral soil derived from mainly non-calcareous parent materials (Fealy *et al.*, 2009). The Quaternary deposits are glacial tills derived from Lower Palaeozoic rocks. These deposits overlie Ordovician metasediments that are classed as a locally important aquifer which is moderately productive only in local zones (L1) (GSI, 2008a). The Quaternary deposit permeability is classed as medium to low.

4.5.7 Differences between fractured-metasediments well-drained arable Site 1 and 2

Two locations were picked within the same catchment because of slight differences in the soils. At site 2 the soil has more clay and as a result is more likely to become waterlogged. Site 1 has more of a “true” Clonroche textured soil (more freely-draining). At both sites prothioconazole, chlorothalonil, and azoxystrobin were frequently used but only site 2 used the herbicides mecoprop-p and MCPA between 2008 and 2012.

4.6 Chapter 4 conclusions

National pesticide usage figures from the Pesticide Control Service (2007a) indicates that arable cereal uses the greatest quantity of pesticide compounds compared to other agricultural land uses. The main arable cereal in Ireland is spring barley (Pesticide Control Service, 2007a). Using ArcGIS physical characteristics associated with arable land use across Ireland were found. Using data obtained across Ireland of the most common physical characteristic associated with arable land use has helped guide the selection process for sites. Sites were selected with acid brown earths, gleys, and grey brown podzolic soils, with regionally important fissure flow fractured aquifers (Rf) aquifer types, and including the bedrock geology Dinantian pure bedded limestones, Ordovician metasediments, and Ordovician volcanics. These land use associations and common physical characteristics were considered when choosing site locations, so sites were representative of the range of conditions existing within tillage areas of Ireland, although every scenario in existence in Ireland could not be included because of a lack of resources and time. Analysis of national scale groundwater monitoring data from the EPA (Chapter 3) were also considered when selecting sites (**Table 3.3**). Seven sites were selected across Ireland with a varying range of physical characteristics and similar land use pressures

(diffuse agriculture). For these reasons two sites with karst springs were chosen with regionally important karst aquifers: KWDg and KWDa. FvWDa and FvPDa are sites located on acid brown earth and gley soils, respectively, with the same regionally important aquifer. I/KWDa is the only site with a gravel aquifer. FmWDa was chosen to represent a theoretically moderate risk to groundwater location with FvPDa a theoretically low risk to groundwater location. **Table 4.8** shows the final seven sites and their characteristics as well as their theoretical risk of pesticide occurrence in groundwater.

Table 4.9 Characteristics of the final cover sites and their theoretical risk to groundwater based on these characteristics.

Site name	Land use	Principal soil association	Soil drainage class	Quaternary deposit (subsoil)	Aquifer type	Theoretical risk category
Source	(European Environment Agency, 2011)	(Gardiner and Radford, 1980)	(Fealy <i>et al.</i> , 2009)	(Fealy <i>et al.</i> , 2009)	(GSI, 2008a)	
KWDg	Grassland	Rendzina	Deep well drained mineral	Bedrock at or near surface	Rkc	High
KWDa	Spring barley	Minimal grey brown podzolic	Deep well drained mineral	Bedrock at or near surface	Rkd	High
I/KWDa	Spring barley	Grey brown podzolic	Shallow well drained mineral	Gravels derived from limestones	Rg and Rkd	High
FvWDa	Spring barley	Acid brown earth	Deep well drained mineral	Bedrock at or near surface	Rf	High
FvPDa	Spring barley	Gley	Deep poorly drained mineral	Irish Sea Till derived from limestone	Rf	Low
FmWDa _{1/2}	Spring barley	Acid brown earth	Deep well drained mineral	Till derived from Lower Palaeozoic sandstones and shales	Ll	Moderate

CHAPTER 5

SITE SOIL, GEOLOGY, HYDROGEOLOGY AND HYDROCHEMICAL CHARACTERISTICS

5.1 *Introduction*

The aim of this chapter is to describe each site's characteristics which have been obtained during the project study period. Data obtained and interpreted included soil/subsoil properties, meteorology and effective rainfall, BH installation logs, interpretation of geophysical surveys, groundwater level monitoring, groundwater flow direction, groundwater age dating, delineation of zones of contribution (ZOC) at each site, and groundwater hydrochemistry. All these factors will be integrated to describe a conceptual model for each site and used later within Chapter 7 to interpret groundwater pesticide occurrence.

Site characteristics at each site were investigated to understand the processes which may affect pesticide occurrence in groundwater. The soil and subsoil was characterised based on its texture, pH, and cation exchange capacity (CEC). During BH installations, geological logs were recorded including water strike records. Geophysics was carried out where MPs were located to better understand subsoil geology. Pressure transducers were installed in BHs to record water level responses to recharging precipitation. The age of the groundwater at selected sites was determined to assist conceptual understanding about residence time. Inorganic chemical parameters were analysed for alongside monthly pesticide samples to indicate the hydrochemistry of the sites using principal component analysis (PCA) of hydrochemical data. These parameters were then amalgamated to decipher hydrogeological and hydrochemical characteristics of each site and used in Chapter 7 to help explain pesticide occurrence.

5.2 *Physical and chemical analysis of soil and subsoil*

5.2.1 *Soil and subsoil analytical methods*

All sites had general data on clay, sand, silt, soil pH, and CEC (m.eq/100g) taken from available national records of these particular soil types by Gardiner and Radford (1980)

and are summarised in Chapter 4. However, for FvWDa and FvPDa soil and subsoil samples were collected and sent to Brookside Laboratories Inc. (Ohio, U.S.A.) for analysis. Samples of unconsolidated vadose zone material were taken every metre during BH installation. The percentages for sand, silt, and clay were determined for the <2 mm fraction. At FvWDa and FvPDa several other soil parameters were measured with results given in **Table 5.1** to include organic matter (OM), organic carbon (OC), and the C:N ratio. Particle size distribution was also carried out by the author on these two sites using a Malvern Mastersizer 2000 laser diffractometer with results for FvPDa shown in **Figure 5.1**. Using the <2 mm fraction of each soil sample, 2 g was placed into the autosampler and 20 ml of 50 g/L sodium hexametaphosphate added and left for 48 hours. Sodium hexametaphosphate helps to deflocculate the particles which aids textural detection. Samples were then agitated for 1.5 hours before analysis on the Malvern apparatus using methods detailed by Sperazza *et al.* (2004) and Eshel *et al.* (2004). Particle size distribution separates the soil based on the size limits encountered following the dispersion of the soil aggregates (Sperazza *et al.*, 2004) which were then categorised according to **Appendix 4**.

5.2.2 Soil and subsoil results

Soils from Counties Carlow, Wexford, Kilkenny, and Mayo were classified by the National Soil Survey of Ireland (Gardiner and Ryan, 1964; Conry and Ryan, 1967; Gardiner and Radford, 1980) based on the Great Soil Groups and subcategorised soil series.

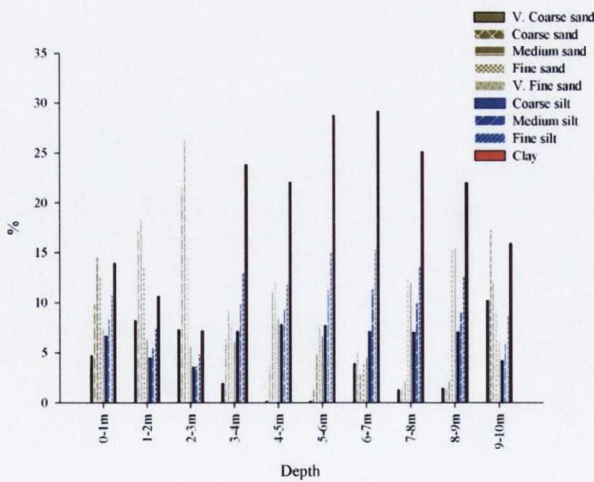


Figure 5.1 Particle size distribution for soils and subsoils from fractured-volcanics poorly-drained arable (FvPDa) collected during borehole installation in October 2008.

5.2.3 Soil and subsoil discussion

Comparing all seven sites, it is FvPDa and I/KWDa that contrast the most regarding soil and subsoil characteristics. I/KWDa has a high percentage of sand which makes this site free draining. This soil will allow recharge to rapidly infiltrate to groundwater beneath (Jahangir, 2012). FvWDa also has a high percentage of sand in its soil, more so in the Upper BH. At the Upper BH the percentage of sand decreases with depth from 70% to 60%. The organic matter in the Lower BH is highest at 0-1 m. More clay is present in the Lower BH at FvWDa.

The two sites (FvWDa and FvPDa) were the only sites to have soil and subsoil samples collected and processed. The results from particle size analysis for FvPDa show more silt and clay, especially below 3 m b.g.l than the FvWDa site (**Figure 5.1**). There was also more soil and subsoil material at FvPDa to obtain results from compared to FvWDa which has a shallower soil in comparison. See BH installation records in **Appendix 3** and section 5.3.1.

Table 5.1 Soil and subsoil results from Brookside Laboratories Inc. for fractured-volcanic well-drained arable (FvW/Da) and fractured-volcanic poorly-drained arable (FvPDa).

Piezo. I.D. and depth	CEC (m.eq/100g)	pH	OM (%)	S (mg/kg)	P (mg/kg)	Ca (mg/kg)	Fe (mg/kg)	Mg (mg/kg)	K (mg/kg)	Na (mg/kg)	OC (%)	Sand (%)	Silt (%)	Clay (%)	Carbon (%)	Nitrogen (%)	C:N ratio
FvW/Da																	
Lower BH 0-1m	7.36	6.7	3.09	18	26	1,121	248	147	128	47	1.44	44.54	35.78	19.68	1.6	0.19	8.42
Lower BH 1-2m	3.56	7.4	0.59	18	18	478	190	94	85	39	0.22	66.19	29.48	4.33	0.24	<0.05	-
Upper BH 0-1m	2.91	7.0	0.47	15	9	323	195	111	81	38	0	69.51	21.05	9.44	<0.2	<0.05	-
Upper BH 1-2m	3.72	7.1	1.38	24	27	466	147	76	186	65	0.43	53.92	41.5	4.58	0.66	0.07	9.43
Upper BH 2-3m	3.47	6.3	0.71	30	11	396	121	96	188	48	0	59.74	39.2	4.06	<0.2	<0.05	-
FvPDa																	
0-1 m	7.86	7.3	1.07	26	7	1,212	179	163	87	50	0.53	60.32	31.46	8.22	0.56	0.06	9.33
1-2 m	6.79	7.4	0.64	23	9	866	193	240	75	61	0.35	63.4	20.8	15.7	0.3	<0.05	-
2-3 m	6.96	7.7	0.49	15	12	1,028	177	176	56	49	0.4	77.4	18.02	4.58	0.3	<0.05	-
3-4 m	20.28	7.9	0.42	41	10	3,540	183	240	138	52	0.95	35.64	40.58	23.78	0.95	<0.05	-
4-5 m	20.99	7.9	0.46	52	12	3,620	206	271	155	55	0.33	29.81	42.96	27.23	1.25	<0.05	-
5-6 m	22.98	8.0	0.51	99	14	3,899	252	329	192	58	0.26	24.17	44.05	31.78	1.31	0.05	35.2
6-7 m	25.11	7.8	0.58	125	14	4,269	293	363	185	62	0.34	20.11	41.35	38.54	1.76	<0.05	-
7-8 m	25.78	8.1	0.38	76	13	4,556	251	285	139	61	0.22	35.52	41.56	22.92	1.49	<0.05	-
8-9 m	22.62	7.9	0.38	71	13	3,907	260	291	132	74	0.23	31.37	39.4	29.23	1.53	<0.05	-
9-10 m	17.84	8.0	0.5	45	11	3,079	222	232	102	58	0.27	43.39	30.97	25.64	0.94	-	-

5.3 *Geology and hydrogeology*

5.3.1 Borehole installations

Air rotary drilling of 20 cm nested piezometer BHs with multi-piezometer levels to target the shallow, interface, and deep groundwater were installed under the authors supervision at the I/KWDa, FvWDa, and FvPDa sites in October 2008, and in November 2009 at FmWDa_{1/2} BH installation was carried out the by the ACP. Across the seven sites used for the project 11 nested piezometer BHs were installed with a total of 33 piezometers. Air rotary drilling was used for all boreholes including the flowing artesian aquifer at FvPDa. As well as air-rotary drilling at FvPDa, a continuous solid stem auger drilling using a spiral welded blade was employed to drill piezometers around the outskirts of FvPDa. The equipment used was called a Giddings Hydraulic Soil Sampling, Coring and Drilling machine. Nested piezometers were sealed in each BH using a bentonite:cement grout mix (3:1) and left to set overnight before installation of the next piezometer above to isolate each MP depth. 60 mm uPVC plastic piping was used for each piezometer and was covered in a geotextile sock to prevent excessive sediment ingress through perforated screen slots in selected sections of the piping (between 1-4 m). BH logs are detailed in **Appendix 3**.

At KWDa no BHs were drilled next to the Boiling Spring however, at two locations within the catchment BH installations occurred using air rotary drilling which was commissioned by the Environmental Protection Agency (EPA). At one site located 1.5 km NWW of the Boiling Spring a water strike was encountered at 29, 38, 59, 62, and 65 m b.g.l. At the same location less than 5 m away another BH was constructed which had a water strike at 1.2 m b.g.l. The other location which had BHs installed were approximately 0.6 km NEE of the Boiling Spring and less than 10 m away from the R. Nuenna channel. Here water strikes happened at 20 and 23 m b.g.l at one BH, while at the other BH (again located less than 5 m away from the other BH) water strikes were found at 1.5 and 6 m b.g.l (**Appendix 3**). This demonstrates the variability across the KWDa site of water saturated pathways within this Dinantian pure bedded limestone aquifer.

BH installations using air rotary drilling methods at I/KWDa clearly show that the upper 4 m is dry sandy deposits with occasional lenses of gravel and sand which may act as water bearing routes (**Appendix 3**). At the site isolated lenses of clay are present but they are not continuous (Premrov, 2011). For example at MP1 no clay was found but at MP2 between 2.2 - 4 m soft silty clay was found with a small water strike in the gravel present above this

discontinuous clay layer. At MP1 three water strikes occurred and these were sealed appropriately using a 3:1 ratio mixture of bentonite and cement slurry to isolate the sample point from hydrological influences both above and below the screened piezometer section. At MP1 these were shallow (6 m b.g.l), interface (10 m b.g.l), and deep (26 m b.g.l) while at MP2 only two water strikes occurred and these were at the interface (10 m b.g.l) and deep (25 m b.g.l). To sample the shallow water at MP2 water was taken from piezometer 17 (P17; **Appendix 3**) which was installed in 2006 by Premrov (2011). A shallow piezometer was not installed at MP2 because no water bearing material was encountered during drilling, hence piezometer 17, located approximately 4 m north east was used. The sample depth here was 4 m b.g.l and in sand and gravelly-sand deposits. The interface and shallow piezometers both sample sand and gravel deposits of which the interface represents an Rg aquifer. The deep piezometers represent water from the Rkd aquifer. No geophysics was carried out at the site but the area has been intensively studied by Hooker (2005), Premrov (2011), and Jahangir (2012) to reveal that amongst the freely draining grey brown podzolic soils (Gardiner and Ryan, 1980) and sand and gravels deposits exists localised clay layers which are discontinuous across the site (Premrov *et al.*, 2009a; Premrov *et al.*, 2009b). A schematical summary of the common material encountered during BH installation can be referred to in **Figure 5.9**.

5.3.2 Geophysical surveys

In October 2009 Minerex Geophysics Ltd. was commissioned by this doctoral study to carry out a geophysical survey consisting of EM31 ground conductivity, 2D resistivity, ground penetrating radar (GPR), and seismic refraction at FvWDa and FvPDa. In June 2008 Minerex were commissioned by the ACP to carry out a geophysical survey at both Site 1 and 2 in FmWDa using EM31 and EM38 ground conductivity, 2D resistivity, GPR, and seismic refraction. Electrical conductivity methods provide a rapid measure of the soil properties such as soil water, clay content, and water content. At KWDa the EPA funded STRIVE Pathways Project employed Apex geophysics to carry out VLF-R apparent resistivity and 2D resistivity survey. **Appendix 5** details additional geophysical maps for the five sites where geophysics was carried out. Summaries from each site are given below.

5.3.2.1 Geophysical survey of the karst well-drained arable (KWDa) site

At KWDa the apparent resistivity highlighted a linear area in the West with values ranging between 1,400-1,800 Ohm compared to elsewhere surveyed, where resistivity values of 200-800 Ohm dominated (blue area in **Figure 5.2**). These higher values represent areas <2m thick and between 2-5 m thick in the west while in the east, thicker deposits were found, of depths between 5-15 m thick in the south east and in the north east greater than 15 m thick. 2D resistivity at transect R8 (**Appendix 5**) in the west indicates a potential fissure. This is more than likely a karst conduit (Rkc) within the mainly dominated karstified diffuse (Rkd) aquifer. This conduit is located up-gradient of the Boiling Spring and may be a good source of water to feed the Boiling Spring. Any other water from the catchment may feed into this conduit, collect and get rapidly transferred, in comparison to diffuse karst areas, to the discharge spring.

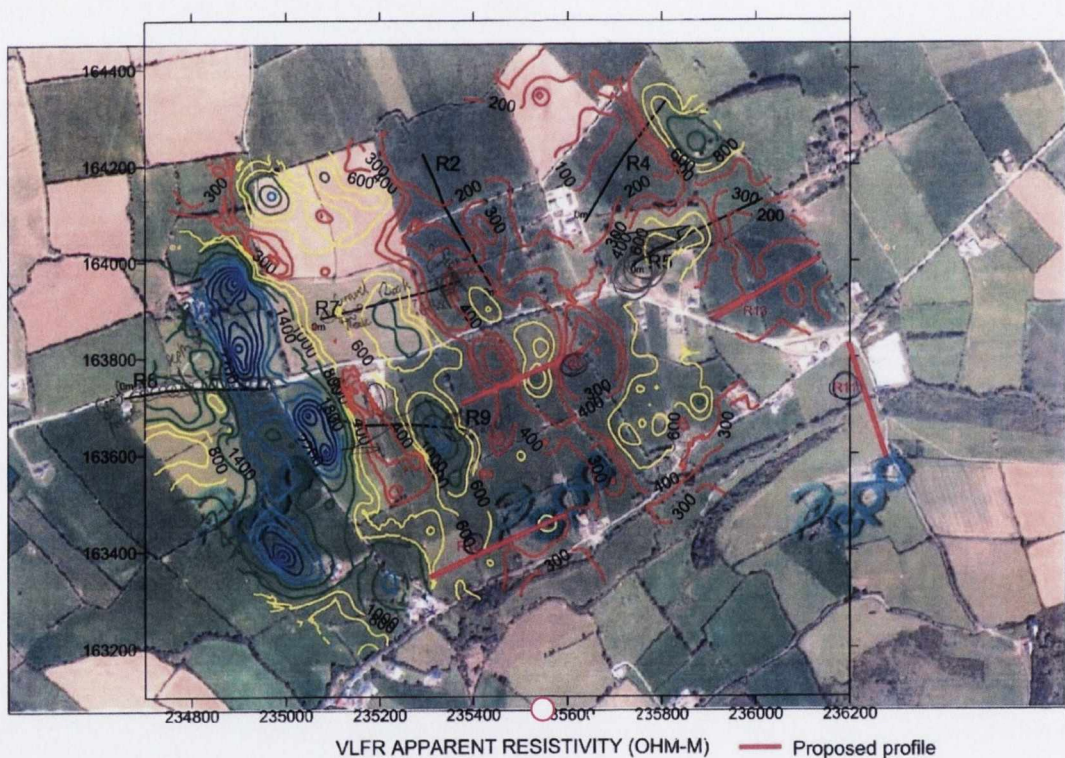


Figure 5.2 2D resistivity for karst well-drained arable (KWDa). Blue areas represent overburdens <2m. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

5.3.2.2 Geophysical survey of the fractured-volcanic well-drained arable (FvWDa) site

At FvWDa 2D resistivity found that across the fields which had geophysics carried out (fields housing Lower BH, Upper BH, Lower Sp. and Upper Sp.) that the rock was highly to moderately weathered with the most weathered rock occurring closest to the surface. EM31 ground conductivity surveys revealed a gravel rich upper layer which also indicates the high degree of weathered rock at FvWDa (**Appendix 5**). To the north of the site and north of the Lower BH and Lower Sp., a significant change in EM31 indicates a change in soil and subsoil to thicker deposits with a higher clay and moisture content (**Figure 5.3**). This change in EM31 coincides with the occurrence of numerous springs. These springs are the source and start of the streams in the catchment (see three tributaries in **Figure 4.7**).

Around the Lower BH resistivity values close to the surface suggest more clay rich soils at or near the surface although one zone of higher resistivity values indicates a lens of sand & gravel. Between 10-12 m depth b.g.l (75-80 mAOD) more compact and less clayey material was found. Seismic refraction data revealed that from 0.5-1 m the overburden was topsoil with a loose compaction. Between 2-5 m b.g.l a stiff and dense material of weathered rock or gravel was encountered. The depth to solid rock was found to be between 5 and 15 m across the site reflecting significant folding and faulting.

At the Lower Sp. high resistivities at depth indicate bedrock with a possible anticline of high resistivity rock below the Lower Sp.s location. Ground penetrating radar (GPR) indicated few features of interest in the upper 1 m apart from at the Lower Sp. where one layer appears to overlap another. This may indicate one soil layer dipping below another or the approach of bedrock to the surface. A number of boulders and bedrock outcrops are also present across the site.

2D resistivity across the Upper BH indicates a 5 m thick layer of highly weathered rock which returns as gravel from the borehole logs (**Appendix 3**). Below this weathered layer, resistivity infers an increased amount of weathering within the rock.

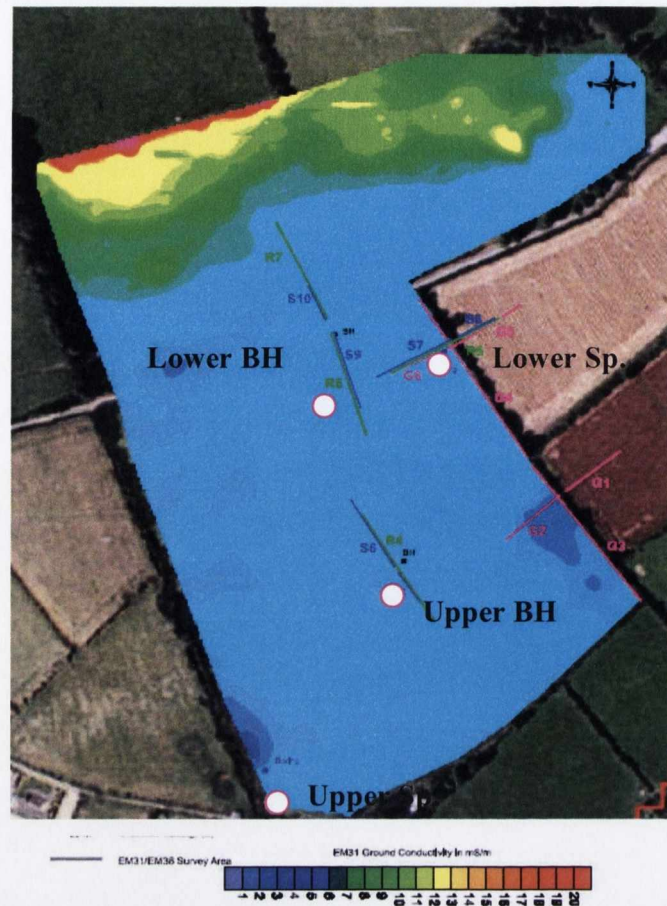


Figure 5.3 2D resistivity for fractured-volcanics well-drained arable (FvWDA). Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

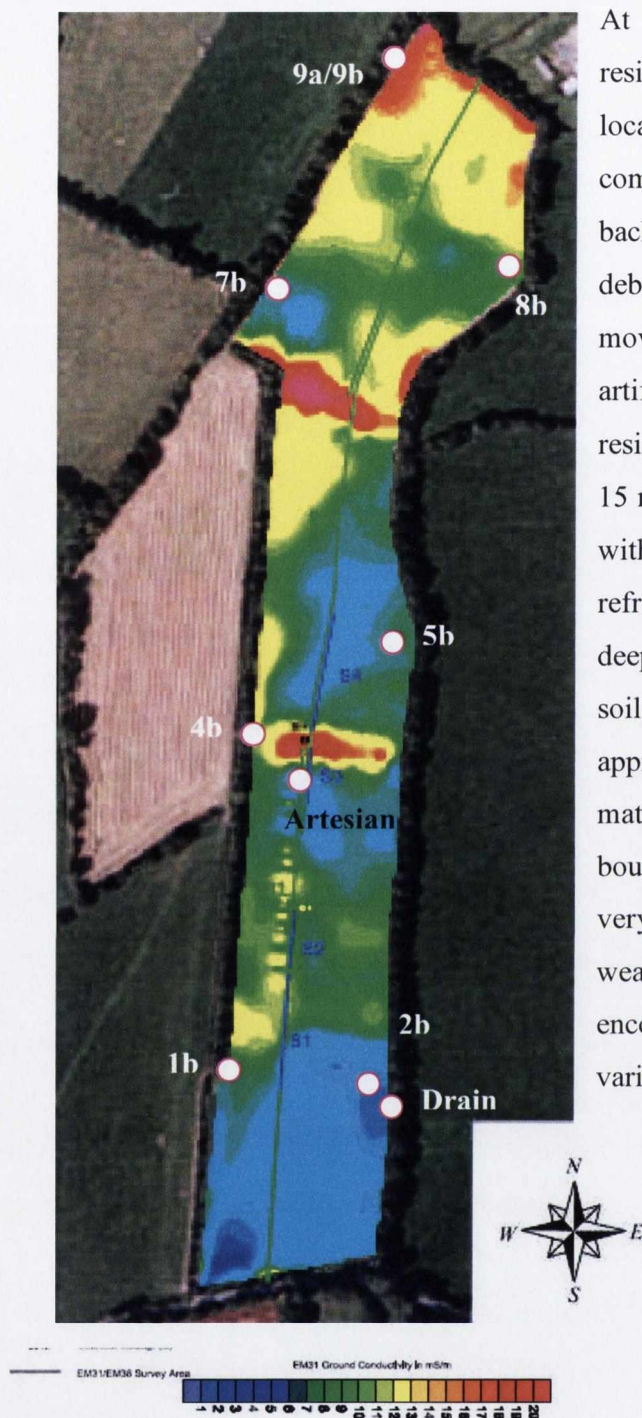
5.3.2.3 Geophysical survey of the fractured-volcanic poorly-drained arable (FvPDa) site

Geophysics at FvPDa revealed thick gravelly clay deposits across most of the site, although some lenses of more sandy and gravelly material were found closer to the surface near the centre of the site (**Appendix 5** and **Figure 5.4**) which are indicated by blue. There were variations in surface resistivity and conductivity values which indicate localised zones of gravel rich material within the thick gravelly clay deposits dominant at the site. It was these locations where additional piezometers were installed using the Gidding's Rig (see section 5.3.1).

The southern most part of the survey area had thin sand and gravel deposits. Near field boundaries, higher conductivities indicate the near surface effects of streams and drains inferring more saturated areas with a higher clay content.

Across the site 2D resistivity indicates low resistivity values (<250 Ohm-m) in the upper 10-15 m which indicate gravely clay or boulder clay material. A few higher resistivity (>400 Ohm-m) zones were encountered close to the surface particularly between 330-430 m where piezometers 4b and 5b are located. These zones of higher resistivity are gravelly deposits in the clay, and extend laterally towards surface water drainage ditches and streams which run alongside the outer perimeter of the site (see red boundary in **Figure 4.8**). **Figure 5.5** shows a summary of the material each piezometer was drilled through using data gathered during the 2D resistivity survey.

The blue areas for EM31 ground conductivity at FvPDa represent areas less water saturated or dominated by clay while red indicates the opposite. At sample point 1b (**Figure 5.4**) and south of this the soil is less clay rich. North of the site, the green symbolises areas wetter with blue patches showing the location of gravelly deposits. The two red linear areas are ditches and field boundaries with trees and hedgerows. In field two where 4b, 5b, and the artesian MP are located, a large patch of gravel extends across the site. MPs 4b and 5b were located here as these gravel lenses represent pathways allowing water movement. The location of 7b and 8b also represent these gravel lenses however, 9b is located in an area of clay rich deposits. The cross section of the area through geophysics indicates that the further north, the soil and subsoil become thicker. The artesian BH at FvPDa samples water from 11.5m b.g.l but the other piezometers collect water from several other depths (**Figure 5.5**). The deepest of these piezometers is 2b which samples water from 8.6 m b.g.l. At this level the well is flowing slightly with a trickle of overflow. This indicates that artesian conditions can be found as far south as 2b should a BH be drilled deep enough another flowing artesian well may occur. At 2b the piezometer taps a mixture of gravel and some groundwater upwelling into the gravel from the confined aquifer beneath. The shallowest piezometer is 8b (**Figure 5.5**) in field 3 but this is because saturated material is closer to the ground surface than elsewhere.



At 45 m north near piezometer 1b a high resistivity feature (**Appendix 5**) indicates a localised gravel lens, which from personal communication with the land owner, was a back-filled ditch with broken bricks and debris following hedge removal. Water moving along this is sampled through the artificial subsurface drain near 2b. 2D resistivity also indicates that at greater than 15 m depth, the bedrock lithology is folded with slates and volcanics. Seismic refraction revealed that from 0.4-1.2 m deep an overburden of topsoil or clay and soil with a loose compaction is present. At approximately 2-3 m b.g.l a stiff dense material was encountered inferred as boulder clay. From 8-20 m b.g.l a stiff to very stiff gravelly clay material with weathered rock at the base was encountered. The depth to solid rock varies from 10-30 m across the site.

Figure 5.4 2D resistivity for fractured-volcanics poorly-drained arable (FvPDa). Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

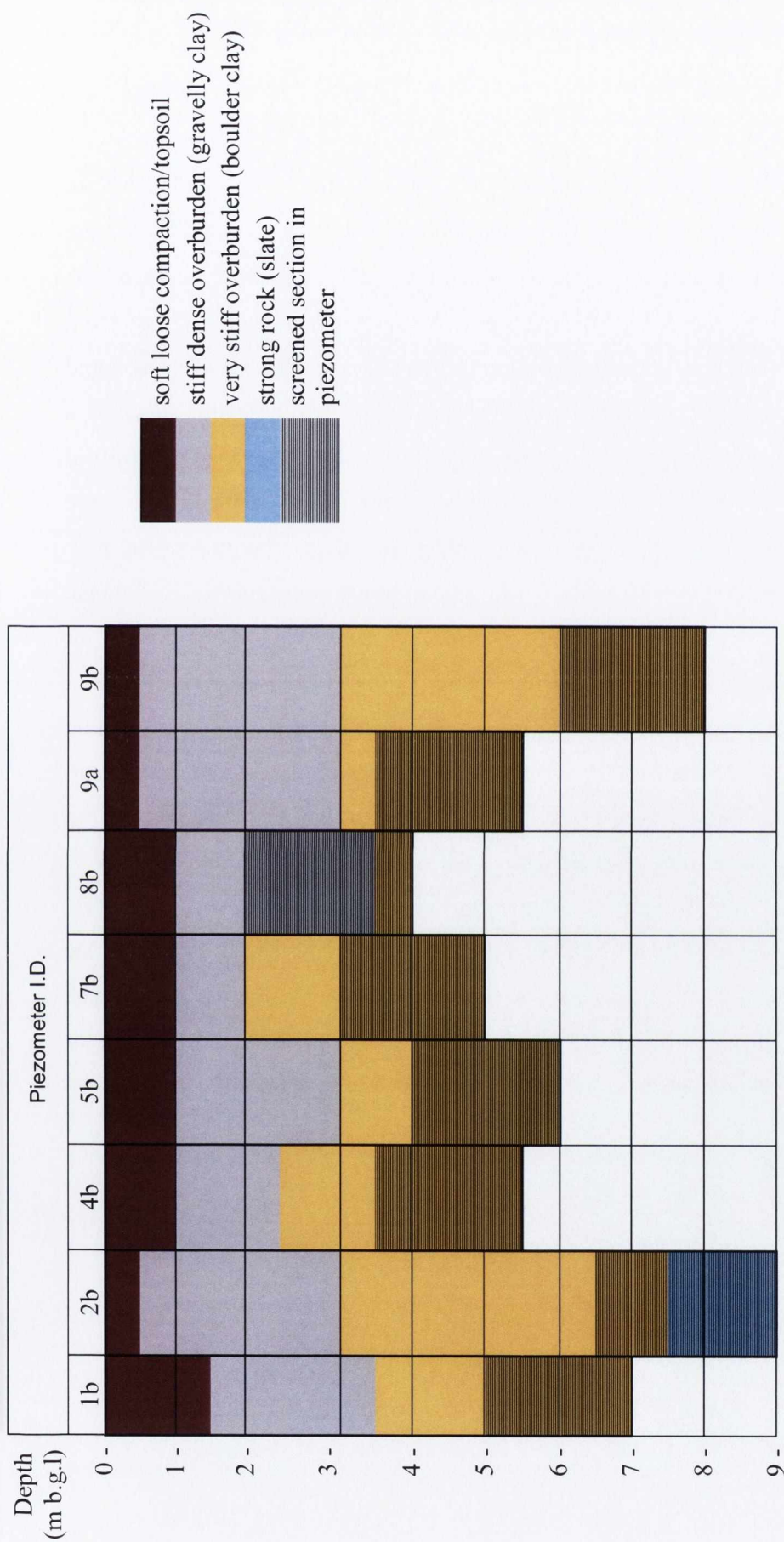


Figure 5.5 Schematic cross section of material encountered at the piezometers drilled using a Giddings Hydraulic Soil Sampling, Coring and Drilling machine at the fractured-volcanics poorly-drained arable (FvPDa) site.

5.3.2.4 Geophysical survey of the fractured metasediments well-drained arable Site 1 (FmWDa₁)

EM31 ground conductivity at FmWDa₁ (**Figure 5.6**) had relatively low conductivities measured which indicate weathered and gravelly deposits. Higher conductivities were found closer to the stream indicating clay-rich overburden and a greater depth-to-bedrock. Little variation was found across FmWDa₁ from EM31 ground conductivity indicating near surface rock and weathered deposits. Between 60-200 m a channel feature was found indicating a change in material type close to the surface (**Figure 5.6**). What is apparent is that high conductivities are present which are associated with saturated or clay rich soils at the eastern end of the site close to the river. Between 80-160 m low conductivities were measured inferring thinner soils or more gravel rich material. 2D- resistivity profiles show clay rich material (red: <100 Ohm-m) to the north-west of the stream running alongside the bottom of the site. Values increase uphill (north west) suggesting more gravelly or weathered material is found uphill. At depth variations in resistivity indicate a change in lithology to strong rock inferred as slate. A cross-section for 2D resistivity and seismic refraction was carried out c.50 m from the stream at the bottom of the hill. The interpreted cross section shows c.13 m of overburden before solid rock was encountered. From geophysics the upper 2 m of this overburden was clayey topsoil, below this was 3 m of gravelly clay, and then 9 m of highly weathered slate separates topsoil from solid rock. GPR data from site 1 shows a thin layer of topsoil 0.1-0.2 m in thickness across most of the site. Below this from 0.2-0.6 m, represents a lower subsoil layer. High amplitude diffractions and features across the transect represent localised cobbles and boulders or zones of increased gravel content.

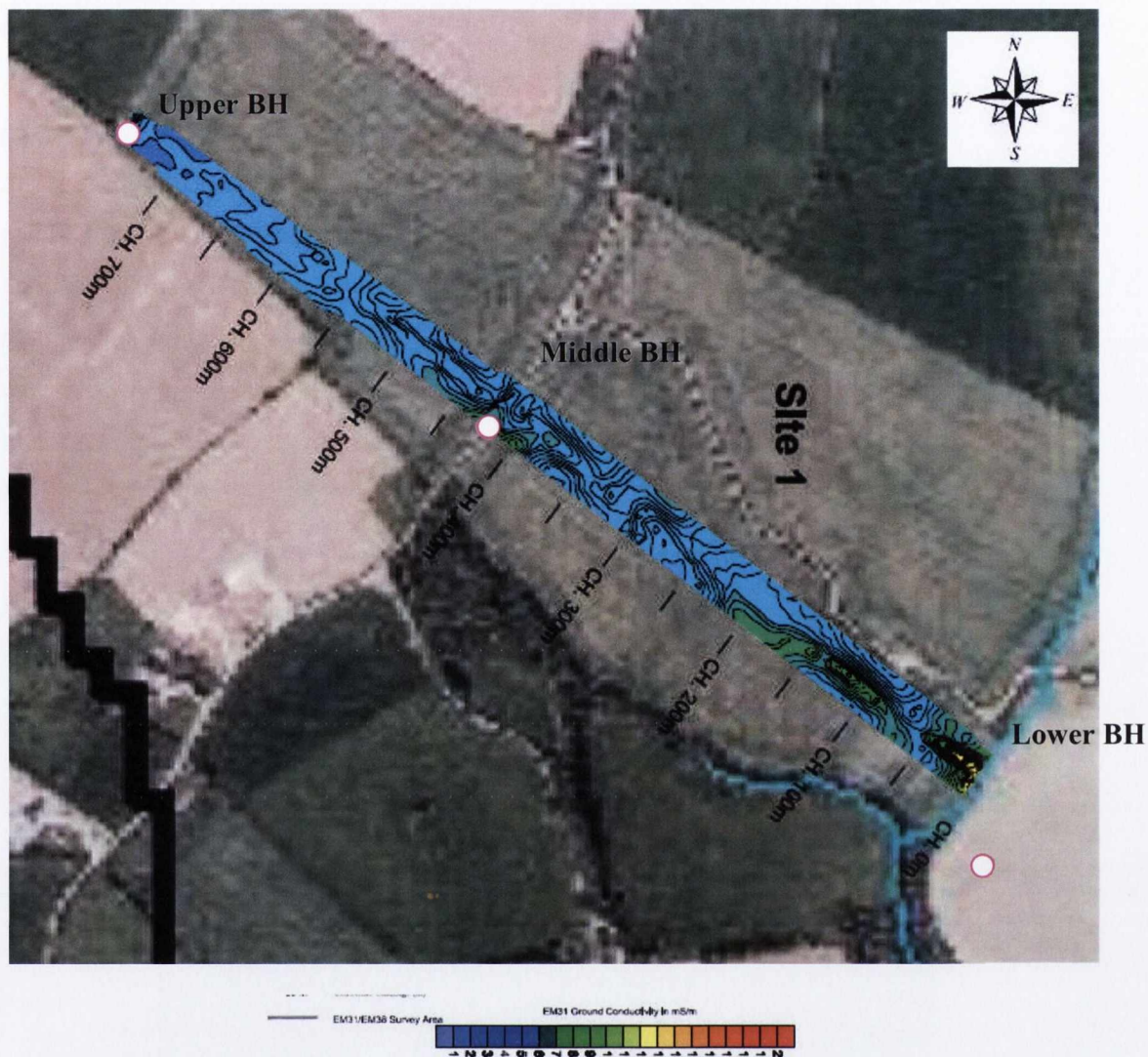


Figure 5.6 2D resistivity for fractured-metasediments well-drained arable site 1 (FmWDA₁). Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

5.3.2.5 Geophysical survey of the fractured metasediments well-drained arable Site 2 (FmWDA₂)

EM31 ground conductivity for FmWDA₂ (**Figure 5.7**) shows a distinct change with low conductivities (green and yellow colour in **Figure 5.7** indicating shallow bedrock or sandy/gravelly overburden) in the lower field which houses the Lower and Middle BHs and then uphill in the field with the Upper BH which borders with the catchment boundary, shallow rock or gravel deposits are present (blue on **Figure 5.7**). Conductivity generally decreased downhill towards the stream (north west) suggesting a deepening of rock or

more clay rich material. Between 30-80 m a zone of higher conductivity was encountered inferring thicker clay rich deposits (yellow colour in **Figure 5.7**). 2D resistivity for FmWDA₂ had a low resistivity from 30-60 m along the profile. This is the area surveyed beside the stream and resistivity infers a zone of gravely clay material to a depth of 10 m. For the rest of the transect, uphill resistivity values ranged from 400-2,000 Ohm-m indicating a gravely overburden overlying rock. Depth of overburden to solid rock fluctuates around 14 m. The top 5 m of this is topsoil of loose compaction and 9 m of gravely clay. This overlies slate from Ordovician metasediments (GSI, 2008b). GPR gave a thin layer of topsoil from 0.1-0.2 m depth. A lower subsoil layer extended from 0.7-1 m b.g.l. High amplitude diffractions and features across the transect represent localised cobbles. A strong reflection at 0.5 m depth between 40-60 m along the transect may indicate the top of the water table. From 225 m along the transect uphill and south east, the material changes from more saturated clay-rich materials to more gravelly deposits.

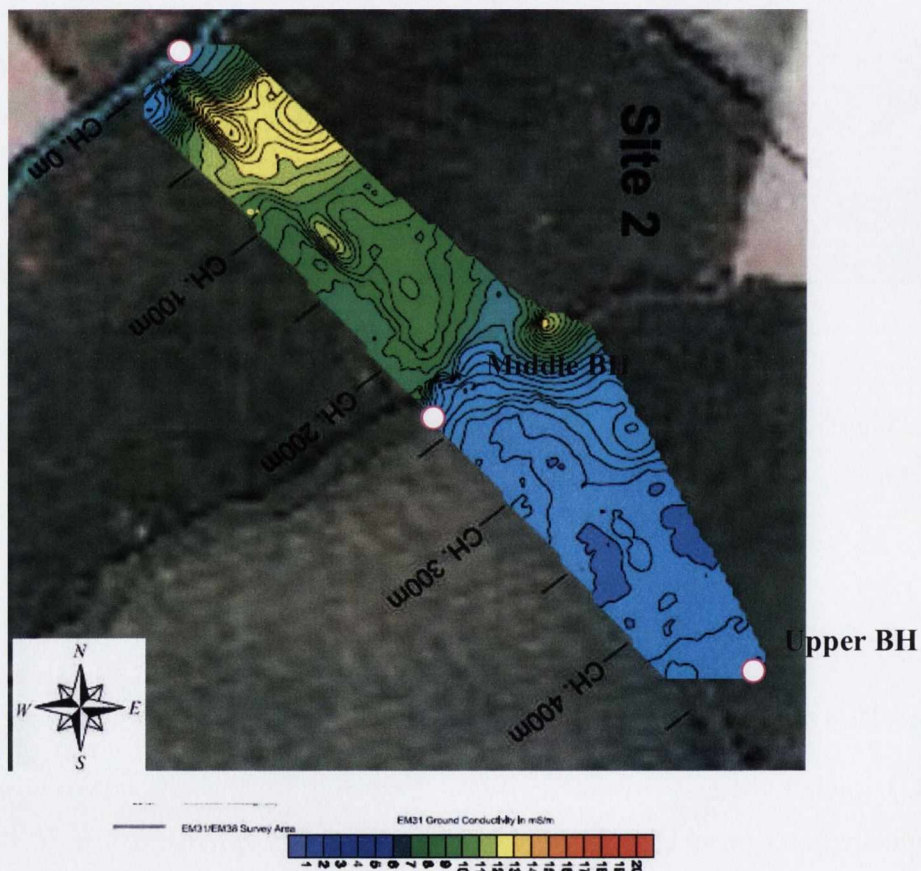


Figure 5.7 2D resistivity for fractured-metasediments well-drained arable site 2 (FmWDA₂). Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

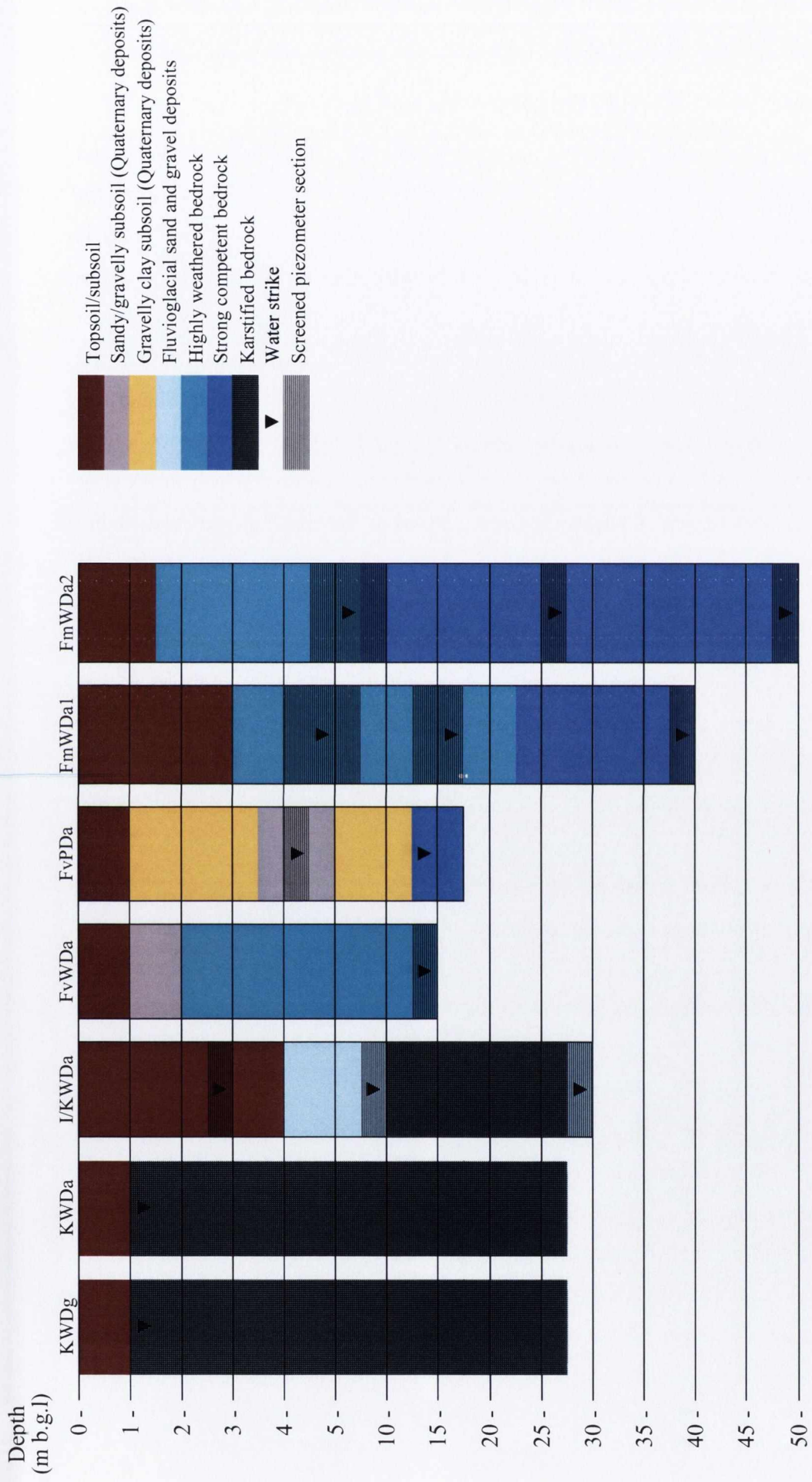


Figure 5.8 Schematic summary and comparison of material encountered across each site using information obtained from borehole installation records and geophysical surveys.

5.3.3 Summary of subsoil and Quaternary deposits at each site

The subsoils of each site have been summarised in **Table 5.2**. The subsoil at KWDa and KWDg is stated by Fealy *et al.* (2009) as bedrock at or near the surface which is correct for both these sites however, the proportion of bedrock at or near the surface in KWDg is much more than KWDa with more numerous karst features present such as swallow holes and turloughs. At the I/KWDa site the subsoil is gravelly and the extent of these gravel deposits has rendered the area an aquifer (GSI, 2008a). Interbedded within the unconsolidated gravel deposits are discontinuous clay lenses (Premrov, 2011). The gravel deposits yield water and piezometers were installed to sample this water between 8 – 10 m b.g.l (**Appendix 3**). At FvWDa the subsoil was stated by the GSI (2009) as bedrock at or near the surface (see section 4.5.4.4). BH installations at the site indicated that highly weathered bedrock was encountered between 2 – 5 m b.g.l. across the site. During BH installation this weathered rock did not have any significant water bearing fractures which would yield water until 16 m b.g.l. and 10 m b.g.l. for the Lower and Upper BHs, respectively. So although the bedrock was highly weathered at FvWDa and piezometers were installed at depths which may potentially yield water, the shallowest groundwater at FvWDa was present below 10 m (**Appendix 3**). More clay is present in the Lower BH at FvWDa supporting the inference from geophysics data that the soil is changing into a gley rather than remaining an acid brown earth. At the FvPDa site the GSI state the subsoil as Irish Sea Till derived from limestone. These deposits were encountered during drilling of both the flowing artesian well and the shallower piezometers across the boundary of the site (**Appendix 3**). Samples collected every metre and analysed for particle size (see section 5.2) revealed that below 3 m the clay fraction of the subsoil increases as the sand and silt fractions decrease (**Figure 5.1**). The increase in clay indicates development from a gley soil to an Irish Sea Till. **Figure 5.9** shows this material encountered at 5.5 m with a screened piezometer section installed below 5.5 m (**Figure 5.5**). At FvPDa significant changes in CEC can be found below 3 m changing from an average of 7.2 m.eq/100g for the top 3 m to an average of 22.23 m.eq/100g between 3-10 m. The pH at FvPDa also becomes more alkaline with depth, Ca in general increases as does K, Na, and the clay content. The subsoil at FmWDa_{1/2} is stated by Fealy *et al.* (2009) as till derived from lower Palaeozoic sandstones and shales. During BH installation at FmWDa₁ the till was highly weathered and had isolated water bearing fractures for the Upper and Middle BHs, but in the Lower BH more saturated deposits were encountered (**Appendix 3**). 2D

resistivity across the site also found this change in saturation at 50 m NW of the stream with a depth of 9 m of weathered rock, more saturated than uphill before stronger rock was encountered. At FmWDa₂ again deposits were more saturated in the near-stream BH than uphill and as with FmWDa₁ highly weathered deposits were found across the site. 2D resistivity indicates the subsoil became less weathered and saturated from the Middle BH to 80 m from the stream where the saturation of material became more saturated (**Figure 5.7**).



Figure 5.9 Material encountered 5.5 m b.g.l at piezometer 1b at the fractured-volcanic poorly-drained arable (FvPDa) site during Gidding’s Rig drilling.

Table 5.2 Summary of subsoil and Quaternary deposits at each chosen site.

Site	Description
KWDg	Bedrock at or near surface with numerous outcrops and karst features.
KWDa	Bedrock near the surface with less outcrops and karst features compared to KWDg.
I/KWDa	Gravel deposits with discontinuous shallow clay lenses.
FvWDa	Highly weathered bedrock with some bedrock outcrops.
FvPDa	Heavy clay.
FmWDa ₁	Highly weathered subsoil with a higher clay content in near-stream zones.
FmWDa ₂	Highly weathered subsoil with a higher clay content in near-stream zones.

5.4 Effective rainfall and meteorology

5.4.1 Introduction

Effective rainfall has been defined by Stuyt *et al.* (2000) as the portion of rainfall which could contribute to groundwater storage. Effective rainfall is rainfall minus the actual evapotranspiration. It represents an estimate of potential recharge which may percolate through the vadose zone. To derive values of effective rainfall, models were employed which would estimate the proportion of effective rainfall that would infiltrate into groundwater which is important for the study of transport of contaminants such as pesticides to groundwater. The models used determine effective rainfall as potential recharge and make no estimation of the actual amount which could recharge. To estimate recharge from effective rainfall a method by Misstear *et al.* (2009) was used.

5.4.2 Effective rainfall calculation method

Two models were used to calculate the effective rainfall for each site used during this study and both models are based on the Penman-Monteith equation for water balance using agro-environmental conditions specific in an Irish context (Premrov *et al.*, 2010). The first was the grassland SMD (soil moisture deficit) model by Schulte *et al.* (2005) and the other the tillage SMD model by Premrov *et al.* (2010). The grassland model was created for use on grassland sites and for three different soil drainage classes (1) well-drained, (2) moderately drained, and (3) poorly drained, whereas the tillage model was created for tillage land but only on one soil drainage type: well drained. The inputs for each model were latitude, longitude, altitude, soil drainage class, and daily averages of the following five variables: minimum temperature, maximum temperature, total rainfall, wind speed, and solar radiation. The output from each model was: potential evapotranspiration (PET), actual evapotranspiration (AET), and effective drainage/rainfall. These five variables were obtained from weather stations installed and managed by the ACP for sites KWDg, FvWDa, FvPDa, and FmWDa_{1/2}. For I/KWDa data was taken from a weather station located 1 km away from the site (Sawmills Field) at the Teagasc Crop Research Centre in Co. Carlow.

5.4.3 Technical note on effective rainfall model comparisons

To ensure that the modelled effective rainfall data was accurate, at five of the sites PET was recorded from weather stations installed by the ACP. PET was calculated at the weather station using the Pennman-Monteith model. This PET although calculated, shall be termed recorded PET from here on. Recorded PET was plotted against modelled PET and a coefficient of determination (r^2) obtained for each. The closer to 1.0 the coefficient, the more accurate modelled effective rainfall data is. For sites which gave poor comparisons between modelled and recorded PET other model scenarios were tested to see if the modelled data for PET was more comparable and had a higher r^2 . Then that model was chosen since it was producing a similar output in comparison to recorded PET. **Table 5.3** shows the calculated PET results between modelled and recorded data for the sites which had PET recorded data available. The highest r^2 values are given in bold in **Table 5.3**, and these are the models used for effective rainfall at each site. For I/KWDa the tillage SMD model by Premrov *et al.* (2010) was used for effective rainfall while for KWDa no weather data was available to input into the model to generate effective rainfall. **Appendix 6** shows the comparisons visually between modelled and recorded PET.

Table 5.3 Coefficient of determination (r^2) results for modelled potential evapotranspiration (PET) and recorded PET.

Site	Grassland model: well drained	Grassland model: moderately drained	Grassland model: poorly drained	Tillage model: well drained
KWDg	0.5722	0.5725	0.5725	-
FvWDa	-	-	-	0.8791
FvPDa	-	-	0.91284	-
FmWDa	0.3774	0.3058	0.3774	0.3775

Two of the sites showed excellent comparisons between modelled and recorded PET, these were FvWDa and FvPDa (**Table 5.3**). Although not ideal the best coefficients of determination for the KWDg was 0.5725 using the grassland SMD model by Schulte *et al.* (2005) and the lowest coefficient was using the tillage SMD model by Premrov *et al.* (2010) for FmWDa however, this was the best r^2 after testing all the model scenarios. Comparison of modelled and recorded PET for the FvPDa site is shown in **Figure 5.10** with other comparisons in **Appendix 6**. Differences between the models indicate site

characteristics which will affect the amount of effective rainfall. From **Table 5.2** differences between the soil drainage class have more of an effect on the r^2 than land use.

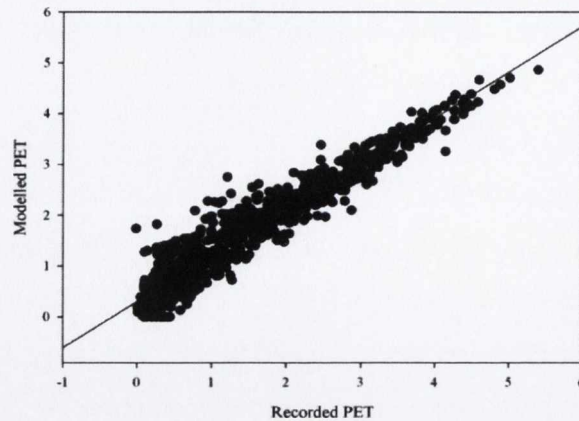


Figure 5.10 Comparison of recorded potential evapotranspiration (PET) from the fractured-volcanic poorly-drained arable site (FvPDa) with modelled PET obtained from the grassland SMD model by Schulte *et al.* (2005) with a coefficient of determination (r^2) of 0.91284.

5.4.4 Results of effective rainfall calculations and meteorology

For each site total daily rainfall has been plotted over time for as much of the monitoring period between March 2010 and March 2012 as was available. Effective rainfall has been modelled for each site except KWDa because no additional weather data apart from total rainfall was available in this site to input into the model. **Table 5.4** details the annual total rainfall, total PET, total AET, total effective rainfall, and the number of days of effective rainfall for each site in 2011.

The highest total amount of effective rainfall to occur at any site in 2011 was at KWDg with 714 mm. The least amount of total effective rainfall for 2011 occurred at I/KWDa with 284 mm (**Table 5.4**). All sites except KWDg in **Figure 5.11** mirror each others total cumulative effective rainfall over the full monitoring period. KWDg does not follow the pattern of the others, especially between July 2011 and October 2011 where cumulative effective rainfall increases at KWDg while at the other sites very little effective rainfall occurs.

Table 5.4 Total rainfall, potential evapotranspiration, actual evapotranspiration, effective rainfall, maximum and average effective rainfall and the number of days of effective rainfall for each site in 2011.

	KWDg	KWDa	I/KWDa	FvWDa	FvPDa	FmWDa _{1/2}
Total rainfall (mm/yr)	1,195	955	736	812	812	845
Total PET (mm/yr)	485	Na	721	622	620	386
Total AET (mm/yr)	437	Na	451	432	498	345
Total effective rainfall (mm/yr)	714	Na	284	380	304	500
Maximum daily effective rainfall (mm/day)	23	39 [†]	32	26	26	39
Mean daily effective rainfall (mm/day)	2	2.6 [‡]	0.8	1	0.8	1.4
Number of days of effective rainfall	139	264 [*]	54	66	135	96

na = not available.

[†] = Maximum daily total rainfall (mm/day).

[‡] = Average daily total rainfall (mm/day).

^{*} = Number of days of total rainfall.

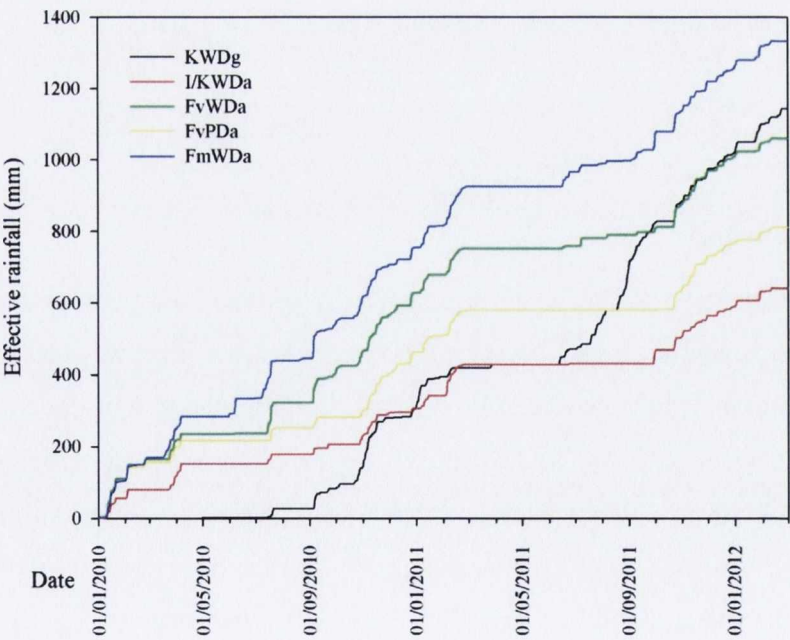


Figure 5.11 Cumulative effective rainfall for each site where effective rainfall was modelled.

The lowest air temperature was found at KWDg and the maximum air temperature remained relatively constant across all sites where meteorological information was collected (**Table 5.5**). The average wind speed was highest at I/KWDa attribute to the flat topography with few wind breaks to deter wind gathering momentum. Solar radiation was highest at FvWDa and FvPDa which are located in the same catchment, the lowest average was at FmWDa.

Table 5.5 Meteorological summary information between sites collected from weather stations.

	KWDg	I/KWDa	FvWDa	FvPDa	FmWDa _{1/2}
Minimum temperature (°C)	-16	-12	-14	-14	-5
Maximum temperature (°C)	26	26	25	25	25
Average temperature (°C)	10	9	9	9	9
Minimum wind speed (10 m/s)	0.001	0.07	0.047	0.047	0
Maximum wind speed (10 m/s)	12	21	9	9	10
Average wind speed (10 m/s)	4	7	3	3	3
Minimum solar radiation (J/cm/day)	50	23	34	34	2
Maximum solar radiation (J/cm/day)	3,118	2,899	3,089	3,089	3,095
Average solar radiation (J/cm/day)	983	882	1,030	1,030	583

5.5 Groundwater level monitoring and spring discharge

5.5.1 Methodology

In many piezometers water level loggers were present and were removed prior to measuring the groundwater level using a dipper. This water level was recorded as a cross-check on the groundwater level being recorded by the pressure transducer. Groundwater level readings were recorded at piezometers in each site where appropriate and where resources would allow. Water levels were monitored using pressure transducers at Site 1 and Site 2 in FmWDa (Solinst LT Levellogger Gold, Waterra, UK) and in MP1 at I/KWDa a pressure transducer (Mini Diver, Van Walt, UK) was installed in each piezometer targeting the piezometer screen in the shallow, interface, and deep groundwater. Pressure and temperature was recorded every 10 minutes. Each MP was surveyed to the common

Ordnance Datum: mAOD (mean sea level). **Figure 5.14** to **5.20** illustrates the daily average groundwater table for each piezometer which had a logger and daily effective rainfall. At FmWDa_{1/2} atmospheric pressure transducers were used for compensation calculations (Solinst Barologger Gold, Waterra, UK).

At KWDa and KWDg weirs were installed by the ACP and the EPA, respectively and data was obtained from these collaborators for use in this study.

5.5.2 Spring discharge results

5.5.2.1 Spring discharge results from the karst well-drained grassland (KWDg) site

Discharge from this spring was measured using a Thermo-Fisher time-of-flight area velocity meter (Mellander *et al.*, 2012). Data was collected by the EPA which was then made available to the ACP and subsequently this project. Data was only available at the time of thesis writing between 11th May 2010 and the 21st March 2011 and this discharge data is displayed in **Figure 5.12** along with the daily effective rainfall between these dates. At KWDg discharge from the spring responds throughout the year to effective rainfall during both summer low flow periods (22nd July 2010) and higher winter flow periods (30th December 2011).

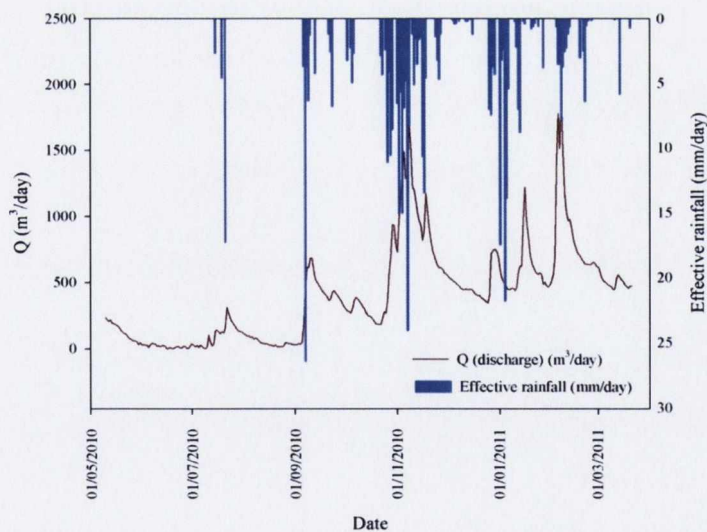


Figure 5.12 Spring discharge and total rainfall from 11th May 2010 until 21st March 2011 from the spring at karst well-drained grassland (KWDg) in Co. Mayo which is used to supply water to a group water scheme (GWS) and which is also monitored by the Agricultural Catchments Programme (ACP).

5.5.2.2 Spring discharge results from the karst well-drained arable (KWDa) site

At KWDa, downstream of the Boiling Sp. the channel splits before eventually the original flow from the Boiling Sp. reaches the R. Nuenna. One tributary leads to the R. Nuenna as a natural phenomenon while a local land owner has dug an additional channel downstream of the spring to sustain a duck pond. Using both these channels the flow was measured by Travers (2011). **Table 5.6** shows the total spring flow from the Boiling Sp. to be an average of $0.0617 \text{ m}^3/\text{s}$ for the dates when flow was measured.

The R. Nuenna receives approximately 93% of its baseflow from spring discharge (Travers, 2011). Of the six springs discharging along the R. Nuenna, Travers (2011) found that 64% of the R. Nuenna's flow was gained downstream of the Boiling Sp. from six flow measurements taken between 22nd June 2011 and 26th July 2011. From this flow measurement point downstream of the Boiling Sp. it was also found by Travers (2011) that the GWS Sp. contributed 26% while the Boiling Sp. contributed 35% to the total flow of the Nuenna.

Table 5.6 Discharge flow measured from the Boiling Spring at karst well-drained arable (KWDa) site in Co. Kilkenny.

Date	Spring flow entering the Duck pond (m^3/s)	Spring flow entering the Nuenna River (m^3/s)	Total spring flow (m^3/s)
5 th March 2010	0.033	0.0235	0.0565
21 st May 2010	0.0494	0.0388	0.0882
29 th June 2010	0.0419	0.0219	0.0638
13 th December 2010	0.0338	0.0355	0.0693
27 th April 2011	0.0282	0.0179	0.0461
22 nd June 2011	0.0363	0.0119	0.0482
28 th June 2011	0.0507	0.0155	0.0662
5 th July 2011	0.0464	0.0116	0.058
12 th July 2011	0.047	0.015	0.062
19 th July 2011	0.0437	0.0173	0.061
26 th July 2011	0.043	0.0169	0.0599

No weir was installed immediately after the Boiling Sp. to record discharge but since the Boiling Sp. contributes a large proportion of its flow to the R. Nuenna a weir approximately 200m downstream of where the Boiling Sp. enters the R. Nuenna was used. This weir is called Rocky weir and has an automatic stage recorder to log the water height every 15 minutes. This is an OTT Thalimedes Shaft Encoder which was installed by the EPA. **Figure 5.13** shows that discharge (Q) responds to total rainfall in November 2010, January 2011, February 2011, November 2011, December 2011, January 2011, and February 2011 (**Figure 5.13**). Between May and November 2011 a recession period exists were rainfall did not cause a response in Q at Rocky Weir. Flows reduce as expected between March and June indicating the summer recession, with the lowest flows expected between August and September (Dillon, 2010). A similar recessionary period exists after mid-February 2012. During these times the amount of effective rainfall would be minimal as evapotranspiration is higher in the summer and the soil moisture deficit is high, requiring more saturation before a response can occur in flow.

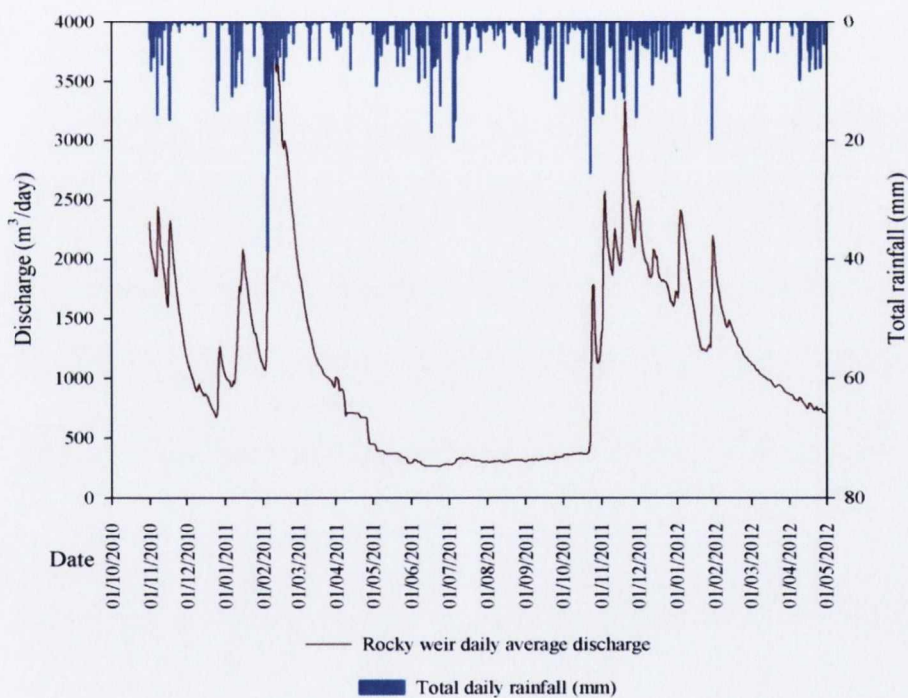


Figure 5.13 Daily average discharge from the Rocky Weir located approximately 200 m downstream from where the Boiling Spring enters the River Nuenna and daily total rainfall at karst well-drained arable (KWDa).

5.5.3 Groundwater level results

5.5.3.1 Groundwater level results for the intergranular/karst well-drained arable (I/KWDa) site

The groundwater table at I/KWDa only responds to effective rainfall during the winter months of late October to mid April. In the summer there was a recession period where the groundwater table is unresponsive to effective rainfall. At I/KWDa the groundwater table fluctuates within 50-55 mAOD. Groundwater table fluctuations (**Figure 5.14**) between January 2010 and February 2011 at the three piezometers with loggers installed in BH MP1, show a recession in groundwater table level from April to November with a steadily decreasing water table (Jahangir, 2012). This recession period was also noted by Daly (1995) as typical of Irish aquifers during these months. Beyond November 2010 and between January 2010 and March/April 2010 all three piezometers respond to effective rainfall. The best example of which is in late March where a prolonged rainfall event caused a response in the groundwater table.

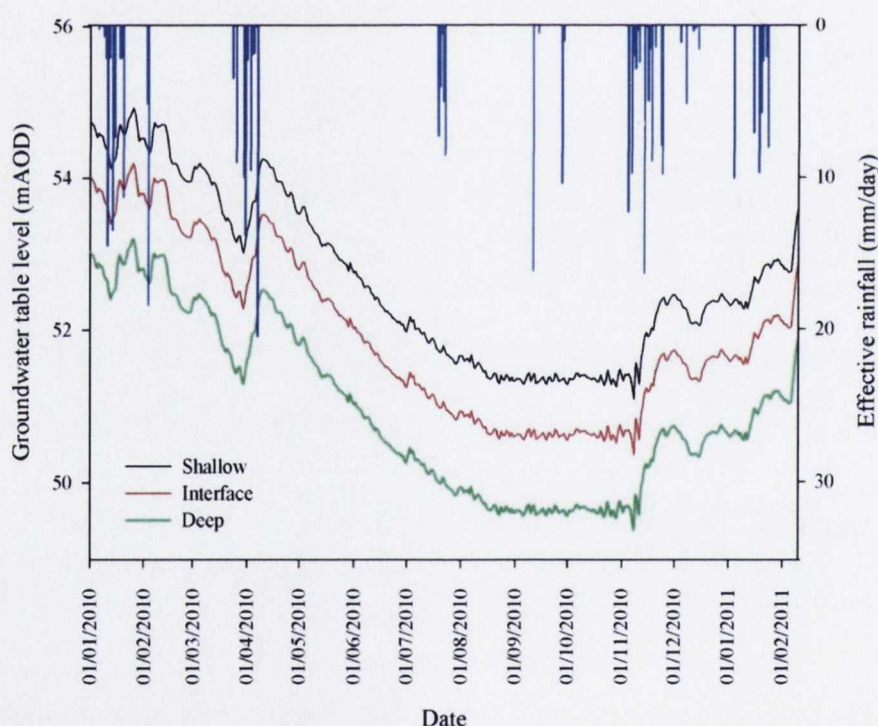


Figure 5.14 Groundwater table fluctuations and effective rainfall at the intergranular/karst well-drained arable (I/KWDa) site.

5.5.3.2 Groundwater level results for the fractured-metasediments well-drained arable site 1 (FmWDA₁)

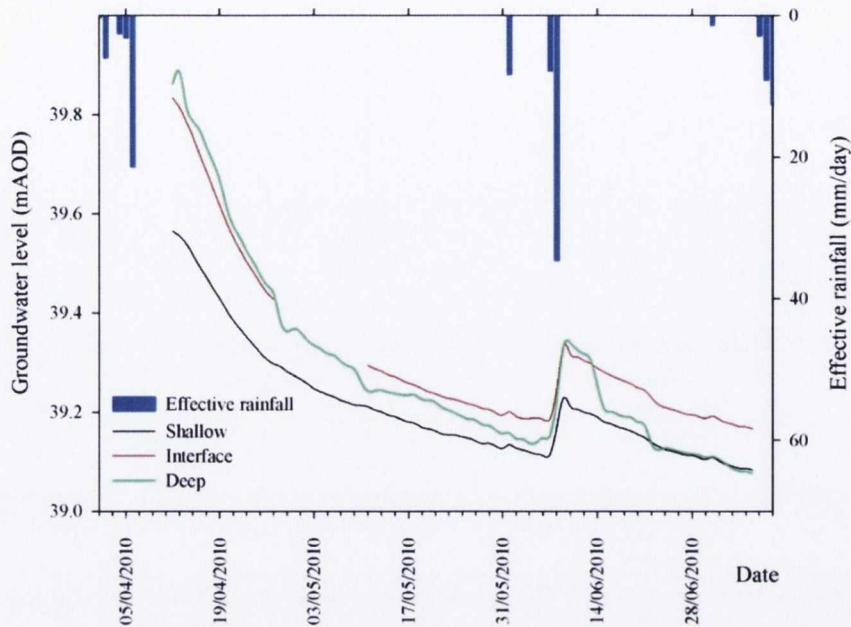


Figure 5.15 Groundwater table fluctuations and effective rainfall at the lower borehole in fractured-metasediments well-drained arable site 1 (FmWDA₁).

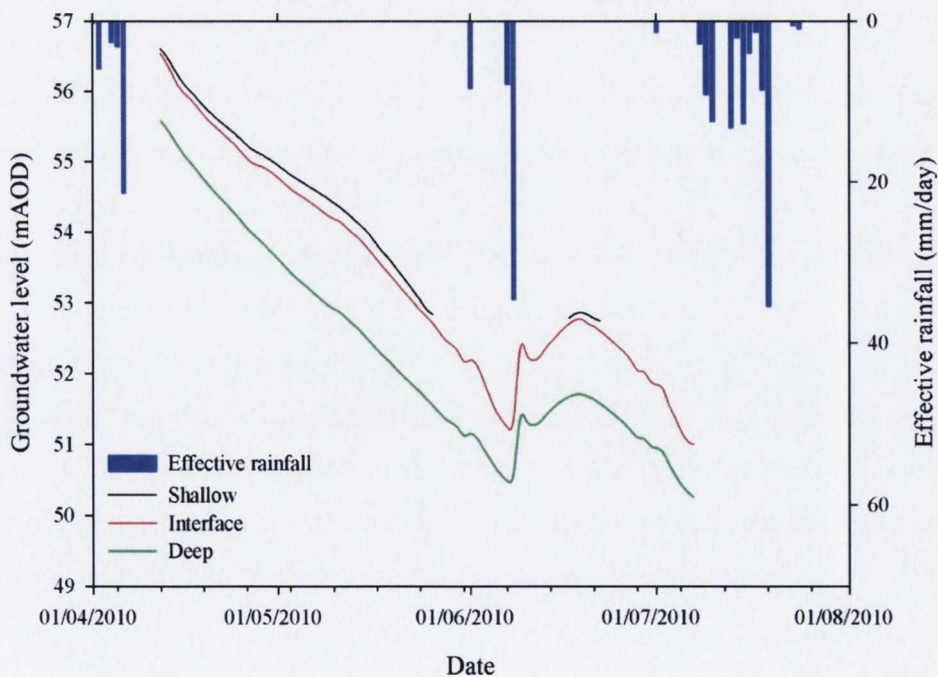


Figure 5.16 Groundwater table fluctuations and effective rainfall at the middle borehole in fractured-metasediments well-drained arable site 1 (FmWDA₁).

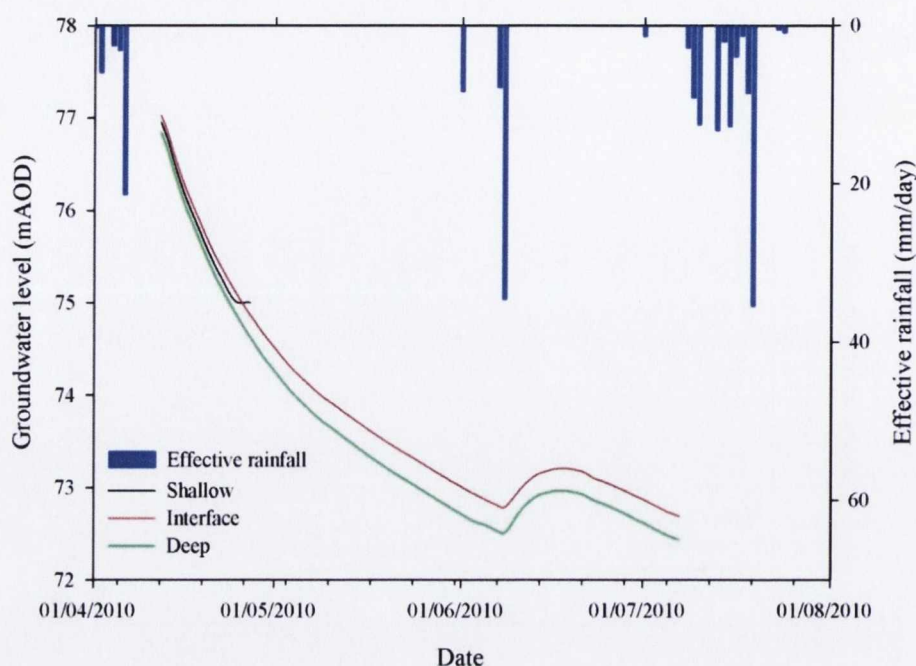


Figure 5.17 Groundwater table fluctuations and effective rainfall at the upper borehole in fractured-metasediments well-drained arable site 1 (FmWDA₁).

Groundwater level fluctuations between the three BHs at FmWDA₁ showed a response to effective rainfall in mid-June 2010. The Middle and Upper BHs show that the interface and deep piezometers mimic their groundwater level, as does the shallow piezometer when water is present. Although during these dry months with little effective rainfall occurred (**Figures 5.15 to 5.17**) the shallow piezometers in the Middle and Upper BHs are usually dry. Groundwater levels fluctuate between 50-57 mAOD for the Middle BH and between 72.5-77 mAOD for the Upper BH. At the Lower BH the groundwater level fluctuates much less between 39.1-39.9 mAOD (**Figure 5.15**). In the shallow piezometer at the Lower BH, even in the driest periods, the shallow piezometer still yields water because it is under the influence of near-stream discharge processes from the stream located approximately 2 m away. During periods when no effective rainfall has occurred the piezometers are not recharged from above ground but are instead influenced by the losing stream discharging water to reserves in the aquifer beneath. But following effective rainfall in mid-June 2010 (**Figure 5.15**) the levels of the interface and deep piezometers switch to those reflecting recharge. Following this recharging groundwater event the deep piezometer groundwater level falls more drastically than the shallow or interface piezometers.

5.5.3.3 Groundwater level results for the fractured-metasediments well-drained arable site 1 (FmWDA₁)

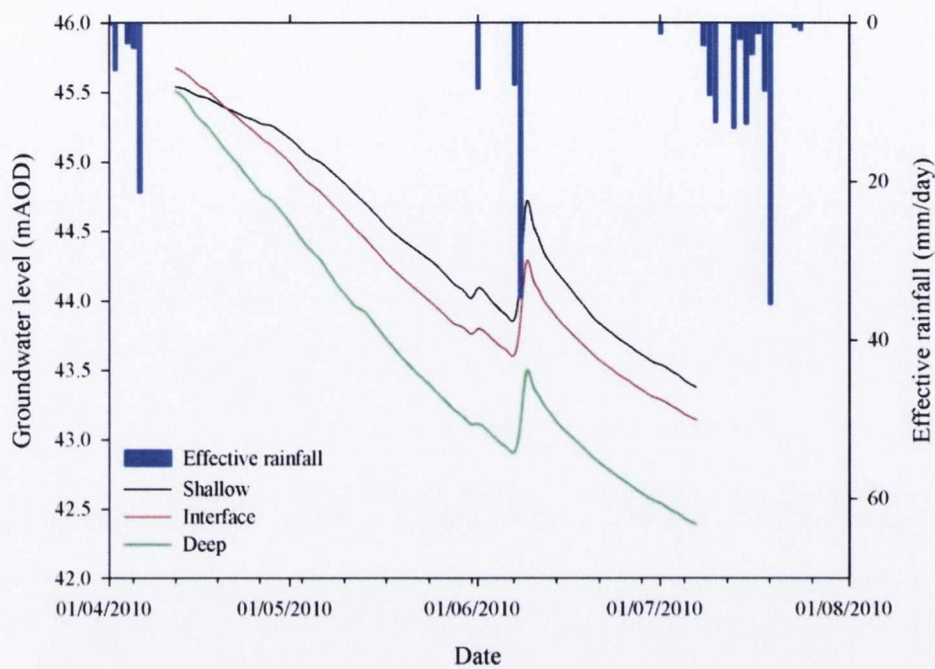


Figure 5.18 Groundwater table fluctuations and effective rainfall at the lower borehole in fractured-metasediments well-drained arable site 2 (FmWDA₂).

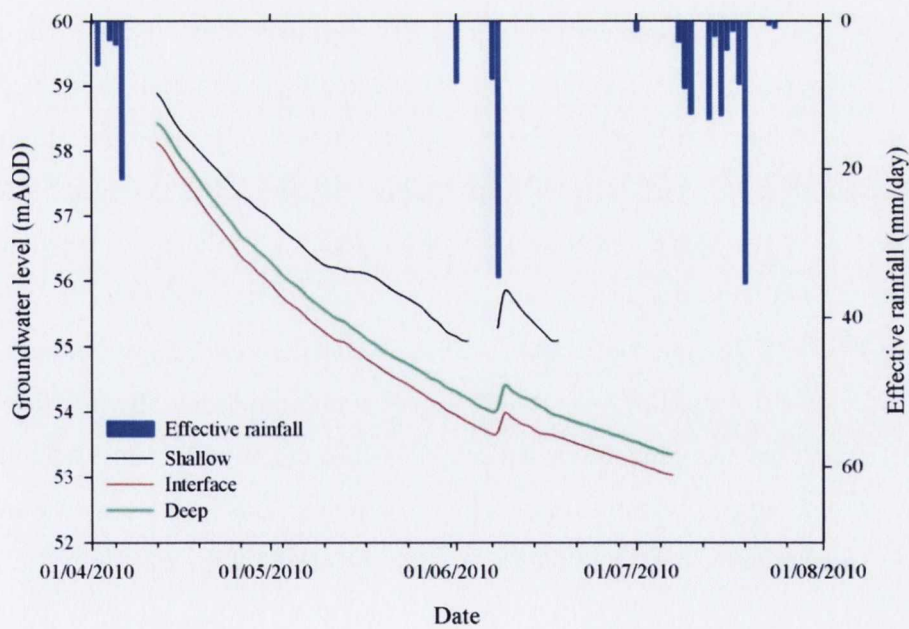


Figure 5.19 Groundwater table fluctuations and effective rainfall at the middle borehole in fractured-metasediments well-drained arable site 2 (FmWDA₂).

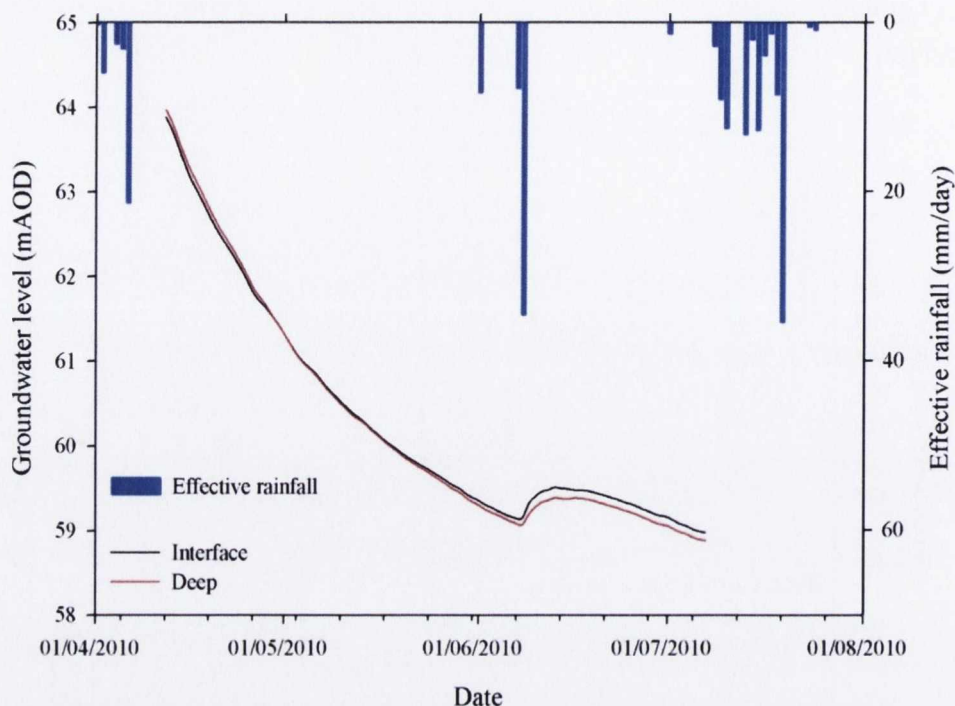


Figure 5.20 Groundwater table fluctuations and effective rainfall at the upper borehole in fractured-metasediments well-drained arable site 2 (FmWDA₂).

Groundwater level fluctuations in the summer of 2010 at FmWDA₂ show a response to effective rainfall in the catchment in all three BHs (**Figures 5.18 – 5.20**). The Lower BH at FmWDA₂ appears to have the quickest response to effective rainfall in June compared to the Middle and Upper BH but this is because of differences in the y-axis scale. The Lower BH fluctuates from 42.7-45.7 mAOD, the Middle BH fluctuates between 59-64 mAOD, while the Upper BH fluctuates between 59-64 mAOD. The shallow piezometer in the Upper BH did not have any water to measure pressure from, hence there is no water level shown in **Figure 5.20**. At the Upper BH the interface and deep piezometers have very similar groundwater levels, its only following effective rainfall that the interface heightens the water level because recharging water reaches here first but soon after groundwater levels return in both piezometers to much the same level. This indicates that water samples collected from here are potentially the same groundwater from the L1 aquifer.

Table 5.7 Summary of each sites hydrogeological properties.

	KWDg	KWDa	Boiling Sp. [†]	I/KWDa	FvWDa	FvPDa	FmWDa ₁	FmWDa ₂
at KWDa								
Minimum Q (m ³ /day)	0.23	264	92	na	0.36*	na	na	na
Maximum Q (m ³ /day)	1,935	3,814	1,335	na	18*	na	na	na
Average daily Q (m ³ /day)	409	1,115	390	na	14*	na	na	na
Minimum groundwater level height (m b.g.l.)	na	na	Na	1.4	3.1	0	0.2	0.1
Maximum groundwater level height (m b.g.l.)	na	na	na	9.0	7.7	2.9	16.4	14.7
Average groundwater level height (m b.g.l.)	na	na	na	5.3	4.7	1.2	5.8	4.2

* House Spring.

[†] Values are 35% of KWDa.

A comparison between each sites hydrology detailed in section 5.5 is summarised in Table 5.7. Between the three sites which have springs as MPs, the highest minimum, maximum, and average discharge was from KWDa however, these discharges were measured from Rocky Weir in The R. Nuenna. Since the Boiling Sp. at KWDa contributes 35% of total flow to the R. Nuenna (Travers, 2011) then the discharge of the Boiling Sp. can be estimated as 35% of total flow at Rock Weir[†]. The Boiling Sp. thus would have a more continuous discharge than KWDg with a higher minimum, but the average of both springs are similar (Table 5.7). The spring at FvWDa called the “House Sp.” is much smaller in comparison to the other springs used throughout this study. Regarding groundwater levels the shallowest groundwater table is at FvPDa which is a reflection of the shallow piezometers installed across this site as opposed to the flowing artesian well. All other sites have an average groundwater table height of between 4.2-5.8 m b.g.l. The most fluctuation in groundwater table height can be found at FmWDa₁ with a 16 m range.

5.6 Groundwater flow direction and zones of contribution

Groundwater flow direction helps understand the hydrology of the site, especially where water is travelling from and too, thus inferring the potential sources of pesticides and the direction where pesticides might travel towards. Groundwater flow can not always be determined from surface water flows and topography, so for this reason a groundwater table contour map must be determined from observed groundwater table levels. All nested BHs were cased off with bentonite slurry: this will allow potentiometric surface water level maps to be drawn reliably for each site. Groundwater will flow in the direction where the water table or potentiometric surface is sloping. Flow direction is indicated by the slope of the water table or potentiometric surface which is called the hydraulic gradient. Water level recordings were recorded in metres above Ordnance Datum (mAOD). Using Surfer software Vs. 8 (Golden software, Colorado) contour maps were drawn to show a two-dimensional representation of three-dimensional data, with contours defining equal Z values (mAOD) across the map (Surfer, 2002). These groundwater flow direction contour plots are from averages of the water levels found at the site throughout monitoring for this project.

In Chapter 4, section 4.5 using already known information about each site, estimates were derived for each sites relative zone of contribution (ZOC) which has been defined in section 3.2.2 as the catchment area which contributes water to a MP (Misstear *et al.*, 2009). Throughout the doctoral study as more information was gathered on the sites a more accurate ZOC has been estimated.

5.6.1 Groundwater flow direction and the zone of contribution at the karst-well drained grassland (KWDg) site

At KWDg groundwater flow direction was determined through dye tracer work carried out by Coxon and Drew (1986). They found that the turloughs Ardkill, Kilgassan, and Skealoghan in the East of the catchment eventually drained to the KWDg spring with average linear velocities of 79-103 m/hr, 47-123 m/hr, and 5-10 m/hr, respectively. Although these three turloughs proved to contribute water to the Sp. sampled for this study, several artificial drains have been dug throughout the catchment, and these along with the numerous other karst features such as sinking streams and swallow holes may also contribute water to KWDg Sp. Water table contour maps from Coxon and Drew (1986) show that the general groundwater flow direction is from East to West.

The ACP commissioned a study of the KWDg catchment in 2011 which involved carrying out additional tracing to work to those traces already accomplished by Coxon (1986) and mapping the entire catchment for karst features. On the 2nd June 2011 four swallow holes across the catchment were injected with different dyes and optical brighteners such as flourescein, rhodamine, and Eosin. Then from each spring in the catchment sampling was carried out twice a day. After one week three of the springs showed positive results. Only Kilrush Spring had flourescein dye, which travelled 3.5 km westwards towards Lissatava. From the Robe 'loop' spring optical brightener was detected after travelling 1.5 km north west from a swallow hole at Lugatallin turlough. For the KWDg Spring sampled as part of this doctoral study, rhodamine was detected. Rhodamine was injected into a swallow hole at Roos, 8.7 km west-southwest. **Figure 5.21** shows the new catchment boundary for KWDg. The total catchment area is now 32 km². The new catchment boundary was developed using results from the 2011 tracer study and also using water balance from four rainfall gauges installed by the ACP across the KWDg catchment. This information is currently being prepared as a paper by Mellander *et al.* for Environmental, Science and Technology. Tracer lines will be included in the article and therefore can not be shown in this thesis prior to their publication. Tracer lines from the GSI carried out by Coxon (1986) are shown in **Figure 5.21**.

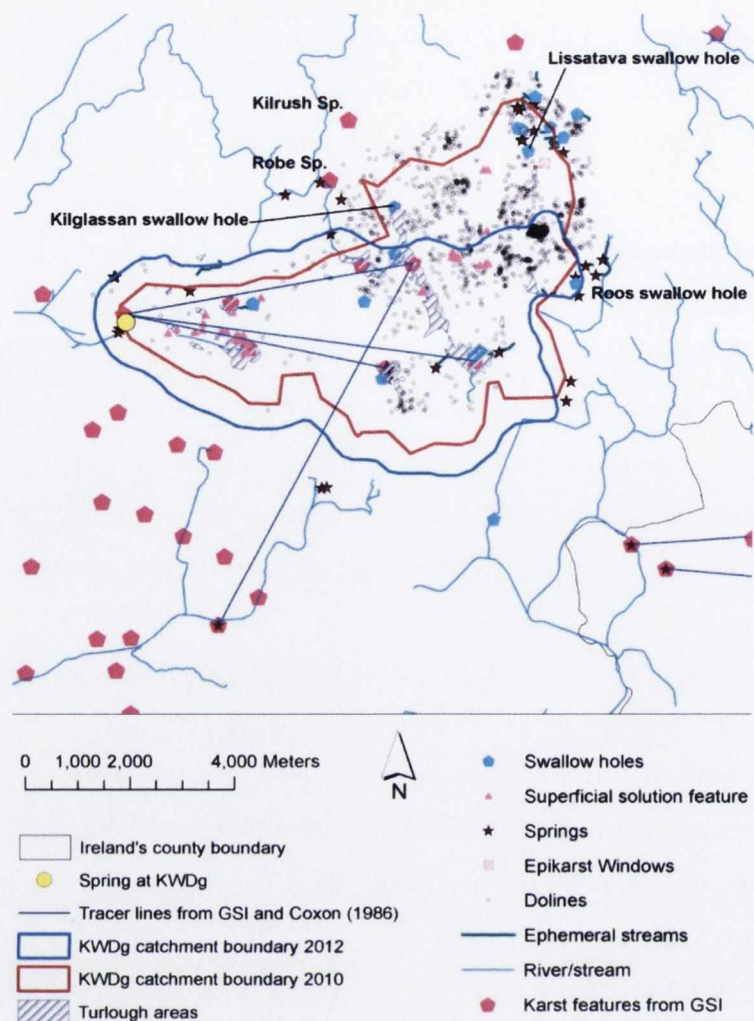


Figure 5.21 The karst well-drained grassland (KWDg) catchment in Co. Mayo, Ireland with mapped karst features commissioned by the ACP and the new catchment boundary.

5.6.2 Groundwater flow direction and the zone of contribution at the karst well-drained arable (KWDA) site

In Chapter 4 it was estimated the ZOC for the Boiling Sp. would be to the NW (**Figure 4.5**). Tracer work carried out by Walsh (2011) who injected fluorescein dye into a swallow hole located 4 km south west away from the Boiling Sp. (**Figure 5.22**) detected fluorescein dye at the GWS Sp. after 124 hours (Walsh, 2011). This successful trace is shown in **Figure 5.22** with the estimated area of the GWS Sp.s ZOC shown in yellow.

The GWS Sp. is located approximately 100 m west of the Boiling Sp. and only background concentrations of fluorescein dye was detected at the Boiling Sp. and in concentrations which did not warrant a link from the swallow hole in **Figure 5.22**. Two swallow holes in

the south of the catchment located and injected by Walsh (2011) did not discharge at the Boiling Sp. Since the GWS Sp. is located nearby to the Boiling Sp., yet the trace only discharged to one Sp., results can infer that the Boiling Sp. is not under the influence of point recharge mechanisms operating at this swallow hole in the south (**Figure 5.22**).

On the 25th July 2011 20 L of sulforhodamine B dye and 5,000 L of water were injected into a doline on the northern boundary of the catchment by Walsh (2011). On the 12th August 2011 sulforhodamine B was detected at concentrations exceeding background concentrations in the R. Nuenna 750 m downstream of where the Boiling Sp. enters the River. This slow yet successful trace from the doline to the R. Nuenna indicates the estimated ZOC of the Boiling Sp. to be in the North of the catchment as indicated in white in **Figure 5.22**. The catchment area contributing to flow from the Boiling Sp. and GWS Sp. was derived by Travers (2011) who found the average catchment area for these two springs along the R. Nuenna to be 17,372 km² with a range in catchment size from 8,591 km² in October 2010 to 27,841 km² in February 2011. In **Figure 5.22** the ZOC has been drawn for the Boiling Sp. using ArcGIS. Although the ZOC was traced back to the headlands with little to no arable land, and thus pesticide application, the low overburden highlighted in **Figure 5.2** (section 5.3.2.1) may allow recharging water through and into the karst conduit beneath.

The time it took for an elevated concentration of tracer dye from the doline in comparison to the swallow hole can indicate more diffuse karst flow pathways in operation in comparison to conduit flow which dominates at KWDg. The hydrochemistry of the Boiling Sp. indicates that its dominant discharge is associated with diffuse flow as opposed to conduit because of high alkalinity values which occur when groundwater is stored in the karst system for a longer period of time allowing for more dissolution processes (Walsh, 2011).

The Boiling Sp. contributes 35% of stream discharge to the Nuenna while the GWS Sp. contributes 34% (Travers, 2011; McAleer, 2012). These two streams located nearby in total contribute 69% of stream discharge to the R. Nuenna with stream flow and spring flow measurements suggesting that 80% of discharge in the R. Nuenna is from springs and drains during base flow conditions (McAleer, 2012). Tracer work and flow velocities measured by Walsh (2011) indicate a relatively poorly developed conduit system at KWDa.

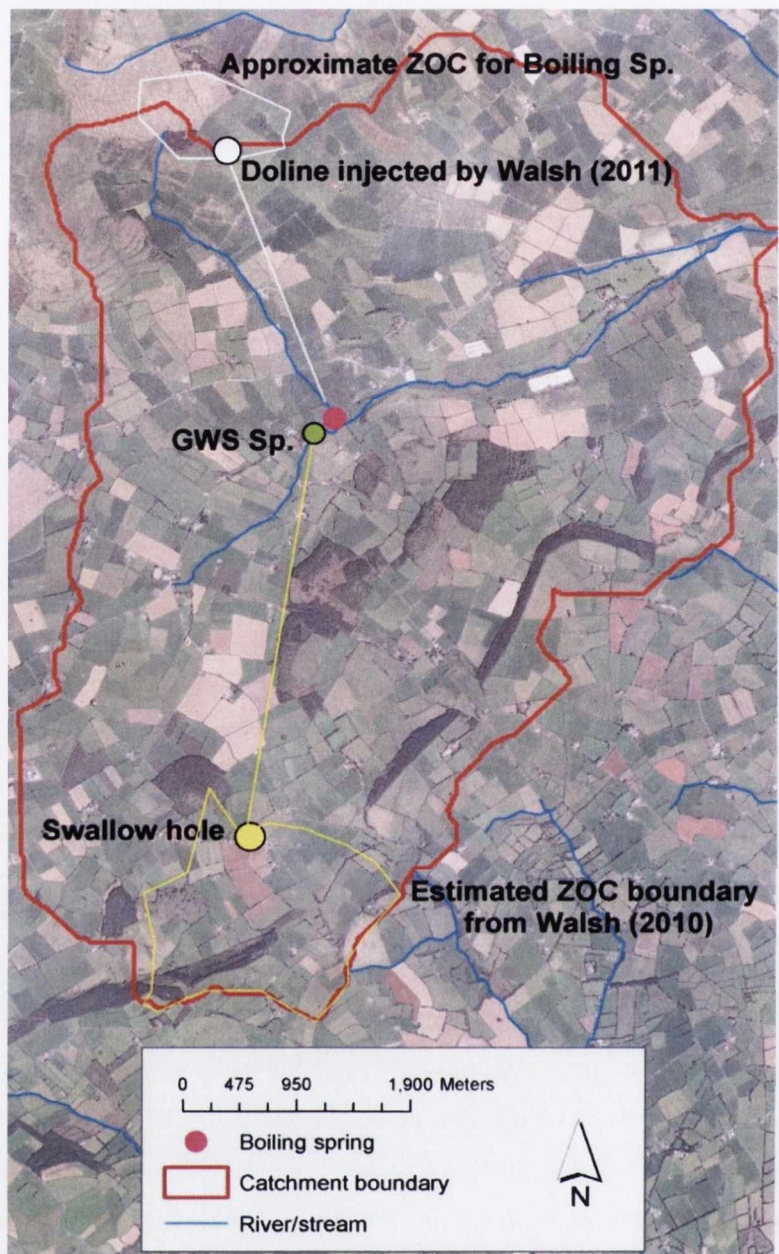


Figure 5.22 The karst well-drained arable (KWDa) catchment in Co. Kilkenny, Ireland showing the estimated ZOC of the Boiling spring and the estimated ZOC from Walsh (2011) following tracer work from a swallow hole in the south west to the Group Water Scheme spring. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

5.6.3 Groundwater flow direction and the zone of contribution at the intergranular/karst well-drained arable (I/KWDa) site

At I/KWDa the general groundwater flow is from MP1 to MP2 and slopes from 56 mAOD at MP1 to 54 mAOD at MP2 (**Figure 5.23**). Bromide tracer tests carried out by Premrov (2011) states that it took 70 days for the bromide tracer to leach vertically to the screened section of the piezometer where the tracer was applied in November 2007 above ground following 155 mm of effective rainfall. Laterally it took the tracer 22 days to reach suction cups buried 0.9 m b.g.l. and 1.5 m b.g.l. located approximately 10 m away from the application area. The application area was approximately 100 m north east of MP2 (Premrov, 2011).

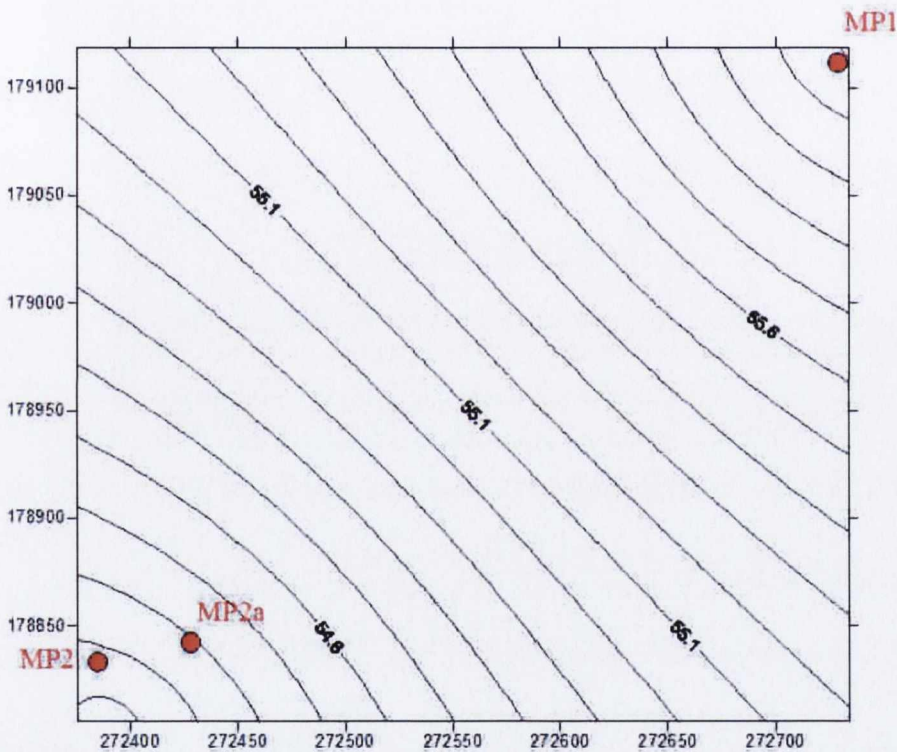


Figure 5.23 Groundwater flow direction at intergranular/karst well-drained arable (I/KWDa).

Due to the flat sloping nature of the I/KWDa site with groundwater flow towards the R. Barrow the ZOC may include the area up-gradient of the Sawmills Field (outlined in red **Figure 5.24**). The area within yellow reflects the area up-gradient of the Sawmills Field and which may receive pesticide applications. This area encompasses a crops research centre with many field trials, each requiring different pesticide a.i. applications. These

applications may contribute to pesticides detected in MP1 and MP2 as all are within the same groundwater body.



Figure 5.24 The intergranular/karst well-drained arable (I/KWDa) site in Co. Carlow with field boundaries in red and arable areas in the ZOC potentially able to receive pesticide applications in yellow. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

5.6.4 Groundwater flow direction and the zone of contribution at the fractured-volcanics well-drained arable (FvWDa) site

At FvWDa (**Figure 5.25**) groundwater flow moves from the catchment boundary (which is also the watershed) and flows towards the Upper BH, but also spreads out to reach the House Sp. where groundwater then flows and curves gently towards the emergence springs and the small stream as seen in **Figure 4.7**.

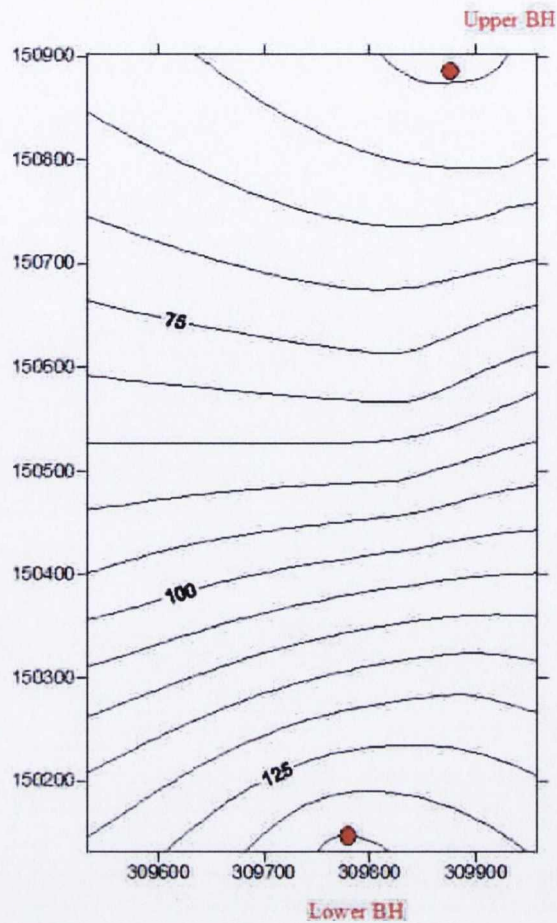


Figure 5.25 Groundwater flow direction at fractured-volcanic well-drained arable (FvWDa).

The two fields at FvWDa are located beside each other (**Figure 5.26**) with one bordering the catchment boundary or watershed. The ZOC for the MPs located in these fields can therefore be extrapolated back up hill towards the catchment boundary and also includes the higher topography area in the south west which in **Figure 5.26** has woodland as its land use.



Figure 5.26 The fractured-volcanic well-drained arable (FvWDa) site in Co. Wexford with field boundaries in red and the estimated ZOC in yellow. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

5.6.5 Groundwater flow direction and the zone of contribution at the fractured-volcanics poorly-drained arable (FvPDa) site

At FvPDa (**Figure 5.27**) groundwater flow has a higher gradient between piezometers 1b to 5b in the two tillage fields, then groundwater flow becomes more gentle in the grassland field nearest the stream.

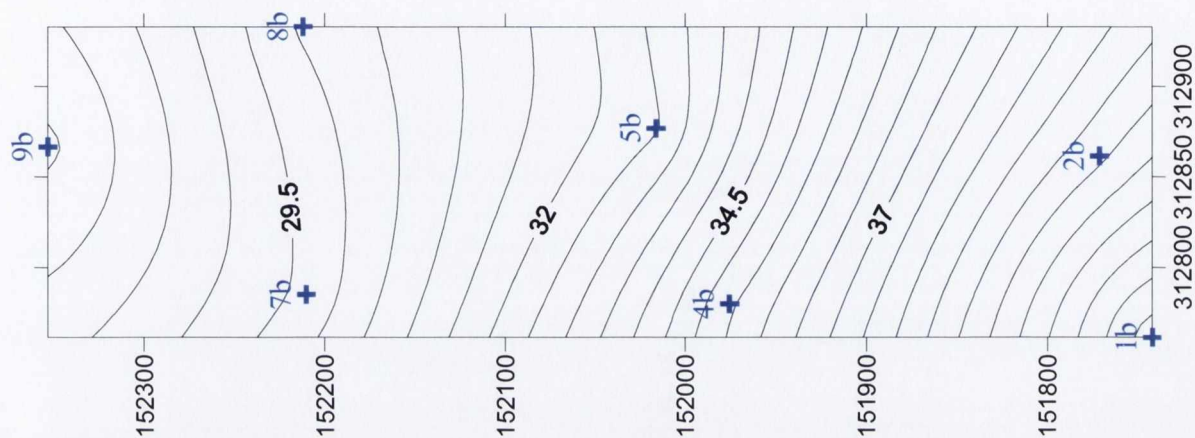


Figure 5.27 Groundwater flow direction at fractured-volcanic poorly-drained arable (FvPDa).

Figure 5.28 shows the estimated ZOC for the fields housing the MPs at the FvPDa site. Artesian conditions are present at the site in piezometer 2b which was drilled to 8.6 m b.g.l and the artesian BH which was drilled to 11.9 m b.g.l. The potentiometric level at the artesian BH is greater than 6 m above ground level which is a consequence of recharging water from Boley Hill located south west of the site. **Figure 5.28** shows the ZOC boundary extending up to Boley Hill which is dominated by forestry and scrub. During BH installation at FvPDa the water content of the soil became increasingly wetter until after 10 m a massive water strike occurred. Above which gravels and shales were encountered, which were weathered Ordovician Volcanics. Water flowed constantly at c.60L/min. The well was artesian with a potentiometric head greater than 6 m above ground level. The well was grouted to 8 m with bentonite slurry and a T-piece connected to 6 inch uPVC piping which could handle up to 60 psi obtained from In-Situ Inc. (UK). Samples were collected from a hose attached to the T-piece with a valve which allowed the artesian water to flow.

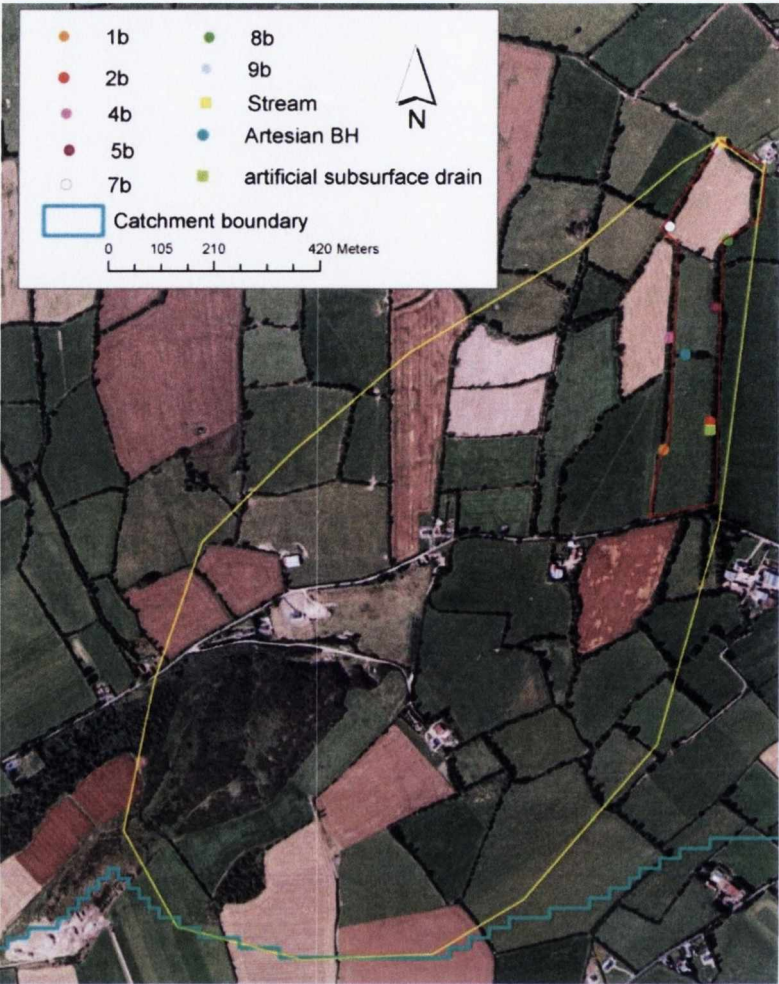


Figure 5.28 The fractured-volcanic poorly-drained arable (FvPDa) site in Co. Wexford with field boundaries in red and the estimated ZOC in yellow. Ortho photography from 2000 printed under Licence No. 6155 from the Ordnance Survey Ireland.

5.6.6 Groundwater flow direction and the zone of contribution at the fractured-metasediments well-drained arable site 1 and 2 (FmWDa_{1/2})

Figure 5.29 shows groundwater flow for the FmWDa₁ site. Here the gradient is steepest from the Upper BH to the Middle BH and then becomes more gentle from the Middle BH to the Lower BH.

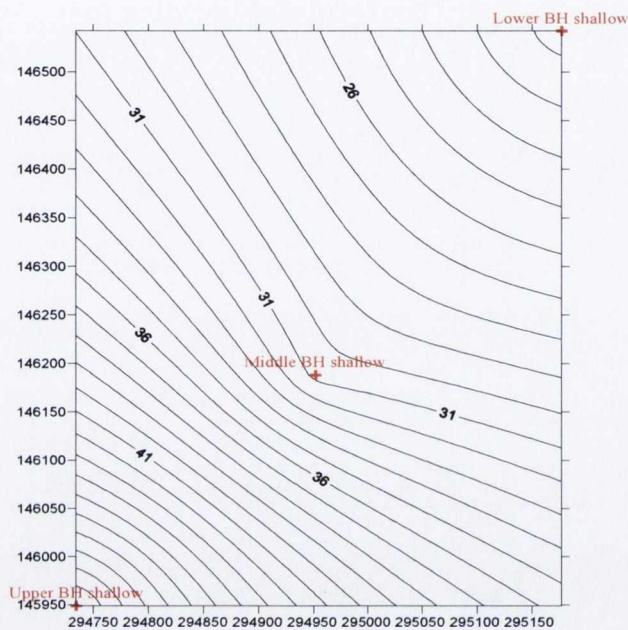


Figure 5.29 Groundwater flow direction at fractured-metasediments well-drained arable site 1 (FmWDa₁).

At FmWDa₂ in Figure 5.30 the steep gradient is between the Upper and Lower BH, while between the Upper and Middle BH the groundwater flow gradient is gentler.

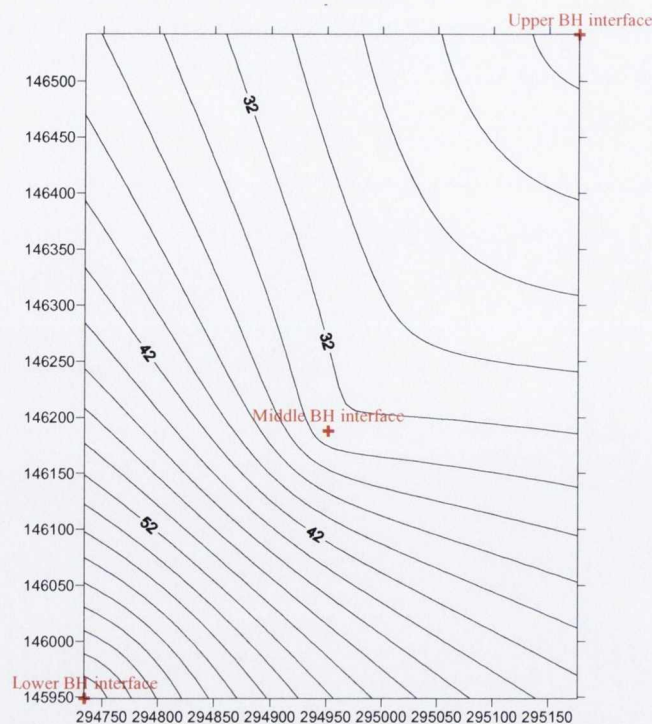


Figure 5.30 Groundwater flow direction at fractured-metasediments well-drained arable site 2 (FmWDA₂).

Both site 1 and 2 in the FmWDA catchment extend up to the catchment boundary and watershed, therefore their estimated ZOC is the same as the field boundaries where the MPs are located (Figure 4.10).

5.7 Groundwater age dating

The concept of groundwater age is one of the most fundamental in hydrology since it enlightens us about contaminant migration (Castro and Goblet, 2005) and residence time (Beyerle *et al.*, 2000; MacDonald *et al.*, 2003). Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆) provide a technique for dating groundwaters up to 50 years old (Gooddy *et al.*, 2006). Other indicators include ³H (tritium), ³⁶Cl, and ⁸⁵Kr (MacDonald *et al.*, 2003). For dating waters 50 to 1,000 years old SF₆/CFC dating is used alongside a flow model but radiocarbon analysis can be useful although this technique is expensive.

Resources available to the project only allowed two piezometers to be sampled for groundwater age (Table 5.8). Groundwater was sampled in April 2010 using a submersible pump (Grundfoss MP1) the piezometer was purged of 3-5 volumes of stagnant water with all air removed from the system. The method for sampling and analysis is

detailed by Beyerle *et al.* (2000) and Aeschbach-Hertig *et al.* (2012). To summarise 45 ml of groundwater was collected in copper tubes which were mounted onto an aluminium channel. Once the sample was in the copper tube, steel clamps were tightened to seal the tube and prevent gaseous exchange of noble gas isotopes.

Table 5.8 The monitoring points sampled to determine the age of groundwater and results.

Monitoring point	Site	Groundwater age (years)
MP1 interface piezometer	I/KWDa	9.5 ± 2.2
Lower BH shallow piezometer	FmWDA ₁	43.4 ± 6.3

5.8 Hydrochemistry

5.8.1 Aims of hydrochemical analysis

Hydrochemistry seeks to determine the origin of the chemical composition of groundwater and the relationship between water and rock chemistry, particularly as they relate to groundwater movement (Zaporozec, 1972). Groundwater chemistry not only relies on the vadose zone but also reactions along the saturated flow system such as the dissolution and precipitation of various minerals and cation exchange (Schwartz and Zhang, 2003) with the aquifer lithology influencing the hydrochemistry of groundwater moving through it (O'Callaghan Moran & Associates, 2007). As a general rule the most rapidly dissolving minerals have the greatest impact on water chemistry (Schwartz and Zhang, 2003). In groundwater over 90% of the dissolved solids are attributed to eight ions: sodium (Na⁺), calcium (Ca²⁺), potassium (K⁺), magnesium (Mg²⁺), sulphate (SO₄²⁻), chloride (Cl⁻), bicarbonate (HCO₃), and carbonate (CO₃²⁻) (Fetter, 2001), although not all these ions are naturally occurring in groundwater. Elevated potassium (K) is usually from organic point sources of contamination, and sodium (Na) may arise naturally from precipitation or geology but also septic tank effluent may be a source. Through obtaining and plotting these inorganic ions for each groundwater sample, the hydrochemistry of each sample can be obtained with the composition inferring groundwater characteristics.

5.8.2 Hydrochemistry methods

5.8.2.1 Sample collection and field measurements

Once a month groundwater samples were collected from each MP at each site. Section 6.1.1 details the method used for sampling pesticides which are also summarised here. Prior to sampling, the weather conditions, ground conditions, time, date, and any other field observations were recorded. Using a bladder pump (Geotech Environmental Equipment, Inc., USA), teflon lined tubing was lowered into the piezometer to the depth of the screen. The groundwater physical and chemical parameters pH, temperature, oxidation-reduction potential (ORP or Eh), residual dissolved oxygen (RDO), electrical conductivity, and turbidity were measured on site using a calibrated In Situ Multiparameter Troll 2000 probe (In Situ Inc., USA). Once these water quality parameters had stabilised to vary by less than 10%, the sample was taken to be representative of the aquifer (British Standards Institution, 2009). An unfiltered 50 ml polyethylene tube was filled for other water quality analysis and stored at 4°C until analysis.

5.8.2.2 Hydrochemical statistical methods

Principal component analysis (PCA) was employed to determine the hydrochemical composition of each piezometer at each site. PCA has become increasingly popular for exploring large environmental monitoring datasets with many variables (Bengraïne and Marhaba., 2003), especially where the water flux is not available (Guggenmos *et al.*, 2011). PCA allows associations between variables to be found without reducing the dimensionality of the dataset, with the participation of the original variables in the principal component given by the loadings. For PCA analysis in this study two principal component scores (PCS) were generated with each PCS corresponding to a particular loading value for the set of variables input. The variables which will most likely reflect changes in lithology and indicate surface water – groundwater interactions include: Ca, Mg, K, Na, HCO_3^- , Cl, and electrical conductivity (EC) (Guggenmos *et al.*, 2011). However, changes in these variables can indicate the influx of contamination, for example through higher conductivity readings. Or should the natural constituents of the groundwater suddenly change this may indicate a pathway or again an influx from other sources including anthropogenic sources.

Section 5.8.2.3 details each variable selected and used for PCA and how it can be interpreted. Here in Chapter 5 the aim is to determine the hydrochemical composition of each site. GenStat 13th Edition (VSN International, UK) was used to carry out PCA for each MP at each site with the results outlined in section 5.8.3. Using samples collected from each MP for the duration of the two year monitoring programme, the following variables listed in **Table 5.9** were input into GenStat. HCO_3^- and CO_3^{2-} were calculated from measured alkalinity using **Eqn. 5.1** and **5.2**.

Table 5.9 The variables (n=15) used for input into GenStat for principal component analysis (PCA) of each monitoring points (MP) hydrochemical composition.

Variables measured in-situ	Variables measured in the laboratory
Electrical conductivity ($\mu\text{S}/\text{cm}$ @ 20°C)	HCO_3^-
pH	Cl
Residual dissolved oxygen (mg/L)	CO_3^{2-}
Temperature ($^\circ\text{C}$)	Na
ORP/Eh (redox potential)	Ca
	Mg
	K
	Fe
	Total carbon (TC)
	Total organic carbon (TOC)

5.8.2.3 Hydrochemical parameters summary

The hydrochemical variables measured and included in PCA are summarised in this section which can then be referred back to as regards each variables interpretation.

Electrical conductivity (EC)

An electrical current can be carried through water by dissolved ions with electrical conductance expressed in microsiemens per centimetre ($\mu\text{S}/\text{cm}$). The electrical conductivity (EC) of water increases with temperature, therefore field probes should be temperature compensated. The In Situ Multiparameter Troll 2000 measured EC at 20°C ($\mu\text{S}/\text{cm}$ at 20°C). EC measurements are particularly useful during monitoring tests to

highlight the intrusion of different types of water. Conductivity provides an estimate of the dissolved ionic matter content in the water and is dependent on the geology of the area (Fetter, 2001). A sudden change in EC can indicate a direct discharge or other source of pollution into the water (Drever, 1997).

pH

The pH reflects the effective concentration of hydrogen- (H^+) and hydroxide- ions (OH^-) in water. The units of pH are the negative logarithm of $[H^+]$ expressed in moles per litre. A pH of 7 indicates neutral water, acidic water has lower values (<6), and alkaline values are higher than neutral (>8). The pH is controlled by various reactions and the presence of different compounds. In freshwater systems the carbonate system $CO_2-HCO_3-CO_3$ plays a role in pH (Drever, 1997). In other cases the presence of H_2S or its oxidised form, sulphuric acid, determines low pH (Fetter, 2001).

Dissolved oxygen (DO)

Rain and subsurface waters equilibrate with air, becoming saturated with DO. Equilibration with soil air goes on until water reaches the saturated zone, where it is isolated from further contact with air. The concentration of DO is controlled by (1) pressure (which is controlled by altitude), (2) temperature (increase in temperature, decreases the oxygen solubility), and (3) salinity (an increase in salinity, decreases the oxygen solubility) (Drever, 1997). Older waters tend to have lost most or all of their DO and heightened biological activity will use up oxygen. In unconfined or phreatic aquifers, water retains a significant proportion of the initial oxygen, whereas in confined aquifers little to no oxygen is retained (Drever, 1997).

DO can infer the following about aquifer characteristics (taken from Apello and Postma, (2006)):

1. DO can indicate if an aquifer is anaerobic or aerobic.
2. DO can infer an increase in biological activity
3. DO can identify systems which are dominated by conduit flow. These systems have limited rock-water contact, fast-flow, and retain their initial DO over long distances.
4. DO can identify older water.
5. DO can identify older strata in depth profiles

6. DO can identify the mixing of different water types through the occurrence of 'forbidden' ion combinations e.g. DO and H_2S .

Alkalinity

Alkalinity measures the buffering ability of water to neutralise an acid to a designated pH (Dillon, 2010). It is related to the sum of the carbon-containing species dissolved in the water: CO_2 , HCO_3^- and CO_3^{2-} . The more carbonate species present in water the "harder" the water. Water with a high water hardness is detrimental to household appliances. Bicarbonate is usually the dominant ion. In unconfined aquifers HCO_3^- dominates while in confined aquifers Cl^- dominates (Chebotarev, 1955). In shallow aquifers the oxygenous ions (HCO_3^- , SO_4^{2-}) are relatively abundant compared to Cl^- , whereas in deep aquifers the opposite is true (Zaporozec, 1972). Higher alkalinity values may arise because water remains in the aquifer system for longer and is subject to greater dissolution thus, point recharge from conduit flow is likely to have lower alkalinity in comparison to water from a diffuse aquifer system (Walsh, 2011).

Oxidation-reduction potential (ORP/Eh)

Sometimes referred to as redox, the Eh is a measure of the tendency for a chemical species to gain or lose electrons with the introduction of a new species. A higher (more positive) reduction potential means the species is more likely to gain electrons from the new species and thereby oxidise the species. The lower the Eh the more likely it is to gain electrons and reduce the new species. Redox processes are often related to the decay of organic matter with oxygen being the primary donor to allow for oxidation of the organic matter, although once oxygen is exhausted other electron acceptors such as nitrate may mediate the oxidation of organic matter (Appelo *et al.*, 2006).

Redox reactions influence natural concentrations of O_2 , Fe^{2+} , SO_4^{2-} , H_2S , and CH_4 among other compounds in groundwater (Appelo *et al.*, 2006). Redox processes in groundwater typically occur through the addition of an oxidant such as O_2 or NO_3^- to an aquifer containing a reductant. These redox processes in turn can influence the leaching potential from agricultural areas and landfills (Appelo *et al.*, 2006).

Temperature

Water temperature is a measure of the heat content. Since the solubility of oxygen, measured using DO, decreases with increasing water temperature, high water temperatures

will limit the availability of DO for aquatic life. Water temperature can influence various biochemical reaction rates that may influence water quality indirectly by controlling the chemical and biological composition of a freshwater body (Belkhiri *et al.*, 2010).

Chloride

Chloride is one of the most abundant anions to be found in water and sewage. Anthropogenic sources of chloride includes farmyard manure, landspreading of organic waste, sewage effluent, road salt, landfill leachate, saline intrusion, coastal precipitation, and urban areas (EPA, 2003). Small amounts of chloride are required for normal functions in plant and animal life. Chlorides have no biochemical sinks or sources in a waterway and may be regarded as a relatively conservative element in water. The presence of chloride in large amounts may be due to natural processes such as the passage of water through natural salt formations, salt water intrusion, or pollution from an anthropogenic source. Potable water should not exceed 250 mg/L of chloride.

Total organic carbon (TOC)

TOC refers to the OC content of an unfiltered sample which is also the non-purgeable organic carbon (NPOC) content. It plays an important role in controlling geochemical processes in groundwater as it can act as a pH buffer or a proton donor or acceptor. TOC is reactive and may interact with other constituents in the groundwater through various precipitation and dissolution reactions, which may ultimately affect the transport and degradation of potential pollutants (Aiken, 1995). The presence of TOC in aquifer material can also act as a colloid to assist in the transport of pollutants (Ryan and Elimelech, 1996). A study by Wang *et al.* (2006) found positive correlations between the observation of TOC and the organochlorine pesticides HCH and DDT.

Sodium (Na)

Na is a naturally occurring monovalent positively charged ion which is one of the principal dissolved constituents present in groundwater. A source of Na in groundwater is precipitation from the atmosphere which recharges into groundwater (**Table 5.9**), where values usually range between 0 – 9.4 mg/L (Oregon State, 2012). Na may also derived from the weathering of bedrock with Na present, salt deposits, brackish water, salt water intrusion, infiltration of surface water laden with road salt, groundwater pollution by sewage effluent or the infiltration of leachate from landfills or industrial sites (The British Columbia Groundwater Association, 2007a).

Calcium (Ca)

Ca is a naturally occurring divalent positively charged ion which is also one of the principal dissolved constituents in groundwater, especially in carbonate aquifer systems. Water that contains a high concentration of Ca is called hard water. The hardness of water is expressed in terms of the amount of CaCO_3 (the principal constituent of limestone). Soft water contains <60 mg/L, medium hard 60-120 mg/L, hard 120-180 mg/L, and very hard >180 mg/L (The British Columbia Groundwater Association, 2007b). Calcium in groundwater can become involved in ion exchange, as groundwater containing Ca flows through the aquifer, Ca^{2+} ions can displace Na^+ ions from the surfaces of clay minerals where present (Oregon State, 2012). Sources of Ca include precipitation but the Ca content will vary considerably from inland areas to coastal areas. Other sources of Ca include the weathering of rocks such as limestone and dolomite which contain carbonate (**Table 5.10**).

Magnesium (Mg)

Mg is a divalent positively charged cation which together with Na, K, and Ca is one of four major cations found in groundwater. Mg also contributes to water hardness, as mentioned above under Ca. Sources of Mg include the weathering of certain minerals such as dolomite (**Table 5.10**).

Potassium (K)

K is a monovalent positively charged cation which can occur naturally in groundwater. Sources of K include the weathering and dissolution of feldspar and mica minerals (**Table 5.10**) which may be present in certain types of bedrock geology. Anthropogenic sources of K include fertiliser, farmyard runoff, land spreading, and sewage (EPA, 2003). Typical concentrations of K in specific Irish aquifers are presented in **Table 5.11**.

Iron (Fe)

Fe is a minor component of groundwater in comparison to the four main cations (Appelo *et al.*, 2006). Groundwater, especially if the water is acidic, in many places can contain excessive amounts of iron, with the presence of iron indicating organic contamination (EPA, 2003). Iron causes reddish stains on plumbing fixtures and clothing. Iron is a naturally occurring element but anthropogenic sources may also be silage and sewage

(EPA, 2003). Other sources of Fe include those listed in **Table 5.9** with **Table 5.10** listing the values of Fe common in Ordovician volcanic rocks in Ireland.

Iron in groundwater can be present in several forms, the most soluble form is Fe^{2+} (Fetter, 2001). Fe^{2+} is ferrous iron but $\text{Fe}(\text{OH})^+$ and $\text{Fe}(\text{OH})^{2+}$ are also forms of ferrous iron. Ferric iron can be in the form Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, and $\text{Fe}(\text{OH})_3$ (Fetter, 2001). When oxygen and ferrous iron are present in groundwater, ferric hydroxide ($\text{Fe}(\text{OH})_3$) can form which is colloidal (Fetter, 2001) and may assist in the transport of contaminants through aquifer systems should the contaminant have an affinity for $\text{Fe}(\text{OH})_3$. In anoxic groundwaters with a reducing environment, iron (III) can be used as an electron acceptor once stocks of oxygen and NO_3^- have depleted. Once stocks of iron (III) has been reduced to iron (II) sulfate (SO_4^{2-}) is used next as an electron acceptor which leads to the production of H_2S (Fetter, 2001), a foul, egg-smelling gas indicative of reducing conditions.

Table 5.10 Major elements and some of their mineral sources in unpolluted fresh water (Appelo and Postma, 2006).

Element	Source
Na^+	Feldspar, rock-salt, zeolite, atmosphere, cation exchange
K^+	Feldspar, mica
Mg^{2+}	Dolomite, serpentine, pyroxene, amphibole, olivine, mica
Ca^{2+}	Carbonate, gypsum, feldspar, pyroxene, amphibole
Cl^-	Rock-salt, atmosphere
HCO_3^-	carbonates, organic matter
NO_3^-	Atmosphere, organic matter
Fe^{2+}	Silicates, siderite, hydroxides, sulfides

Table 5.11 Typical groundwater hydrochemistry values for inorganic variables in Ireland.

Source: EPA (2003) and units are in mg/L.

Variable	Ordovician volcanics	Carboniferous limestone	Sand and gravel
Ammonium	0.1	0.13	0.05
Calcium	80	102	118
Chloride	35	26	22
Hardness as CaCO ₃	60	307	320
Iron	0.1	nd	nd
Magnesium	9.7	12.9	6.3
Manganese	Nd	nd	0.01
Nitrate	0.5	0.9	2.8
Potassium	3.1	3.0	0.6
Sodium	24	8.8	12

nd = not determined.

5.8.3 Hydrochemical results for individual sites

For each monitoring point (MP) sampled every month between March 2010 and March 2012 the average hydrochemical variable for each site was recorded in **Table 5.12** along with the standard deviation (SD). **Appendix 7** contains the average and SD for each MP within each site. The hydrochemical composition of the water was also determined using multivariate statistics known as PCA. The following sections detail the hydrochemistry of each site.

Table 5.12 Descriptive statistics for hydrochemical variables at each site.

		KWDg	KWDa	I/KWDa	FvWDa	FvPDa	FmWDa ₁	FmWDa ₂
pH	Mean	7.3	7.5	7.6	6.4	7.4	6.5	6.87
	SD	0.2	0.3	0.3	0.4	0.3	0.5	0.4
ORP (mV)	Mean	126.6	192.8	139.8	172.8	-75	151.6	124.1
	SD	109.4	51.5	69.4	80.4	49	73	92.7
RDO (mg/L)	Mean	-	7.8	15.7	8.3	2.4	9.3	7.1
	SD	-	1.7	38.5	1.3	1.4	1.7	2.3
Conductivity (μS/cm)	Mean	559.3	447.1	439.7	155.4	281.4	178.8	218.9
	SD	41.6	60	101.9	43.6	57.3	49.7	43.4

Table 5.12 Descriptive statistics for hydrochemical variables at each site contd.

		KWDg	KWDa	I/KWDa	FvWDa	FvPDa	FmWDa ₁	FmWDa ₂
Turbidity (NTU)	Mean	0	33.4	242.7	195.8	238.6	249.4	148.6
	SD	0	56.2	276.2	264.8	245.1	353.4	230.8
Temperature (°C)	Mean	10.8	10.4	11.6	11.4	11.9	10.5	10.8
	SD	3.4	0.3	2.5	3.2	2.2	1.9	2.4
Ca (mg/L)	Mean	72.6	62.2	62.6	9.5	25.9	10.6	14.9
	SD	53.5	52.6	41.8	9.4	18.5	11.5	11.7
Cu (µg/L)	Mean	0.4	0.6	0.5	0.5	0.4	0.5	0.5
	SD	1	1.1	0.9	1.6	0.7	1	0.9
Fe (µg/L)	Mean	10.5	11.6	76.2	125.8	308	149.4	51.7
	SD	19.2	28	182.8	246.6	650.5	338.5	121.8
K (mg/L)	Mean	2.2	1.6	2	1.4	1.8	1.3	1.5
	SD	1.4	1.4	1.1	0.9	1.3	0.8	1
Mg (mg/L)	Mean	3.3	6.1	5.8	3.5	6.5	4.4	5.1
	SD	2.7	5.9	5.1	3.3	5.1	3.4	3.8
Mn (µg/L)	Mean	0.9	0.5	28.1	23	258.3	12.3	11
	SD	3.4	1.3	101.9	58.7	264.6	35.3	34.2
Na (mg/L)	Mean	6.8	5.3	7.6	8.2	14.2	8.4	9.9
	SD	3.3	3.4	5	4.6	10.2	4.5	6.6
Zn (µg/L)	Mean	0.2	0.1	0.2	0.8	0.8	0.7	1.3
	SD	0.5	0.5	0.6	1.7	2.3	1.8	2.5
NPOC (mg/L)	Mean	2.6	7.3	1.1	2.7	2.6	1.7	0.8
	SD	0.9	18.1	2	9.6	3.5	4.8	0.9
Total Nitrogen (mg/L)	Mean	2.1	5.4	12.2	7.1	1.2	6	7.2
	SD	1.6	2.1	2.9	1.7	1.1	1.4	1.8
Chloride (mg/L)	Mean	16.4	12.7	14.9	19.9	18.9	14.9	19.3
	SD	2.3	2.3	5.2	2.5	5.2	3.8	4.7
Ammonium- N (mg/L)	Mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
	SD	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Total oxidised nitrogen (mg/L)	Mean	1.5	5	10.9	6.4	0.7	5.3	6.6
	SD	0.7	2.3	3.4	1.6	0.7	2.2	2.3
Nitrite (mg/L)	Mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
	SD	<MDL	<MDL	0.2	<MDL	<MDL	<MDL	<MDL

Table 5.12 Descriptive statistics for hydrochemical variables at each site contd.

		KWDg	KWDa	I/KWDa	FvWDa	FvPDa	FmWDa ₁	FmWDa ₂
Nitrate (mg/L)	Mean	1.5	3.8	10.7	6.3	0.7	5.2	6.5
	SD	0.8	2.6	3.4	1.7	0.8	2.3	2.5
total reactive P (mg/L)	Mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.2
	SD	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Bicarbonate alkalinity as CaCO₃ (mg/L)	Mean	348.9	305.3	236.7	28.6	189.4	41.7	55.8
	SD	46.4	58.7	80.1	10.8	42.6	22.5	16.2

<MDL = less than the method detection limit.

5.8.3.1 Hydrochemistry of the karst well-drained grassland (KWDg) site

The pH of the Sp. at KWDg is neutral and with a low ORP of 126 mV. Unfortunately, no data was able to be gathered for RDO because of a faulty probe in the In-Situ MP TROLL. Conductivity at the site was high at 559 μ S/cm, the highest conductivity average measured at all the sites (**Table 5.12**). Turbidity was zero indicating clear waters and temperature was an average of 10.8°C. The main metals encountered in samples were Ca at 2.6 mg/L, chloride was 16.4 mg/L, and TC was 59.2 mg/L. Bicarbonate alkalinity as CaCO₃ was an average of 349 mg/L.

The typical value for Ca in Irish Carboniferous limestone groundwater is 102 mg/L (**Table 5.11**). Ca was an average of 73 mg/L at KWDg. The typical value for CaCO₃ in Irish Carboniferous limestone groundwater is 307 mg/L, CaCO₃ was an average of 349 mg/L at KWDg. The typical value for NO₃⁻ in Irish Carboniferous limestone groundwater is 0.9 mg/L, NO₃⁻ was an average of 1.5 mg/L at KWDg.

PCA data for the Sp. at KWDg using Ca, Fe, K, Mg, Mn, TOC, Cl, total carbon, HCO₃⁻, CO₃²⁻, and CaCO₃ was used from 23 samples to show that 81.19% of the variation could be explained by principal component score (PCS) 1 which had a loading of 0.69418 for HCO₃⁻, 0.569 for CaCO₃, and 0.3414 for CO₃²⁻. This infers that the three alkalinity variables have the most influence on the chemistry of the groundwater flowing at this Sp.

5.8.3.2 Hydrochemistry of the karst well-drained arable (KWDa) site

The pH of both springs at KWDa were near neutral (**Table 5.12** and **Appendix 7**). ORP was an average of 193 mV, RDO 8 mg/L, and conductivity 447 $\mu\text{S}/\text{cm}$. Turbidity was one of the lowest averages in comparison to the other sites (**Table 5.12**) and average temperature was 10.4°C. Ca was the main ion present at 62.2 mg/L with the Boiling Sp. having more Ca than the Sp. under the bridge (66 mg/L compared to an average of 58 mg/L). NPOC at KWDa had the highest average in comparison to the other sites at 7.3 mg/L. The Sp. under the bridge contributed the most to this average with 13.3 mg/L (**Appendix 7**). The Sp. under the bridge is an overflow spring for the Boiling Sp. which only yields water when flow is greatest at the Boiling Sp. (Archbold *Pers. Comm.* 2011). The Boiling Sp. alone only had an average of 1.4 mg/L. Along with KWDg, this site with arable land use had a high TC at 57.8 mg/L in comparison to the other sites.

The Boiling Sp. and the Sp. under the bridge differ in several hydrochemical variables. The Boiling Sp. had higher averages of the bicarbonate fractions, higher average NO_3^- , and higher conductivities in comparison to the Sp. under the bridge. While the Sp. under the bridge had higher average turbidity than the Boiling Sp. and a higher average NPOC.

The typical value for Ca in Irish Carboniferous groundwater is 102 mg/L (**Table 5.11**). Ca was an average of 62 mg/L for KWDa. The typical value for NO_3^- in Irish Carboniferous limestone groundwater is 0.9 mg/L. NO_3^- was an average of 4.8 mg/L for the Boiling Sp. and 2.8 mg/L for the Sp. under the bridge.

At the Boiling Spring (Sp.) 86% of the variation could be explained by PCS 1 which had a loading of 0.58827 for HCO_3^- (**Figure 5.31**). The overflow spring 10 m up gradient of the Boiling spring, under the bridge, showed that 93% of the variation could be explained by PCS 1 which had a loading of 0.50641 for HCO_3^- .

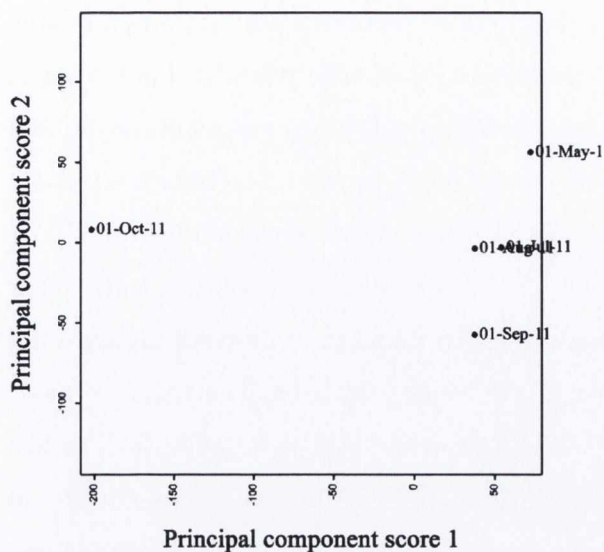


Figure 5.31 Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the Boiling Spring at karst well-drained arable (KWDa).

5.8.3.3 Hydrochemistry of the intergranular/karst well-drained arable (I/KWDa) site

The average pH for all MPs at I/KWDa was neutral at 7.6, ORP was an average of 140 mV, and RDO for the site was 15.7 mg/L, the highest RDO average in comparison to all the other sites in **Table 5.12**. This high RDO was attribute to the deep piezometer at MP1 which had an average RDO of 55 mg/L but a SD of 210 (**Appendix 7**). Conductivity at I/KWDa was an average of 440 $\mu\text{S}/\text{cm}$. The three sites with karst present in their geology all had higher conductivity values (**Table 5.12**; **Appendix 7**). The average turbidity of samples were all high at I/KWDa, except for the deep piezometer at MP1 (**Appendix 7**). The main ions present were Ca with an average of 63 mg/L but a SD of 42. Fe had an average of 73 $\mu\text{g}/\text{L}$ but a SD of 183 (**Table 5.12**). This high average for Fe was attribute to MP1 shallow, with an average Fe concentration at MP1 shallow of 241 $\mu\text{g}/\text{L}$ (**Appendix 7**). The other MPs at I/KWDa had a range of averages between 9.3-95.1 $\mu\text{g}/\text{L}$ for Fe. Mn was also high at this site with an average of 28 $\mu\text{g}/\text{L}$ (**Table 5.12**). The lowest Mn average was found in MP2 shallow and MP1 deep with the highest average of Mn found at MP2 interface (**Appendix 7**). NPOC had the lowest average at I/KWDa compared to the other six sites with 1.1 mg/L (**Table 5.12**). But I/KWDa had the highest TN and nitrate as nitrogen average across all the sites with 12.2 mg/L and 10.7 mg/L, respectively. TC was highest at MP1 shallow (57 mg/L; **Appendix 7**). Regarding alkalinity, the average at I/KWDa was 269 mg/L with MP1 shallow having the highest average bicarbonate alkalinity as HCO_3^- of all the MPs at I/KWDa.

The typical value for Ca in Irish Carboniferous limestone groundwater is 102 mg/L (**Table 5.11**). Ca averages ranged between 49-72 mg/L at I/KWDa. The typical value for Mg in Irish sand and gravel groundwater is 6.3 mg/L. In MP1 shallow Mg was an average of 8.2 mg/L. The other MPs at I/KWDa ranged between 5.1 and 7.7 mg/L. The EPA (2003) only give typical groundwater concentrations for sand and gravel groundwaters for Mn of 0.01 mg/L which is 10 µg/L (micrograms per litre are the units Mn was measured in). Four MPs at I/KWDa exceeded the typical Mn concentration found in this type of groundwater (**Appendix 7**). The typical value for K in sand and gravel Irish groundwaters is 0.6 mg/L and at I/KWDa the range averages at each MP was between 1-4.5 mg/L, MP2 shallow had 4.5 mg/L of K. The deep piezometers represent Carboniferous limestone groundwater at I/KWDa. Typical values of NO_3^- for these groundwaters is 0.9 mg/L (**Table 5.11**) and both deep piezometers at MP1 and MP2 exceeded this value with 10.1 and 10.7 mg/L, respectively. For sand and gravel aquifers the value is 2.8 mg/L, both shallow and interface piezometers at both BHs exceeded this typical NO_3^- value given by the EPA (2003).

At the shallow piezometer in MP2 the hydrochemical composition can be explained by turbidity, accounting for 89% (**Figure 5.32**). At the interface in MP1 the hydrochemical composition can also be explained by turbidity, accounting for 73% (**Figure 5.33**), while at the deep piezometer at MP1 91% of the hydrochemical composition can be explained by PCS 1 which had a loading of 0.9991 for RDO (**Figure 5.34**).

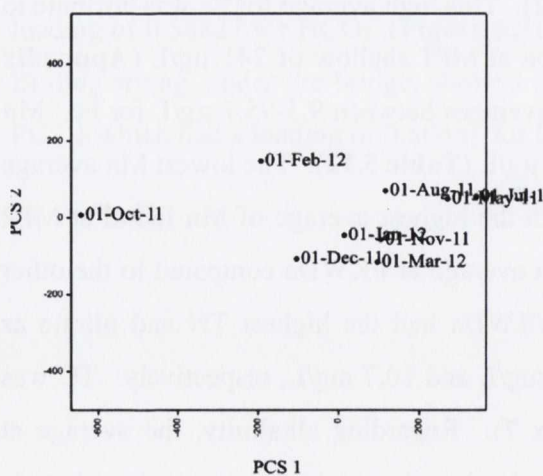


Figure 5.32 Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the shallow piezometer at MP2 at the intergranular/karst well-drained arable (I/KWDa) site. PCS 1 = turbidity.

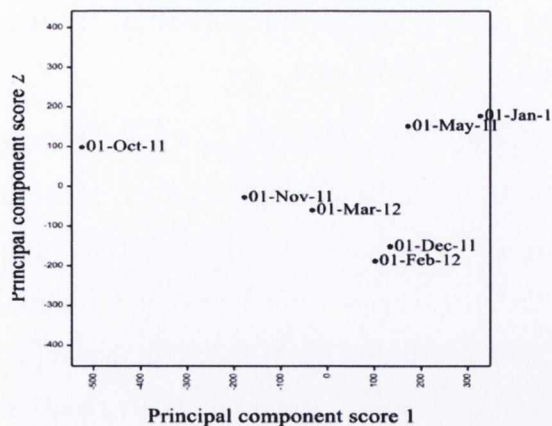


Figure 5.33 Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the interface piezometer at MP1 at the intergranular/karst well-drained arable (I/KWDa) site. PCS 1 = turbidity.

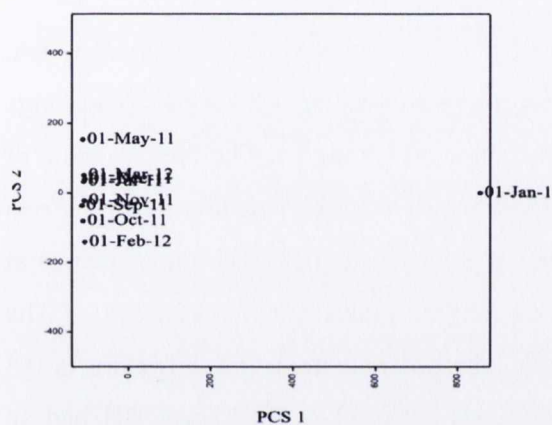


Figure 5.34 Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the deep piezometer at MP1 at the intergranular/karst well-drained arable (I/KWDa) site. PCS 1 = residual dissolved oxygen (RDO).

5.8.3.4 Hydrochemistry of the fractured-volcanics well-drained arable (FvWDa) site

The average pH of the five MPs at FvWDa throughout the course of monitoring was 6.4, the lowest average pH of all the sites (**Table 5.12**). The ORP was the second highest at 173 mV and RDO was an average of 5.3 mg/L for FvWDa. Average conductivity was the lowest at FvWDa out of all the seven sites in **Table 5.12** with 155.4 $\mu\text{S}/\text{cm}$. Turbidity was an average of 196 mg/L for all MPs at the site with **Appendix 7** revealing that the two BHs contributed to this turbidity value with the three springs on site ranging in turbidity from 40 – 168 mg/L.

The main ions at FvWDa were Fe with 126 $\mu\text{g}/\text{L}$ with the Lower and Upper BHs having an average of 233 $\mu\text{g}/\text{L}$ and 339 $\mu\text{g}/\text{L}$ for Fe, respectively. The three springs at FvWDa ranged in average Fe concentrations of between 12-24 $\mu\text{g}/\text{L}$. Zn was highest in these two BHs at 1.1 $\mu\text{g}/\text{L}$ for the Lower BH and 2.2 $\mu\text{g}/\text{L}$ for the Upper BH, however, these

averages did not exceed the DWS for Zn of 5 µg/L. Chloride was highest at FvWDa compared to the other sites (**Table 5.12**) with an average of 20 mg/L.

NPOC for the five MPs at FvWDa was an average of 2.7 mg/L but the Lower Sp. had an average higher than the site average with 9.1 mg/L. TN at FvWDa was 7.1 mg/L with the two BHs, Upper Sp., and Lower Sp. contributing the most to the average TN concentration encountered at this site. The average TN for the House Sp. was the lowest at 3.9 mg/L. TC at the site was the lowest in comparison to the other sites at 10.2 mg/L with the Upper BH and Lower Sp. having a higher average than the other MPs at the site with 12 and 21 mg/L, respectively. Alkalinity at FvWDa had the lowest averages for each of the bicarbonate components compared to the other sites (**Table 5.12**).

Table 5.11 lists typical values for groundwater from Ordovician volcanic bedrock (EPA, 2003). The typical Ca value for Ordovician volcanic groundwater is 80 mg/L. The range of Ca found at FvWDa was much lower of between 4.1-15.4 mg/L. The typical value of Fe in these groundwaters is 0.1 mg/L or 100 µg/L. At FvWDa Fe was highest in the two BHs (Lower BH with 233 µg/L and the Upper BH with 339 µg/L). The three springs at FvWDa had considerably smaller amounts of Fe ranging between 12 and 24 µg/L. The typical NO₃⁻ value for groundwater from Ordovician volcanic Irish groundwaters is 0.5 mg/L. At FvWDa the average NO₃⁻ for the site was 6.3 mg/L. The Lower BH had an average of 7.3 mg/L, the Upper BH had 7.2 mg/L, the Lower Sp. had an average of 7.6 mg/L, the Upper Sp. an average of 6.6 mg/L, and the House Sp. had the lowest NO₃⁻ average at 3 mg/L (**Appendix 7**).

The five MPs at FvWDa were analysed using PCA. Both deep piezometers at each BH (lower and upper) had greater than 96% of their hydrochemical composition explained by PCS 1 which had loadings greater than 0.97 for Fe (**Figure 5.35** and **5.36**). The House Spring and Lower Spring only had 65.1% and 61.91% of their variation explained by PCS 1. These low percentages do not warrant an explanation of the hydrochemical composition since the percentage should be greater than 70% to confirm a variable which dominates the hydrochemical composition. However, the Upper Sp. had 97.9% of its variation explained by PCS 1 which had a loading of -0.99858 for turbidity (**Figure 5.37**).

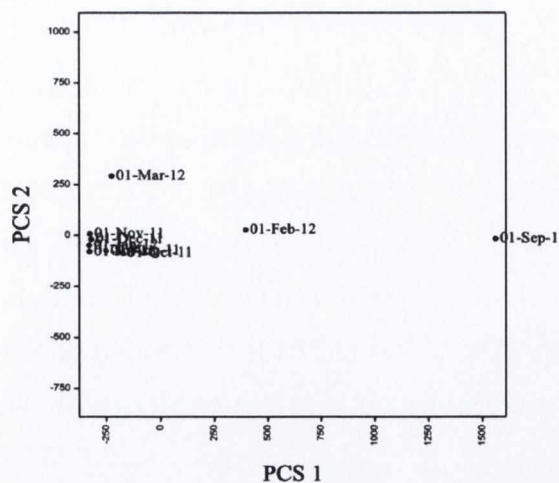


Figure 5.35 Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the deep piezometer at the Lower borehole in the fractured-volcanic well-drained arable (FvWDa) site. PCS 1 = Iron.

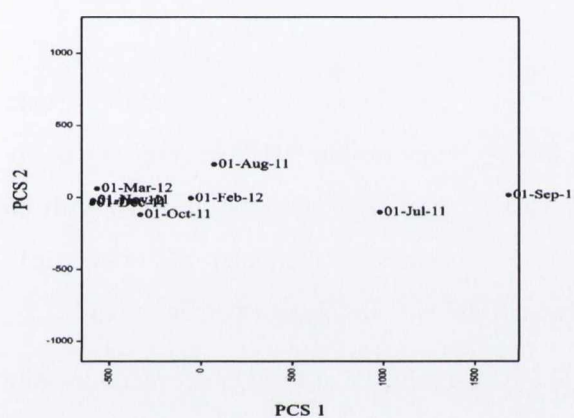


Figure 5.36 Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the deep piezometer at the Upper borehole in the fractured-volcanic well-drained arable (FvWDa) site. PCS 1 = Iron.

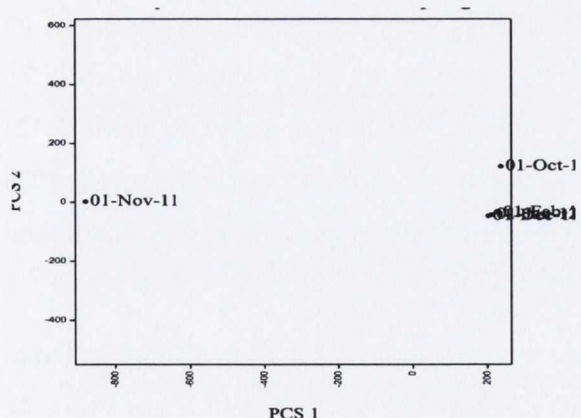


Figure 5.37 Principal Component Analysis (PCA) of groundwater taken every month between March 2010 and March 2012 for the deep piezometer at the Upper Spring in the fractured-volcanic well-drained arable (FvWDa) site. PCS 1 = turbidity.

5.8.3.5 Hydrochemistry of the fractured-volcanics poorly-drained arable (FvPDa) site

From **Table 5.12** the average pH from all the MPs at FvPDa is neutral at 7.4. The average ORP at FvPDa is -22.4 mV: the only site of the seven to have a negative ORP (**Table 5.12**). Although not all MPs at the site had a negative ORP (**Appendix 7**). 2b, 4b, 9a, and the drain did not have an average ORP value that was negative. Average RDO was 8.6 mg/L at FvPDa with 5b and 8b having on average higher RDOs than the other piezometers at the site. 27 mg/L for 5b and 24 mg/L for 8b. Other MPs ranged from 1.9 mg/L to 9.8 mg/L (**Appendix 7**). Average conductivity was 281.4 $\mu\text{S}/\text{cm}$ with piezometers 7b, 8b, 9a and 9b having the highest conductivities (**Appendix 7**). Turbidity was an average of 238.6 NTU with 4b and 9a having the highest averages of 416 NTU and 616 NTU, respectively. Temperature was an average of 12°C for the site, with 9a having an average temperature of 14.2°C (**Appendix 7**).

The main ions at FvPDa were Ca, Fe, Mn, and Na. Piezometers 5b, 7b, 8b and the stream had the highest Ca averages throughout monitoring. The artesian BH, piezometers 1b, 2b, 4b, 5b, 9a, and 9b had the highest averages of Fe. The highest Mn was in 1b with an average of 868 $\mu\text{g}/\text{L}$. The other MPs at FvPDa ranged between 135-494 $\mu\text{g}/\text{L}$. Piezometers 1b, 5b, 8b, 9a, and 9b plus the artesian BH had the highest values of Na.

NPOC was an average of 2.6 mg/L for the site but several MPs at FvPDa exceeded the site average. 1b had 4.7 mg/L, 5b had 3 mg/L, 8b had 2.7 mg/L, 9a had 4.7 mg/L, 9b had 3.6 mg/L, and the stream had 4 mg/L of NPOC. Ammonium as nitrogen was highest out of all the MPs at each site in 9b at FvPDa with an average of 0.7 mg/L. Total carbon was an average of 36.5 mg/L with 1b, 5b, 7b, 8b, and 9b exceeding the site average (**Appendix 7**). Bicarbonate alkalinity as HCO_3^- was much higher at FvPDa than FvWDa (**Table 5.12**) with a site average of 211 mg/L compared to 32 mg/L (**Table 5.12**). The MPs at FvPDa which contribute the most to this sites average were the artesian BH, 1b, 5b, 7b, 8b, and 9b.

The typical value for Ca in Irish Ordovician volcanic groundwaters is 102 mg/L (**Table 5.11**; (EPA, 2003)). At FvPDa the Ca range was between 3.7-53.4 mg/L (**Appendix 7**). The typical value for CaCO_3 in Ordovician volcanic groundwaters is 60 mg/L (**Table 5.11**). This value was exceeded in every MP at FvPDa except the stream and at 9a and 4b where alkalinity wasn't analysed. The range in CaCO_3 at FvPDa was between 82.4-355.2 mg/L. The typical value for Fe in Irish Ordovician volcanic groundwaters is 100 $\mu\text{g}/\text{L}$. At FvPDa the average Fe values were greater than this typical value in nine of the 11 MPs at

FvPDa, ranging between 193.3-796.6 $\mu\text{g/L}$. The typical value for Mg in Ordovician volcanic rocks is 9.7 mg/L. At FvPDa the majority of MPs have averages around this typical value. The MPs at FvPDa with the highest average for Mg throughout monitoring was 8b with 12.7 mg/L and the lowest average for Mg throughout monitoring was 4b and 9a with 1.2 mg/L (**Appendix 7**). At FvPDa the MPs had Na concentrations at less than the typical value of 24 mg/L for Na in groundwater from Ordovician volcanic areas. The typical NO_3^{2-} value for Ordovician volcanics is 0.5 mg/L. At FvPDa only 9b, the drain, stream, and 4b exceeded this value (**Appendix 7**).

At FvPDa the majority of the MPs had their hydrochemical composition using PCA explained by Fe. This included the stream, 2b, 5b, 7b, 8b, 9b, and the artesian BH. However, 4b had 98% of its hydrochemical composition explained by PCS 1 which had a loading of 0.9912 for turbidity. The artificial subsurface drain had 70% of its hydrochemical composition explained by PCS 1 which had loadings of 0.50157 for HCO_3^- , 0.41112 for CaCO_3 , and 0.24667 for CO_3^{2-} .

5.8.3.6 Hydrochemistry of the fractured-metasediments well-drained arable site 1 (FmWDa₁)

At FmWDa₁ the average pH found across all ten MPs was 6.5, the ORP was 152 mV, the RDO 9.3 mg/L, the conductivity 179 $\mu\text{S/cm}$, turbidity was 249 NTU (the highest average at any of the sites), and the average temperature was 10.5°C (**Table 5.12**). The turbidity was highest in the shallow and interface piezometers of the middle BH with 407 and 400 NTU, respectively (**Appendix 7**).

The main ions at FmWDa₁ were Ca, Fe, and Mn (**Table 5.12**). Ca was highest in the stream at FmWDa₁ compared to the other piezometers. And Fe was highest in the shallow and interface piezometers of the Upper BH however, the SD for these two Fe values are very high indicating much variation among sampling occasions.

NPOC is highest in the interface and deep piezometers of the Middle BH but SD is high indicating much variability among sampling occasions. Nitrate at this site was highest in the stream with an average of 6.2 mg/L. No typical groundwater values are given for Ordovician metasediments as they are for other bedrock geologies in **Table 5.11**.

Table 5.13 summarises the hydrochemistry of each MP at each site in the FmWDa catchment. These variables are the loadings which are from principal component scores

which are greater than 60%. **Appendix 8** shows the scree diagrams for each piezometer at each site in FmWDa₁.

5.8.3.7 Hydrochemistry of the fractured-metasediments well-drained arable site 2 (FmWDa₂)

From all the ten MPs at FmWDa₂ the average pH was 6.9, ORP was 124 mV, RDO was 7.1 mg/L, conductivity was 219 μ S/cm, turbidity was 149 NTU, and temperature was 10.8°C (**Table 5.12**). The most notable difference between averages for each MP at FmWDa₂ was for turbidity. The shallow piezometer in the Middle BH had the highest average of 567 NTU with the other MPs ranging between 11 and 247 NTU (**Appendix 7**). No typical groundwater values are given for Ordovician metasediments as they are for other bedrock geologies in **Table 5.11**.

The main metal ions at FmWDa₂ were Ca and Fe. Ca had an average of 15 mg/L across the site and Fe 52 μ g/L, but with a very high SD of 122 (**Table 5.11**). Ca was highest in the Middle BH shallow with an average of 168 μ g/L of Fe and a high SD of 529. Na was highest in all the deep piezometers at FmWDa₂. The highest average concentration of Zn in any of the MPs across all seven sites was found in the Lower BH deep at 4 μ g/L (**Appendix 7**).

The lowest NPOC for all seven sites was at FmWDa₂ with 0.8 mg/L (**Table 5.8**). Among the MPs at this site the highest nitrate concentration was in the Upper BH shallow with 8.1 mg/L. The only detectable amount of ORP was at FmWDa₂ in the middle BH interface with 1 mg/L (**Appendix 7**).

Table 5.11 indicates the dominant variable which has the greatest impact on the hydrochemical composition at each MP in the FmWDa catchment. These variables are the loadings which are from principal component scores which are greater than 60%. **Appendix 9** shows the scree diagrams for each piezometer at each site in FmWDa₂.

Table 5.13 Summary of the hydrochemical composition from the output of principal component analysis (PCA) for each monitoring point (MP) at fractured-metasediments well-drained arable (FmWDa) site 1 and 2.

	Piezometer Shallow	Interface	Deep
<i>FmWDa₁</i>			
Lower BH	Fe	Fe	Turbidity
Middle BH	Fe	Turbidity	Turbidity
Upper BH	na	Turbidity	Fe
Stream		na	
<i>FmWDa₂</i>			
Lower BH	ORP	Fe	ORP
Middle BH	Turbidity	Fe	Fe
Upper BH	na	Fe	Fe
Stream		na	

na = the percentage variation of PCS 1 could not be applied because it was less than 60%.

5.8.3.8 Hydrochemical comparison between sites

The KWDg site had the highest bicarbonate alkalinity across all the sites and the highest conductivity (**Table 5.12**). The other site dominated by karst was KWDa, had the second highest average bicarbonate alkalinity after KWDg. NPOC was highest at KWDa with turbidity very high on average at the spring under the bridge. The highest RDO occurred at I/KWDa compared to the other sites (**Table 5.12**). Within site I/KWDa the highest average RDO was at MP1 deep which targets the Rkd aquifer. PCA of MP1 deep indicates the hydrochemical composition is dominated by RDO (**Figure 5.34**). Turbidity was high at all MPs at I/KWDa except MP1 deep. PCA of MP2 shallow (**Figure 5.32**) and MP1 interface (**Figure 5.33**) show turbidity dominates the hydrochemical composition of this groundwater. At FvWDa the two BHs had on average higher turbidity values than the three springs at the site. The BHs also had high Fe concentrations (**Appendix 7**). Chloride had the highest average at FvWDa compared to the other sites. PCA for the Lower and Upper BH revealed that Fe dominated the hydrochemical composition while for the Upper Sp. turbidity dominated the hydrochemical composition (**Figure 5.37**). Fe also explained the hydrochemical composition of the majority of MPs at FvPDa. At this site the ORP was negative for over half the MPs. FvPDa was the only site with anaerobic conditions. Turbidity was highest at FmWDa₁, especially in the shallow and interface piezometers in the Middle BH.

5.9 Discussion of site characteristics

5.9.1 Karst well-drained grassland (KWDg)

In addition to those properties already known and detailed in section 4.5.1, effective rainfall at KWDg was modelled from total rainfall and four other atmospheric variable inputs detailed in section 5.4.4 using a grassland SMD model by Schulte *et al.* (2005). Out of the seven sites used by this project for monitoring, KWDg had the highest total amount of effective rainfall in one year with 714.5 mm falling in 2011. This is because the site is located in the west of Ireland (**Figure 4.3**) which receives more precipitation in general than other coastlines in Ireland. Although Fealy *et al.* (2009) states that the soil drainage class in the catchment of KWDg is deep well-drained mineral soils, through modelling PET from the Schulte *et al.* (2005) grassland SMD model, and comparing modelled PET with recorded PET, the modelled data gave a slightly better co-efficient of determination for moderately drained soils, although the r^2 was not very different to that of well-drained or poorly-drained soils which were also modelled with the Schulte *et al.* (2005) model (**Table 5.2**). This may infer that although the principal soil association for the catchment is a shallow brown earth and rendzina, the other associations of a smaller proportion, such as gleys and peats are influencing the amount of effective rainfall able to occur at KWDg. The technical note on effective rainfall (section 5.4.3) has raised awareness about the influence soils have on effective rainfall.

Although the soils are displaying an influence on effective rainfall, their influence does not hamper the response of the spring discharge to effective rainfall as **Figure 5.12** shows that the KWDg Sp. responds to effective rainfall throughout the year in both summer low flow periods and winter higher flow periods. Mellander *et al.* (2012) states that the presence of numerous karst features at KWDg (**Figure 5.21**) will allow for both point and diffuse recharge mechanisms to control groundwater recharge at the spring outflow, which may sometimes lead to sporadic discharge at the KWDg Sp.

Groundwater flow direction at the KWDg catchment is from east to west (Coxon and Drew, 1986). Tracer lines from the GSI which were obtained by Coxon (1986) are shown in **Figure 5.21** and each tracer line indicates a karst conduit pathway moving from east to west through the KWDg catchment. Although one trace leads to a spring located outside of the catchment in the south west. From the traces by Coxon (1986) linear velocities ranged from 5-10 m/hr to 47-123 m/hr for some turloughs in the east draining to the

Risings Sp. in the west. Additional traces carried out by the ACP (see section 5.6.1) show that Roos swallow hole was a point recharge feature supplying groundwater to the Risings Sp. 8.7 km away. These new traces also verified a new catchment boundary delineated by the ACP and supplemented with water balance calculations, so the new boundary does not include the northern section of the catchment (**Figure 4.4** and **Figure 5.21**).

The hydrochemistry of the Sp. at KWDg indicates an unconfined aquifer with a high proportion of HCO_3^- in the hydrochemical composition (see section 5.8.3.1) (Chebotarev, 1955). This MP also had the highest average conductivity out of all the sites (**Table 5.12**) which can be attributed to the high concentration of Ca ions present in the groundwater.

The high amount of effective rainfall at KWDg coupled with fast response times of the spring to rainfall will mean that any pesticide compounds applied will not remain for very long in the soil and subsoil before being flushed through the karst conduit system to the spring outlet.

5.9.2 Karst well-drained arable (KWDa)

As well as those properties already known about KWDa (section 4.5.2) the variable heterogeneity at this site was emphasised when six BHs were installed at two locations in the catchment. For example two BHs drilled approximately 5 m away from each other, where one BH had a water strike at 1.2 m b.g.l and the other had a water strike 20 m b.g.l (see section 5.4.1 and **Appendix 3**). Geophysical investigation at this site (section 5.3.2.1 and **Appendix 5**) revealed shallower overburden material north NNW of the Boiling Spring of approximately less than 2 m deep and a fissure across resistivity profile R8 in **Appendix 5** which is located west of the blue area highlighted in **Figure 5.2**. This implies that a conduit is present, with the possibility of it reaching the Boiling Spring. Tracer work carried out by Walsh (2011) indicated that a doline present in the north of the catchment boundary eventually delivers water to the R. Nuenna, and the outlet point of this could be the Boiling Spring located 750 m upstream. An estimation of the Boiling Springs ZOC is given in **Figure 5.22** based on the doline injected by Walsh (2011) and the geophysics which revealed a fissure underneath a shallow overburden area NW of the Boiling Spring. Hydrochemistry is diffuse (GSI, 2008a; Walsh, 2011) and the Boiling Spring contributes around 35% of total flow to the R. Nuenna (Travers, 2011).

The hydrochemical composition of groundwater at the Boiling Sp. is indicative of a karst system with high alkalinity values (**Table 5.12**). Comparing alkalinity with KWDg, a proven developed conduit system with recent tracing work, averages are less in KWDa than KWDg with NPOC and ORP higher at KWDa than KWDg. PCA of groundwater at KWDa showed its composition to be dominated by HCO_3^- which indicates an unconfined aquifer (Chebotarev, 1955). Walsh (2011) found the hydrochemistry of the Boiling Spring to be typical of a spring dominated by diffuse recharge and flow. The slow trace from the doline combined with hydrochemistry indicative of a diffuse system, indicates that flow here is dominated by diffuse rather than conduit which occurs at KWDg.

Pesticides detected at the Boiling Spring will have undergone diffuse flow through a karst system where the source of recharge is an upland area north of the catchment and which contributes between 35 of flow to the River Nuenna..

5.9.3 Intergranular/karst well-drained arable (I/KWDa)

The high percentage of sand in the soil at I/KWDa as stated in section 4.5.2.4 indicates this site is free draining and may be limited in its ability to retain water in the unsaturated and saturated zones above the aquifer (Premrov, 2011). Effective rainfall calculations in section 5.4 reveal that groundwater at I/KWDa responds quickly to effective rainfall during the winter months, but in the summer a recession occurs where effective rainfall does not cause a response in groundwater levels (**Figure 5.14**). Out of all the seven sites used in this monitoring programme, I/KWDa had the lowest total amount of effective rainfall in 2011 with 284.3 mm. The difference in groundwater response to effective rainfall between seasons will affect travel time. Premrov (2011) found hydraulic conductivity to be in the range of 25 - 43 m/day in November 2007 when bromide tracer tests were conducted. This lateral movement of bromide tracer will be affected by the amount of effective rainfall able to leach to the unsaturated zone. Due to the flat topography at I/KWDa and the general groundwater flow direction being from north east to south west, research crop trials located up-gradient of the BHs can be estimated to be part of the BHs ZOC (**Figure 5.24**).

I/KWDa had the highest average RDO in comparison to all the other site averages (**Table 5.12**). This high RDO was attributable to the deep piezometer at MP1 22-30 m b.g.l (**Appendix 3**). As with the two other karst sites (KWDg and KWDa), the conductivity at I/KWDa was also high (**Table 5.12**) indicating the high amount of dissolved ions present

in the groundwater which are supplied through dissolution processes operating in Carboniferous limestone geologies. The average turbidity in all the MPs at I/KWDa (**Appendix 7**) was high except for MP1 deep, where the highest RDO average was also found. The low turbidity and high RDO at MP1 deep indicates groundwater from an unconfined aquifer (Drever, 1997) and the differences between the interface and deep piezometers at MP1 further indicate that groundwater is from a different depth profile (Appello and Postma, 2006). The average NPOC at I/KWDa was the lowest from any of the other sites at 1.1 mg/L (**Table 5.12**) with Wang *et al.* (2006) and Ryan and Elimelech (1996) stating that a higher NPOC content in groundwater may assist in the colloidal transport of contaminants. TN and NO_3^{2-} had the highest site average compared to any of the other sites (**Table 5.12**) because the site is freely-draining and aerobic which will allow for elevated NO_3^{2-} concentration in groundwater (Jahangir, 2012).

The freely-draining and permeable nature of the soil and gravel deposits at I/KWDa will allow soluble pesticides to travel with recharging water relatively easily to deeper groundwater. The deep piezometers are sampling groundwater with a high RDO from an extensive Rkd aquifer.

5.9.4 Fractured-volcanics well-drained arable (FvWDa)

Aside from general soil information about FvWDa gathered from soil series maps of Co. Wexford and from Fealy *et al.* (2009), additional soil and subsoil information was gathered for FvWDa from material drilled through during BH installation. The Lower BH had 2 m of soil and subsoil material before bedrock was drilled through, while the Upper BH had 3 m of material (**Table 5.1**). The Lower BH had more OM and OC present indicating the transition from an acid brown earth soil into a gley soil at the base of the slope, further north of the catchment and also highlighted from 2D resistivity geophysics (**Figure 5.3**) which coincides with the increase in the clay fraction in soil in the Lower BH (**Table 5.1**).

Geophysical investigation revealed a relatively homogenous site until north of the Lower BH where the transition to a more clay-rich and water saturated material occurs. A large amount of weathered rock was highlighted from geophysics which was also drilled through during BH installation in October 2008. The material was dry and crumbly whilst being drilled through, and the air-rotary drilling rig found the material relatively easy to drill through – further indicating the high proportion of weathering across FvWDa. Although

the material was not saturated in water during drilling any potential water yielding fractures and material were noted in BH logs (**Appendix 3**). Although two piezometers were installed in each BH, only the deep piezometer yielded water.

The groundwater flow direction is in **Figure 5.25** and shows groundwater flowing from the Upper BH, then spreading towards the House Sp. and Lower BH, and then flowing north where the source of the R. Bracken originates. The R. Bracken runs through the catchment (**Figure 4.9**). This site is located next to the catchment boundary and watershed and as a result recharge will be derived from these upper reaches of the catchment (**Figure 5.26**) which includes other tillage land of spring barley and woodland further west.

The springs at FvWDa appear to be acting as discharge points for recharging water from the upper reaches of the catchment, and as the groundwater flows through the shallow unsaturated zone it reaches the base of the hill, coinciding with the onset of gley soils causing the water to hit an impermeable layer and force the water upwards into contact springs.

The Fe content between the BHs and springs is significantly different with the BHs having more Fe than the springs. This is because the BHs have groundwater in contact with Ordovician volcanic rocks which have higher deposits of Fe than for example Carboniferous limestone rocks. The Fe concentrations detected in the BHs exceed the typical value of 100 µg/L of Fe given by the EPA (2003) for Ordovician volcanic geology (**Table 5.11**). From PCA the hydrochemical composition of each BH is dominated by Fe but the springs are not (**Figure 5.35 – 5.37** and section 5.8.3.4).

Rainfall that falls at FvWDa may travel in shallow groundwater and eventually discharge at contact springs across the site or may recharge through freely-draining topsoil and highly-weathered Ordovician volcanic rocks to reach deeper groundwater below.

5.9.5 Fractured-volcanics poorly-drained arable (FvPDa)

In addition to the information already known about FvPDa at the beginning of the project in section 4.5.5, soil and subsoil material was collected from the artesian BH during air rotary drilling to a depth of 10 m b.g.l. **Table 5.1** shows the results for the sand, silt, and clay component of the soil plus nutrients and other soil properties such as pH and CEC. The top 1m of soil collected had 60% sand, 31% silt, and 8% clay (**Table 5.1**). The sand content remained between 60-77% between 0-3 m b.g.l but after 3 m declined. With the

sand percentage decline the silt and clay content both increase after 3 m b.g.l with in general more silt with clay present (**Figure 5.1**). These figures coincide with observations recorded in the field during BH drilling (**Appendix 3**) where between 1-2 m b.g.l more gravelly deposits were found with more sand present between 1-3 m than deeper. After 3 m grey coloured wet deposits were found very similar to those encountered in **Figure 5.9** and these deposits infer the location of the Irish Sea Till subsoil which was drilled through before reaching a confined aquifer beneath with a potentiometric surface above ground level, causing flowing artesian conditions.

Figure 5.4 shows the location of the flowing artesian aquifer at FvPDa. This was the only BH drilled at FvPDa using air rotary drilling methods. Shallower piezometers were installed across FvPDa once geophysics revealed the site is not homogenous in its deposits above the confined aquifer. 2D resistivity in **Figure 5.4** revealed that more gravelly deposits were present across the site (blue areas). These less clayey deposits with gravel may act as water bearing pathways, so shallow piezometers were installed to target these gravelly clay deposits and the boulder clay at FvPDa. At FvPDa the confined aquifer below was sampled as well as the deposits overlying this aquifer.

FvPDa is the only site with a negative ORP, which indicates the anaerobic conditions which dominate at the site. Shallow cores were collected at FvPDa in November 2011 and 2012 for demonstration purposes, and mottling was present at cores collected in the top 50 cm beside the artesian BH and 1b. The grey and brown coloured mottles produced in the soil at FvPDa are a result of reducing conditions and lack of oxygen present for soil microbes to use in their respiration processes. The lack of oxygen causes soil microbes to use Fe and Mn in the soil as electron donors during redox processes, which then causes the production of mottles which were present in the gley soil at FvPDa. One MP at FvPDa during monitoring always had a smell of hydrogen sulphide gas ($\text{H}_2\text{S}_{(\text{g})}$). This was 1b and indicates severely reducing conditions present here, where sulphate is reduced to sulphide and some is lost as $\text{H}_2\text{S}_{(\text{g})}$ (Rowell, 1993). MP 1b had a high average of total Fe present in the groundwater here, other MPs with high Fe contents included the artesian BH, 2b, 4b, 5b, 9a, and 9b (**Appendix 7**). PCA of the hydrochemical composition of MPs at FvPDa revealed that the MPs 2b, 5b, 7b, 8b, 9b and the artesian BH had Fe dominating the groundwaters hydrochemical composition. The low nitrate conditions at FvPDa coupled with the high concentrations of Fe and Mn in groundwater, infers the groundwater here is being locally confined (Stuart *et al.*, 2006). The artificial subsurface drain had a highly

mixed hydrochemical signature of Fe , CO_3^{2-} , CaCO_3 , and HCO_3^- . This may be because the source of this water comes from several areas including Boley Hill which is located south east, this then travels under a road and through a backfilled ditch.

This site is complex and MPs have been chosen to reflect potential pathways and reservoirs of pesticide occurrence. The artesian BH represents groundwater which is dominated by receiving recharging water from Boley Hill with the ZOC in **Figure 5.28**. The artificial drainage ditch located upstream of MP 2b represents water from several different sources including a debris-filled ditch and road run-off hence the mixed hydrochemical composition using PCA. The piezometers installed using a Gidding's Rig sample water above the confined aquifer in areas which may act as a reservoir of pesticide occurrence or where pesticides may move through FvPDa. Water seepage out of 2b implies that the potentiometric surface here is slightly above ground level, which means that water is recharging here from a higher area of land, much the same as the artesian aquifer which taps the Rf aquifer beneath, piezometer 2b is the deepest piezometer and taps competent rock; from schematics in **Figure 5.5**. Groundwater recharge is entering the bedrock aquifer upslope, then passing through the aquifer to FvPDa but the gravel deposits highlighted as blue and green areas in **Figure 5.4** do not act as a completely confining layer because of the presence of these more permeable deposits. Water from the piezometers sampled here at FvPDa is a mixture of water that entered the gravel lenses directly as local recharge and some of the groundwater from the bedrock aquifer which has moved upwards into the gravel lenses.

The heavily-textured, saturated soil and subsoil at FvPDa should help to protect groundwater in the underlying confined aquifer from pesticides leached from above. The anaerobic conditions at this site may have an affect on pesticide occurrence.

5.9.6 Fractured-metasediments well-drained arable site 1 (FmWDa₁)

In an off centre transect at FmWDa₁ multi nested piezometer BHs installed to target the shallow, interface, and deep groundwater show that with distance from the stream the depth to the deep piezometer increases: 33.5 m b.g.l compared to 40 m b.g.l. The rock encountered during drilling was highly weathered spanning a range of 3 m b.g.l to 15 m b.g.l. for each of the three BHs (**Appendix 3**). The high degree of weathering at FmWDa₁ was also indicated from geophysics at the site, with rock and gravel deposits dominant

except at the Lower BH near the stream which has saturated clay-rich deposits. With distance uphill away from the stream, EM 31 ground conductivity indicated thinner gravel rich deposits further up hill away from the stream (**Figure 5.6** and **Appendix 5**).

These highly weathered deposits at FmWDa₁ allowed a relatively quick response of groundwater level to effective rainfall within ten days for the lower borehole and slightly less time for a response at the Middle and Lower BHs (**Figures 5.15** to **5.17**). Although the groundwater level responded within ten days or less to effective rainfall the groundwater age at the shallow piezometer in the Lower BH (6.5 m b.g.l) was measured at 43.4 years old $\pm$ 6.3 years (**Table 5.8**). At FmWDa₁ effective rainfall is displacing water stored in the unsaturated zone which is then causing the response in groundwater level. The water reaching the shallow piezometer is not that which recharged the surface ten days ago, but older water stored in the unsaturated zone and this would explain the discrepancy between the groundwater age at 43.4 $\pm$ 6.3 years compared to a response in groundwater level ten days after effective rainfall.

Out of all the sites monitored during this study, FmWDa₁ had the highest site average for turbidity (**Table 5.12**) with the shallow and interface piezometers in the Middle BH accounting the most to these average (**Appendix 7**). Average NPOC was also high for the interface piezometer in the Middle BH and this may allow for colloidal transport of contaminants with an affinity for the particular colloidal matter causing the high average of turbidity and NPOC. **Table 5.13** indicates the main hydrochemical composition of groundwater at each of the MPs at FmWDa₁. Fe dominates indicating water running through weathered deposits of Ordovician metasediments and turbidity dominates the variation in PCA in the interface and deep piezometers.

The combination of weathered Ordovician metasediments across FmWDa₁ with effective rainfall will cause a response to groundwater level within ten days, potentially moving pesticides into deeper groundwater below. In near-stream zones discharge processes are in operation, with the stream discharging water to groundwater during low- precipitation events.

5.9.7 Fractured-metasediments well-drained arable site 2 (FmWDa₂)

The soils at both sites in FmWDa are listed by Gardiner and Ryan (1964) as the same however, through speaking with land owners the soil at FmWDa₂ has more clay present and is more prone to being water saturated although no soil analysis was undertaken to confirm differences in soil texture. The soil at FmWDa₂ is particularly wet in near-stream areas and this was recorded during BH installations in November 2009 (**Appendix 3**) and geophysics (**Appendix 5**). As with FmWDa₁, a transect of BHs was installed. The shallow piezometers targeted depths between 2.5 and 5 m b.g.l. which is water travelling through saturated clays and highly weathered gravel material (as verified during BH logs in **Appendix 3**). The interface piezometers targeted depths between 13-28 m b.g.l. and where water strikes occurred, BH logs state fractures within the rock filled with clay. Deep piezometers at FmWDa₂ are between 30-52 m b.g.l. The Lower BH is the deepest MP at 52 m b.g.l. and the shallowest the Upper BH (**Appendix 3**). As with the interface piezometers these deep piezometers are tapping water bearing fractures (**Appendix 3**). EM 31 (**Figure 5.7**) shows more saturated material in the lower fields especially in near-stream areas while EM 38 picked out a band of conductive material moving north east to south west which may allow water to travel through to the Lower BH. As with FmWDa₁, the upper field has thinner soils and a lower clay content. These fields were also very dry during fieldwork, even during high precipitation events. Gravel was detected in these upper fields (EM 38; **Appendix 5**) which will allow for a rapid infiltration of water.

Groundwater flow direction at FmWDa₂ in general travels from north to south west and groundwater table fluctuations at FmWDa₂ respond within around ten days for all three BHs (**Figure 5.18 – 5.20**).

The site average for NPOC from **Table 5.12** shows that FmWDa₂ had the lowest average compared to all other sites used for monitoring. The hydrochemical composition of groundwaters sampled at FmWDa₂ was dominated by Fe except in the Shallow piezometers of the Lower and Middle BH and the deep piezometer of the Lower BH where the hydrochemical composition was dominated by ORP.

The combination of weathered Ordovician metasediments across FmWDa₁ with effective rainfall will cause a response to groundwater level within ten days, potentially moving pesticides into deeper groundwater below at the Lower, Middle, and Upper BHs.

5.10 Chapter 5 conclusions

The objective of Chapter 5 was to detail information about the characteristics at each site that were obtained during the course of this project and to conceptually describe the seven sites regarding their hydrogeology which may then relate to pesticide occurrence in groundwater. This data will also be used in Chapter 7 to investigate the relationship between site characteristics and the risk of pesticide occurrence in groundwater. The outcomes of this chapter are summarised below:

- The most poorly drained site is FvPDa with anaerobic soil conditions causing gley soils, mottling, and $\text{H}_2\text{S}_{(\text{g})}$ production at MP 1b. A flowing artesian aquifer also exists here with a negative average ORP over the course of monitoring further inferring anaerobic conditions in the soil, subsoil, and groundwater.
- Fe was a common hydrochemical component in groundwater across all the sites except KWDg, KWDa, and I/KWDa, because here Carboniferous limestone aquifers are present as opposed to Ordovician age volcanic and metasediments bedrock geology. At the three sites with Carboniferous limestone present, conductivity measured *in-situ* is much higher than at the other sites.
- Effective rainfall calculations were carried out for each site except KWDa. In 2011 the highest total amount of effective rainfall occurred at KWDg and the least at I/KWDa. Comparing modelled and recorded PET allowed the most accurate model and soil drainage class to be chosen for each site.
- In the karst sites conduit flow dominates at KWDg but diffuse then dominates at KWDa (Walsh, 2011).
- At I/KWDa the hydrochemistry of the interface and deep piezometers are different indicating groundwater present here is from different recharge zones and that the ZOC for the deep piezometers, targeting the Rkd aquifer may have a higher ZOC than groundwater from the shallow and interface piezometers.
- The springs at FvWDa have high RDO values indicating shallow water from rainfall (Drever, 1997). This water then travels close to the ground surface where it is then forced upwards once it reaches the impermeable gley soil and saturated conditions at the base of the slope.

- FvPDa is waterlogged for the majority of the year and within the deposits above the high yielding aquifer, piezometers were installed to sample water from gravel lenses shown in geophysical investigation extending across FvPDa.
- The high degree of weathering at FmWDa site 1 and 2 allows groundwater levels to respond within ten days of effective rainfall however, groundwater age dating at FmWDa₁ indicates the displacement of water stored in the unsaturated zone which is then causing the response in groundwater level. The water reaching the shallow piezometer in the Lower BH at FmWDa₁ is not that which recharged the surface ten days ago, but older water stored in the unsaturated zone and this would explain the discrepancy between the groundwater age at 43.4 ± 6.3 years compared to a response in groundwater level ten days after effective rainfall.

CHAPTER 6

PESTICIDE ANALYTICAL METHODOLOGY

6.1 Introduction

The aim of this chapter is to detail how groundwater samples were sampled and analysed for pesticides. Groundwater was collected so it was representative of the water body being examined. This collection process is described in section 6.2.1. A technical note on the stability of raw and extracted groundwater samples was investigated to make sure no sample degradation occurred. A mini literature review of analytical chemistry methods used to quantify pesticides is detailed in section 6.3. All the analytical methods are described in the final sections. These include the methods external laboratories used and the two methods developed for this project to quantify 21 compounds in groundwater. Both the analytical methods developed by this project have been prepared as journal articles. One method has been accepted for publication.

6.2 Collection and storage of samples for pesticide analysis

6.2.1 Collection of groundwater samples from piezometers and springs

Once a month groundwater samples were collected from each MP. Prior to sampling, the weather conditions, ground conditions, time, date, and any other field observations were recorded. From piezometers and BHs approximately 1,500 mls of stagnant water was removed using a bladder pump (Geotech Environmental Equipment, Inc., USA). Stagnant water may be physically, chemically or biologically altered due to contact with air in the well, casing, screen or packing material was thus removed. Teflon lined tubing of (I.D. 0.6 cm) was lowered into the piezometer to the depth of the screen. Using low-flow sampling and *in-situ* flow through cells prior to sample collection field water quality variables could be determined, which indicate when the sample being purged has stabilised. A multi-parameter TROLL[®] 9500 flow through cell from In-Situ Inc. (Oxfordshire, UK) was used to take readings from unaltered water samples since the sample is not exposed to the air. The variables included pH, turbidity, dissolved oxygen, specific conductivity, temperature, and redox. It is advised they are monitored every 30 sec until values have stabilised to less

than 10% for turbidity and dissolved oxygen, less than 3% for conductivity and temperature, and ± 0.1 units and millivolts for pH and redox, respectively. Once the sample has stabilised 500 mL amber glass bottles with PTFE lined lids (Lennox, Ireland) were first rinsed with the sample and then filled so no air was present. Using low flow purging techniques recommended by BS ISO 5667-11:2009 (British Standards Institution, 2009) at an approximate rate of 100 mL/min, 500 mL of groundwater was collected into an amber glass bottle with a Teflon lid (Lennox, Ireland) so as to contain no air bubbles. The benefits of using low-flow purging includes consistency in results, minimising sampling artefacts, reduced aeration of the sample, and will reduce induced contaminant loading provided a flow rate of 100 mL/min or less is used. Amber glass is required since some pesticides are photosensitive and may degrade in sunlight. Glass and PTFE are the preferred storage vessels for organics as some organic compounds may diffuse through plastic bottles and caps or some may sorb to plastic materials (British Standards Institution, 2003). The inclusion of air in the sample can also increase pesticide degradation within the sample. Glass and Teflon were used since other plastics are porous and may allow compounds to diffuse through the vessel. Glass and PTFE are chemically inert and do not allow for this phenomenon. PTFE tubing was also used for drawing water from the stainless steel GeoTech Bladder pump GEO1.66SS18 (GeoTech Environmental Equipment Inc., USA) to the flow through cell, and into the glass bottle. A GeoTech Geocontrol PRO bladder pump (GeoTech, USA) was used in combination with the stainless steel bladder pump. An additional unfiltered 50 mL tube was filled for other water quality analysis using the same low flow purging technique immediately after the 500 mL pesticide sample was collected (see section 5.8.2.1). Low flow sampling conditions have been demonstrated to remove water from only the screened zone, without the need for packers to isolate the overlying stagnant water (USEPA, 1996) and does not pull sediment from the aquifer into the sample (Sundaram *et al.*, 2009). Low-flow purging sampling mechanisms are specified as being the best for obtaining a truly unaltered and representative sample as they do not change the chemical equilibrium of the sample which may deteriorate some organic compounds (British Standards Institution, 2003; British Standards Institution, 2009). Collected samples should then be stored in a cool box during transportation and packed to ensure minimal agitation. Once the sample was collected it was stored at 4°C until analysis, the water level logger returned to the piezometer, and the monitoring well secured. Samples should then be stored in the fridge between 1 - 4°C and analysed as soon as possible.

6.2.2 Technical note on storage of raw groundwater samples and extracted samples

An organochlorine herbicide stability study was carried out using spiked samples in duplicate fortified with 0.5 µg/L. The calculation of each analytes stability over time was carried out by using the solution of the analyte freshly prepared at the time of analysis (C_o) and compared with the concentration found at each subsequent time point (C_i) to determine the percentage of analyte remaining in the vial as recommended by EU Council Directive 2002/657/EC (European Commission, 2002). Samples were tested every two days until the analytes began to show a loss in concentration.

Analyte remaining (%) = $C_i \times 100 / C_o$

(E.q. 6.1)

Organochlorine compound stability over time in prepared vials (Figure 6.1) revealed that heptachlor was the most unstable organochlorine analyte when stored at room temperature in the dark. *Exo*- and *endo*- heptachlor epoxide started to degrade on day five with *endo*-heptachlor epoxide degrading more quickly than *exo*-heptachlor epoxide. Lindane was found to be stable for at least 17 days. This study indicates that once vials are prepared they must be analysed by SPME and GC-MS within 24 h otherwise heptachlor, *exo*- and, *endo*- heptachlor epoxide will start to degrade.

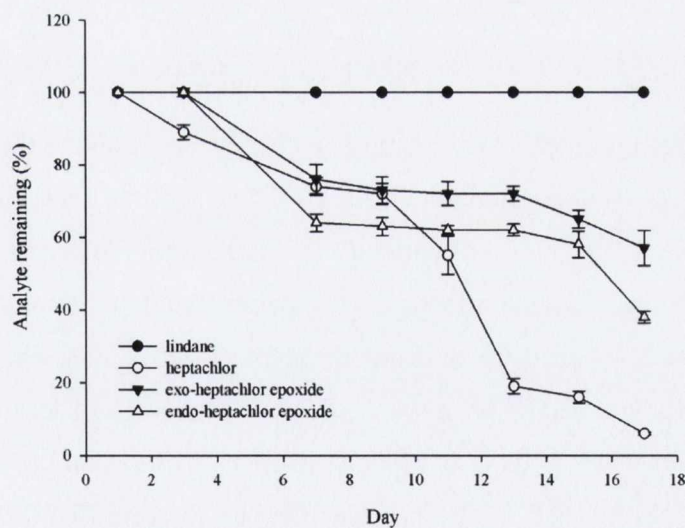


Figure 6.1 Stability over time of analytes in prepared vials calculated as the percentage of analyte remaining after day 1. Error bars represent standard error of the sample mean.

To test the stability of phenoxyacid herbicides in groundwater, groundwater samples were collected in amber glass bottles with PTFE lids in duplicate from the Boiling Spring at

KWDa and spiked with 200 μL of 500 $\mu\text{g/L}$ phenoxyacid and benzonitrile herbicide analytical working standard to yield the concentration 0.1 $\mu\text{g/L}$. These samples were then stored in the dark in a fridge between 0 - 4°C. Samples from the spring were determined for herbicides and miniscule quantities were quantified. Every seven days samples were extracted and analysed for phenoxyacid herbicides to determine how stable each analyte was during a 42 day monitoring period. Compound stability was calculated using **Eq. 6.1**. Experiments show that the most unstable compounds are TBA followed by fluroxypyr, triclopyr, 3,5-dibromo-4-hydroxybenzoic acid (BrAc), and 4-chloro-2-methylphenol (4C2MP) (**Figure 6.2**). The concentration of 4C2MP begins to increase after day 14. 4C2MP is a transformation product (TP) of MCPA, mecoprop, and mecoprop-p (FOOTPRINT, 2006). As these three compounds degrade they are adding to the concentration of 4C2MP, hence the increase of 4C2MP on day 14. MCPA begins to degrade on day 14 and mecoprop(s) fluctuates in concentration between day 14 and day 28 before falling drastically on day 35, which coincides with a sharp increase in 4C2MP. 3,5-dichlorobenzamide (BAM), 3,5,6-trichloro-2-pyridinol (T2P), 2,4-dichlorophenol (DCP), and phenoxyacetic acid (PAC) are the more stable compounds.

6.2.3 Technical note on filtering samples for phenoxyacid and benzonitrile herbicide analysis

Filtering samples could underestimate the concentration of analyte in the sample as particulates carrying compounds may be removed if they are bound to the material filtered off especially colloiddally bound compounds. No study has yet determined if this is the case for the list of herbicides in **Appendix 10**. Filtering may be necessary if the sample contains a large amount of sediment, which when passed through the solid phase extraction (SPE) cartridge may block the sorbent bed and also block active sites which retain analytes of interest, resulting in a reduction in pesticide concentration and loss of sample. It is possible to not filter samples, allow the sediment (if present) to settle to the bottom of the sample bottle and siphon off the water sample but filtering should not be used to compensate for poor sampling technique or inappropriate analysis methods (Ministry of the Environment, 2003). SPE will act to filter samples not heavily laden in sediment as many cartridges now contain frits on top of the sorbent bed for this purpose and recoveries may be improved on unfiltered samples as any particle-bound compounds will be recovered provided the sample can be loaded without blocking the cartridge.

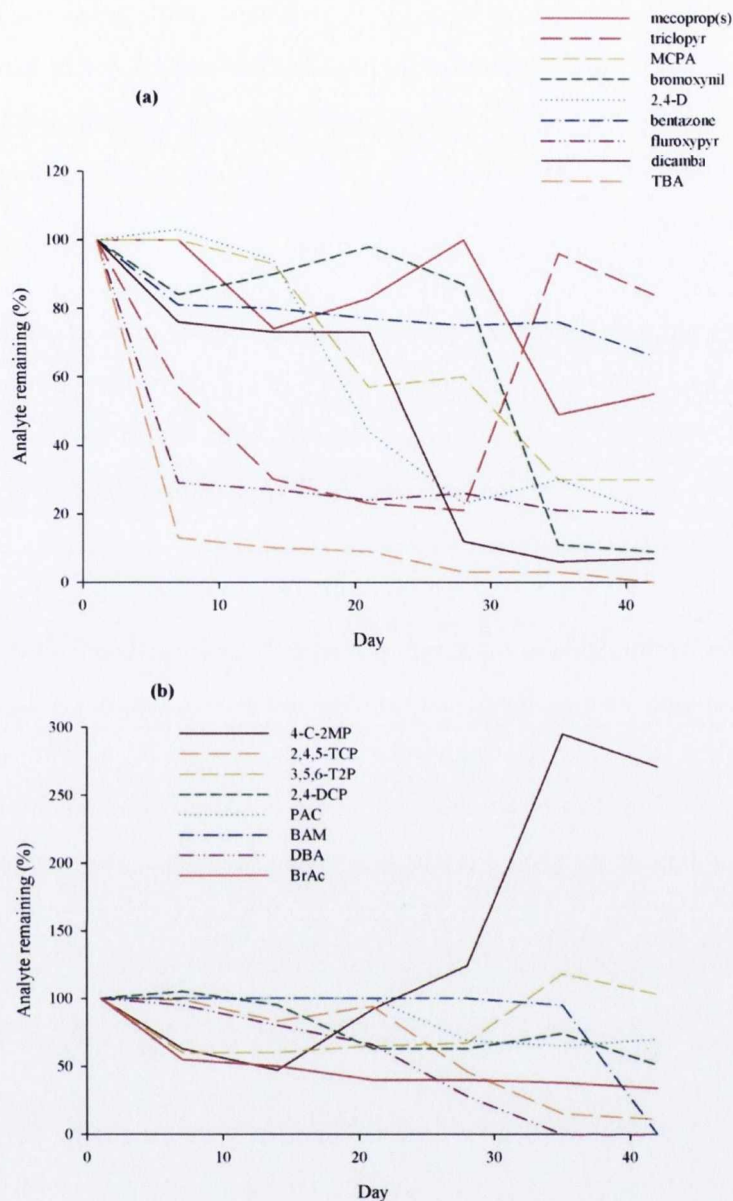


Figure 6.2 Stability over time of (a) phenoxyacid and benzonitrile herbicides and their (b) transformation products (TPs), calculated as the percentage of the analyte remaining after day 1.

A simple experiment was conducted to determine if filtering plays any role in reducing recoveries from real groundwater samples. Six replicates were taken from the same MP, sediment stirred up from the bottom of the piezometer pipe, and 6 x 500 mL of groundwater samples collected. Before the sediment was stirred up a normal, representative sample was collected from the piezometer for comparisons. This sample

will act as guidance for both the effect of filtering on the sample concentration and also not filtering a particularly 'dirty' sample. All analyses was carried out in triplicate. Filtered samples were filtered through a Buchner funnel fitted with a Whatman[®] (Kent, England) 541 hardened ashless 125mmØ filter papers to a vacuum pump within 24 h following sample collection and extracted on the same day.

Results were inconclusive following this experiment. For example the sample which was taken from the piezometer before sediment was agitated had a concentration of 0.029 µg/L for MCPA. For samples taken for the filtration study, all three replicates of filtered samples had 0.005 µg/L of MCPA and for unfiltered samples 0.006 or 0.005 µg/L of MCPA was present. 4C2MP was also present in the actual sample at a concentration of 0.029 µg/L but this compound was not present when sediment was dislodged from the piezometer and a sample taken. Compounds which were detected during the filtration study i.e. from samples taken after dislodging sediment, were DCP, 2,4-D, fluroxypyr, and PAC. These compounds were not found in the actual sample taken prior to dislodging the sediment indicating that these particular compounds were bound to the sediment in the piezometer rather than from groundwater in the aquifer itself. As a consequence of this experiment samples were not filtered so that any pesticide detections present were from the groundwater being sampled as opposed to compounds present in sediment in the piezometer.

6.3 Literature review of analytical techniques to quantify for pesticides in groundwater

6.3.1 Extraction methods

6.3.1.1 Solid phase extraction

Solid-phase extraction (SPE) is a simple method of sample preparation that concentrates and purifies solutions by sorption onto a disposable solid phase cartridge which is then followed by elution of the analyte with an appropriate solvent. It is one of the most widely used and trusted sample preparation techniques used in laboratories (Richardson and Ternes, 2011; Ramos, 2012). The mechanisms of retention include reversed phase, normal phase, adsorption, and ion exchange (Simpson, 2000). SPE was invented in the 1970s as an alternative approach to liquid-liquid extraction which has since become obsolete due to

the large volumes of solvent required (Solymosné-Majzik *et al.*, 2006). SPE cartridges are typically constructed of polypropylene or polyethylene and filled with an appropriate sorbent bed or packing material with different functional groups depending on the analyte needing to be retained (Simpson, 2000). A liquid sample is passed through the cartridge and analytes are concentrated and purified. The goal of SPE is to quantitatively remove the analyte from solution and quickly recover it with an appropriate solvent. The benefits of SPE include high recoveries of analytes, purified extracts, ease of automation, compatibility with chromatographic analysis, and reduction in the amount of organic solvents as would be used during liquid-liquid extraction techniques (Pico *et al.*, 2007).

During method development the nature and the amount of sorbent, solvent nature, and flow rate should be considered so analyte recoveries are not hampered by common contributing factors such as reduced sorbent capacity or too strong retention of analytes or slow kinetics of sorption (Ramos, 2012). Once a suitable cartridge is found and tested several other steps are involved before and after a sample is loaded onto the cartridge. Cartridges need to be conditioned prior to sample loading so the sorbent bed is activated and all active sites within are receptive to any analytes of interest loaded onto the cartridge (Pico *et al.*, 2007). Many new cartridges do not require this step but its recommended practice to condition prior to loading e.g. using methanol. Solvents are usually added first for conditioning followed by the matrix to be loaded to activate the cartridge. Once conditioned the sample of the same matrix added previously can be loaded. This should be carried out at a low flow rate, drop-wise tends to work best for a large range of analytes (Simpson, 2000), although volatile compounds may need a quicker flow rate. Once all the sample has been passed through the cartridge, the cartridge should be washed with water to remove any impurities. For water matrices, ultra-pure water can be used as this will not remove the analytes of interest from the sorbent bed. The final step is to elute the compounds of interest. For elution a suitable solvent should be picked that's strong enough to remove the analytes into the eluate but not any remaining impurities (Simpson, 2000).

6.3.1.2 Solid phase microextraction

Solid phase micro extraction (SPME) is a sample preparation technique developed by Belardi and Pawliszyn (1989). It is a simple solvent free method which uses a fibre coated with a particular stationary phase to extract analytes from a matrix. The coated fibre is

exposed to the sample matrix with the analytes extracted from the sample matrix through the fibre absorbing the compounds of interest whilst submerged in the sample. The analyte partitions between the polymer and the water (Louch *et al.*, 1992). The analytes to be extracted from the polar aqueous solution are absorbed into the less polar stationary phase. Only a small fraction of the analytes present in the sample are extracted since this is an equilibrium method (Pecoraino *et al.*, 2008). An equilibrium is formed between the concentration of compound in the organic layer and the concentration of the compound in the aqueous medium based on the analytes partition co-efficient (Pawliszyn, 2004). Once the fibre is removed from the sample, it is transferred to the heated inlet of an injector system. SPME is advantageous compared to SPE because it is automated, combines several sample preparation steps to reduce solvent usage, processing time, and is independent of sample size (reducing another possible source of human error). However, SPME can suffer when a large range of analytes are needed to be extracted through competition for active sites and many commercially available stationary phases on fibres are only able to cope with a certain type of compound although progress has been made in recent years in developing coatings which can extract a greater number of compounds (Ramos, 2012). Some of the most commonly quantified analytes extracted using SPME are lindane, heptachlor, aldrin, dieldrin, DDT, DDE, DDD, and endosulfan because they are chlorinated compounds.

The fibre exposed to the aqueous medium must be composed of a suitable polymeric coating for the analyte of interest. Available coatings include polydimethylsiloxane (PDMS), polyacrylate (PA), polydimethylsiloxane/Carboxen (PDMS/Carboxen), polydimethylsiloxane/divinylbenzene (PDMS/DVB) and Carbowax/divinylbenzene (Carbowax/DVB). PDMS and PA are 'liquid' coatings which extract by the less permanent phenomenon of absorption whereas PDMS/DVB, PDMS/Carboxen, and Carbowax/DVB are 'solid' coatings which extract by adsorption, a more permanent mechanism (Pawliszyn, 2004). PDMS and PA fibres are the most suitable for samples containing unknown concentrations of several types of compounds, since displacement of any analytes of higher affinity are of minor concern (Pawliszyn, 2004). When fibres are submerged in the aqueous sample they are agitated and heated to accelerate the transfer of analytes. To aid this transfer of analytes to the fibre the ionic strength of the aqueous medium can be increased by adding salt in the form of sodium chloride or sodium sulphate (Scheyer *et al.*, 2006). Although Sauret-Szczepanski *et al.* (2006) indicates that sodium

sulphate can cause salting on the fibre which will in turn decrease fibre longevity. Organic solvents should not be present in quantities greater than 1% and also humic substances should be removed, preferably through centrifugation so less material for pesticide compound to sorb on to (Pawliszyn, 1989).

6.3.2 Separation methods

6.3.2.1 Gas chromatography

Gas chromatography (GC) is a separation technique used to separate a liquid or gas sample mixture before detection. GC is the preferred technique for non-polar, relatively volatile, and thermally stable compounds (Bueno *et al.*, 2012). It offers good resolution and peak shape if used with capillary columns. Capillary columns were introduced in 1959 but not used widely until 1980. Capillary columns have greater separation power compared to packed columns. Capillary columns consist of open tubes of silica glass with a thin film of liquid phase coating the inner wall. Columns can be up to hundreds of meters in length which enables them to efficiently separate complicated mixtures, however this length also adds to overall run time for separation. Thin films provide high resolution and fast analysis, but have very limited sample throughput while thicker films have good sample capacity but show lower resolution and are typically only used on very volatile compounds. GC uses either helium or nitrogen as the carrier gas. Nitrogen with packed columns is the gas of choice as it is heavier than helium and produces more efficiency. With capillary columns, especially those with thin films, hydrogen gas may be preferable because it allows faster diffusion with the mobile phase with minimal loss in efficiency. The theory of chromatography states that the rate of passage through the capillary column is determined by the relative partitioning behaviour of the solute between the stationary and mobile phases (Gustafson, 1989).

During GC analysis a small amount of liquid (usually 10 μ L) is injected into a hot injector. The heat from the injector and the carrier gas (either nitrogen, helium or a mixture) vaporises the sample onto the column. This is an important step since the sample needs to be introduced onto the column quickly otherwise peak shape will be poor causing lower sensitivity and resolution. The capillary column is coated with a stationary phase which has a different affinity for certain compounds. This affinity coupled with a temperature

gradient in the column oven which houses the column aids separation of analytes before they reach the detector.

6.3.2.2 Liquid chromatography

Liquid chromatography (LC) is an analytical chromatographic technique used to separate compounds which are dissolved in a suitable solvent. LC-MS/MS is the technique most referenced for the analysis of polar and semi-polar organic compounds in environmental samples (Bueno *et al.*, 2012). The sample solution is in contact with a stationary phase in a suitable column and as the sample passes through the column, the compound interacts with the phase. The degree of interaction with the column depends on the compound. For phenoxyacid herbicides and benzonitriles ion exchange mechanisms induce the best response (Hu *et al.*, 2010; Hassan *et al.*, 2011). The interaction differences then allow the ions to separate on the column, eluting at different times and entering the detector at different times to aid detection. The sample is pumped through the column at 1000 – 5000 psi along with two mobile phases pumped at different percentages to create a gradient elution. An aqueous and an organic phase are used, sometimes with an additive such as formic acid which will encourage sharper peak shape. At the start of an injection the aqueous phase dominates and then is gradually replaced with the organic phase to help elute ions off the column. Some ions will require more organic phase to elute them from the column, hence why steps are added into the gradient profile. At the end of the injection 99.9% organic phase should be pumped through the column to elute any lingering ions from the column so the next injection does not suffer from cross contamination. LC coupled with mass spectrometry (MS) has grown in popularity over the past few years for environmental analyses, especially for environmental TPs which tend to be more polar than parent active ingredients (Richardson and Ternes, 2011). Ultra performance liquid chromatography is a recently developed LC technique that uses small diameter particles of around 1.7 μm in stationary phase columns with higher pressures to create narrower peaks of between 5 – 10 secs wide which reduces overall method run times (Richardson, 2012).

6.3.3 Mass spectrometry detection

With mass spectrometry (MS) the GC or LC is coupled with a bench top mass spectrometer providing a lot of information on the qualitative detection of unknown

compounds such as structure, elemental composition, and molecular weight. MS is a powerful tool since it can not only identify a compound but also quantify it. In GC-MS, the most widely used ionisation technique is electron ionisation, in which sample molecules are in the first phase bombarded by high-energy electrons (70 eV), creating high-energy, single charged molecular ions. This is then followed by a loss in excess energy via fragmentation, producing a collection of fragment ions characteristic of the compound (Hajšlová, J and Čajka, 2007). Tandem mass spectrometry offers higher performance than single quadrupole instruments in terms of sensitivity and selectivity (Bueno *et al.*, 2012). Analyte molecules must be first ionized in order to be attracted or repelled by the proper magnetic or electrical fields situated within the MS. Electron impact (EI) is the oldest and most common and will be used for this project for the GC method. EI is employed for generating spectra under controlled conditions to produce fragments of the compounds ion which can be reproduced (Hajšlová, 2007). These fragmentation patterns can be stored in downloadable software libraries (NIST). EI is preferred for the identification of unknowns, determination of molecular structure, and confirmation of the target compound (Hajšlová, 2007). However, the use of selective ion storage (SIS) or selective ion monitoring (SIM) in MS detection reduces the capability of selection of unknowns over sensitivity (Hajšlová, 2007). The ionisation source is heated and under vacuum so most samples are easily vaporised and then ionised. Effluent from the GC column passes into a heated ionisation source at low vacuum and electrons are drawn out from the tungsten filament by a collector voltage of 70eV. This voltage defines the energy of the electrons. These high energy electrons then strike the neutral analyte molecules, causing ionization (usually loss of an electron) and fragmentation. After ionisation, the charged particles are repelled and attracted by charged lenses into the mass analyser. Here the ionic species are separated by their mass-to-charge ratio (m/z).

For the LC method the more sophisticated triple quadrupole MS was used. A triple quadrupole MS consists of two quadrupole MS in series with a radio frequency quadrupole between them which acts as a collision cell. The first- and third- quadrupoles serve as mass filters and the middle a collision cell. The collision cell uses inert gas such as nitrogen to provide collision induced dissociation of a selected precursor ion which was selected in the first quadrupole. Subsequent fragments are then pass into the third quadrupole where they may be filtered and scanned.

6.4 External laboratory analysis

6.4.1 Phenoxyacid herbicide analysis

Samples collected in March and April 2010 were shipped to an external laboratory in Hertfordshire, England within five days of collection. This external laboratory used SPE and GC-MS to quantify for 21 phenoxyacid herbicides with detection limits of 0.02 µg/L.

Appendix 11 lists the compounds analysed in this analyses. Unfortunately the external laboratory are not permitted to disclose details on this method.

Phenoxyacid herbicide analysis was also carried out at the Northern Ireland Environment Agency (NIEA) in Lisburn in the autumn and winter of 2010. A total of 191 samples were processed using equipment and methodology already in place at the NIEA. The method used SPE and LC-MS/MS to quantify for the following nine phenoxyacid herbicides: mecoprop, mecoprop-p, 2,4-D, MCPA, triclopyr, bentazone, fluroxypyr, bromoxynil, and phenoxyacetic acid. SPE was carried out using a Zymark AutoTrace system fitted with six reservoirs. Separation was carried out using a Varian L200 Liquid Chromatogram and detection was carried out using Varian Triple Quadrupole Mass Spectrometer. To 500 mL of groundwater sample, 2.5 mL of methanol was added to increase wetability on the cartridge followed by 2.5 mL of 1 mol dm⁻³ hydrochloric acid and then 500 µL of the internal standard MCPA-D₆. The internal standard was added before SPE clean up for relative recovery information. Strata-X 100µm 500mg 6 mL tubes (Phenomenex, Cheshire) were conditioned at 15 mL/min prior to loading the sample. **Table 6.1** details the SPE cartridge conditioning steps.

Table 6.1 Solid phase extraction (SPE) cartridge conditioning steps for phenoxyacetic acid herbicides analysed at the NIEA.

Step	Description
1	5 mL of methanol:MTBE (10:90, v/v) containing 0.001% formic acid.
2	5 mL of methanol
3	5 mL of deionised water
4	5 mL of 0.13% (v/v) hydrochloric acid

Once cartridges were conditioned, samples were loaded at 6 mL/min onto the cartridges. Once all the sample was loaded, 10 mL of ultra-pure water was flushed through the cartridge at 15 mL/min to remove any impurities and then dried under nitrogen for 35 min. Each cartridge was then soaked to elute with 3 mL of freshly prepared methanol:MTBE (10:90, v/v) containing 0.001% formic acid. Analytes were then eluted off the cartridge at 3 mL/min into 14 mL disposable borosilicate glass test tubes using 8 mL of methanol:MTBE (10:90, v/v) containing 0.001% formic acid. This extract contains the analytes of interest.

The eluted solution was then concentrated to near-dryness under a gentle stream of nitrogen gas generated on-site and in a water bath at 45°C in a Zymark TurboVap System. The concentrated extract was then re-dissolved in acetonitrile:water (60:40, v/v) with 0.001% formic acid, vortexed for 30 sec and transferred to a 2 mL vial for analysis using LC-MS/MS. A Varian 410 autosampler was used and 10 µL of sample was introduced by electrospray injection using a partial loop set up onto a C18 5 µm analytical column at 0.25 mL/min. The aqueous mobile phase was ultra-pure water with 0.02% formic acid and the organic phase used was acetonitrile with 0.02% (v/v) formic acid. **Table 6.2** details the mobile phase gradient programme used for analyte separation on the column. Equilibration time was 5 min.

MS detection details were set as follows on the instrument: needle set points at -4500 V : -3 µA, nebuliser gas at 53 psi, housing at 50°C, shield at -600 V, drying gas at 200°C : 19 psi and CID gas pressure at 1.5 mTorr. The system used the following m/e ratios in **Table 6.3** of parent and daughter ion transitions to undertake the identification, calibration and quantification of each herbicide..

Results were processed from four calibration standards ranging from 0.025 – 8 µg/L with correlation coefficients greater than 0.993 and curves fitted with a linear or quadratic fit. Quality controls (QCs), limits of quantification (LOQ), and blanks were processed with each batch to monitor method performance. This method was capable of detecting MCPA, mecoprop, mecoprop-p, 2,4-D, bentazone, and bromoxynil in aqueous samples to 0.025 µg/L with fluroxypyr, triclopyr, and phenoxyacetic acid having LOD of 0.035, 0.035, and 0.45 µg/L, respectively. This method was unable to differentiate between mecoprop and

mecoprop-p because both compounds have the same transitions (**Table 6.3**). Therefore results quote mecoprop(s) when a detection of mecoprop or mecoprop-p was detected.

Table 6.2 Mobile phase gradient programme used for the NIEA phenoxyacid herbicide method.

Time (min)	Aqueous mobile phase (%)	Organic mobile phase (%)
0	90	10
1	70	30
2	70	30
10	45	55
12	10	90
17	90	10

Table 6.3 Parent and daughter transitions used for identification and quantification during the NIEA phenoxyacid herbicide method.

Compound	Parent (m/e)	Daughter (m/e)
phenoxyacetic acid (PAC)	151	106
MCPA	199	141
Mecoprop(s)*	213	141
2,4-D	219	161
Fluroxypyr	254	196
Triclopyr	256	198
Bentazone	239	197
Bromoxynil	274	81

*mecoprop and mecoprop-p

6.4.2 Organophosphorous herbicide analysis

Samples collected in March 2012 were shipped to the same external laboratory in Hertfordshire, England within five days of collection as the phenoxyacid herbicide samples were sent to in section 6.3.1. This external laboratory used SPE and GC-MS to quantify for 27 organophosphorous herbicides with detection limits of 0.02 µg/L. **Appendix 11** lists the compounds analysed for in this analyses. Unfortunately the external laboratory are not permitted to disclose details on this method.

6.5 Analysis of organochlorine pesticides using gas chromatography*

Until now no other method has determined both TPs of heptachlor during the same chromatographic run or taken into consideration the EU DWS(i) for validation for the four organochlorine compounds quantified in this method. The objective of this work was to be able to quantify the compounds lindane, heptachlor, *exo*- and *endo*- heptachlor epoxide in groundwater matrices with LOQ half the EU DWS(i) for these compounds which is 0.03 µg/L.

6.5.1 Experimental

HPLC grade methanol was purchased from Reagecon (Shannon, Ireland) and deionised water with a conductivity of 0.055 µS/cm was generated on site using a Sartorius Arium® 611 µV water purification system (Sartorius Stedim UK Ltd, Dublin, Ireland). SPME fibres were all purchased from Supelco™ (Sigma Aldrich, Arklow, Ireland) to include the coatings DVB/CAR/PDMS 23GA, 50/30 µm; PDMS-DVB 23GA; Polyacrylate 23GA, 85 µm, and Carboxen/PDMS 23GA, 85 µm. HPLC p.a. puriss sodium chloride (NaCl) was purchased from Sigma Aldrich (Arklow, Ireland). 10 mL headspace vials with screw caps and PTFE septum 1.5 mm were purchased from InfoChroma (New Haven, USA).

Lindane, heptachlor, *exo*-heptachlor epoxide and *endo*-heptachlor epoxide standard solutions (100 µg/mL in methanol) were purchased from AccuStandard (NewHaven, CT, USA). The deuterated internal standard α -HCH-D₆ (100 ng/µL in Cyclohexane) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). A primary stock standard solution was prepared at a concentration of 100 µg/L in methanol to contain all four compounds of interest. From this primary stock, intermediate working standards for a six point calibration were prepared in deionised water so as to contain less than 1% (v/v) solvent to target the concentrations: 0.015, 0.1, 0.5, 1.0, 2.0 and 5.0 µg/L. For validation studies intermediate working solutions were made to target the concentrations: 0.015, 0.03, 0.05, 0.1 and 0.15 µg/L.

*This chapter section is the basis for a paper accepted for publication in the Journal of Chromatography A volume 1284 page 1 – 7 in November 2012 as: Sarah-Louise McManus, Catherine E. Coxon, Karl G. Richards and Martin Danaher 'Quantitative solid phase microextraction – gas chromatography mass spectrometry analysis of the pesticides lindane, heptachlor and two heptachlor transformation products in groundwater.'

A working internal standard solution of 25 µg/L was prepared and was used to spike all samples for validation and application work to achieve 0.1 µg/L of internal standard in each sample. Five mL of sample was transferred into a 10 mL headspace vial containing 2.5 g NaCl to achieve 50% (w/v) saturation. The addition of salt improves extraction efficiency by reducing the solubility of analytes in the sample by increasing the ionic strength of the sample (Pawliszyn and Alexandrou, 1989; Louch *et al.*, 1992). Five mL of H₂O was used because when the fibre was immersed in the sample this volume did not allow any sample to touch the barrel of the SPME fibre syringe which may allow for carry over and cross contamination. The penetration depth of the fibre was set to 28 mm.

Extraction was carried out using a CTC Combi-pal auto-sampler (CTC Analytics AG, Switzerland) configured for SPME extraction using a Combi PAL SPME kit (CTC Analytics, Switzerland). Disposable SPME polyacrylate (PA) fibres were directly immersed in the sample vial and extracted at 50°C for 45 min with agitation at 250 rpm. Agitation was used to accelerate the extraction, reducing time spent extracting (Pawliszyn and Alexandrou, 1989). Desorption of the fibre took place in a Varian 1079 injector at 250°C in splitless mode for 4 min following extraction. A Varian GC glass insert SPME inlet liner for 1078/1079 injectors (0.8mm I.D) was used (Sigma Aldrich, Arklow, Ireland). A splitless injection was carried out to help focus the vaporised sample on the column during desorption. The split was initially on at a ratio of 10, and then turned off following injection. After one minute the split was turned on at a ratio of 10 for four min. The fibre was then baked out at 250°C for 10 min following desorption in a parallel Varian 1079 injector installed on the instrument to remove non-desorbed analytes and to prevent sample carry over. The PA fibre began to lose sensitivity after 51 injections, including a six-point calibration and was replaced. The PA fibre was conditioned prior to any analysis for 60 min at 280°C as recommended by SupelcoTM (Sigma Aldrich, Ireland) in the additional Varian 1079 injector installed on the instrument.

Analysis was carried out on a GC-MS ion trap (Varian CP 3800 and Varian MS Saturn 2000) coupled to a split/splitless Varian 1079 injector operated in splitless mode with a Merlin MicrosealTM (Sigma Aldrich, Arklow, Ireland) at 250°C during chromatographic runs. The use of a Merlin MicrosealTM helped reduce the appearance of phthalate plasticisers which would otherwise occur with use of a normal plastic septum. Separation was achieved using a Zebron ZB-5 capillary column (film thickness 0.25 µm; 30m x 0.25

I.D) purchased from Phenomenex (Cheshire, UK). Grade A helium gas was used as the carrier gas (BIP[®], Air Products) at a flow rate of 1.0 mL/min. The oven temperature was as follows: 50°C held for two min and then increased to 280°C at 8°C/min. The chromatographic run time was 30.75 min.

Analytes were acquired in EI ionisation mode at -70eV with SIS. The MS transfer line, trap and manifold temperatures were set to 300, 245, and 45°C, respectively. The retention time of each analyte was identified by injection of individual standards and the MS was segmented using SIS with the analytes unique ions monitored (**Table 6.4**). SIS optimised the MS by using only the dominant ions for each compound of interest based on their compound structures. For example heptachlor with ions: 100, 272, 274, 270, and 102 m/z. SIS improves sensitivity by discarding ions which may interfere or compete in the MS trap. During SIS, the scan time was 0.4 sec, the target total ion count (TIC) was 20,000 counts, the pre-scan ionisation time was 100 µsec, the background mass was 49 m/z, and the RF dump value was 650 m/z. The multiplier offset was 275 V, the emission current 30 µA, and the count threshold at 1 count. *Exo*- and *endo*- heptachlor epoxide were acquired in the same segment because both analytes eluted closely together, which made separating them in two windows impractical without increasing overall GC run time. **Figure 6.3** shows a typical chromatographic trace at 0.1 µg/L. Peak area was measured for quantitation with the ratio of the sample peak area to that of the internal standard ratio derived for each calibration standard.

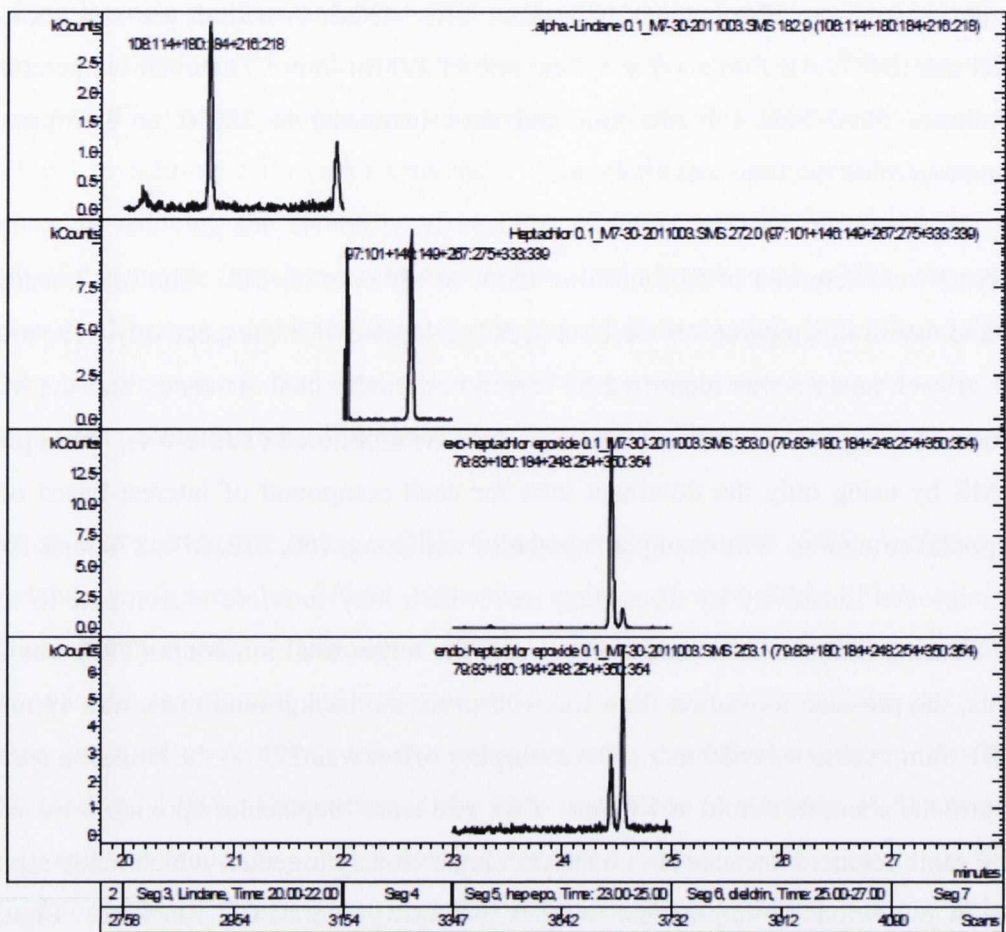
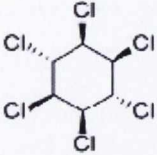
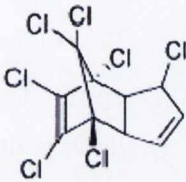
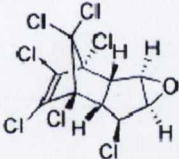
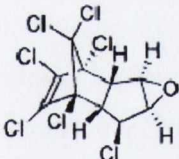
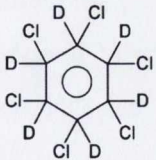


Figure 6.3 Chromatographic trace, showing the sum of all ions, for each compound at 0.1 μ g/L.

Table 6.4 Average compound retention time from 18 replicates, characteristic ions, and the quantification ions monitored using selective ion storage (SIS).

Analyte	Retention time (min)	Characteristic ions in order of decreasing abundance (m/z)	Quantification Ion (m/z)
lindane 	20.79	<u>183</u> , 219, 217, 109, 221	183
heptachlor 	22.62	100, <u>272</u> , 274, 270, 102	272
<i>exo</i>-heptachlor epoxide 	24.46	81, <u>353</u> , 355, 351, 357	353
<i>endo</i>-heptachlor epoxide 	25.57	81, <u>253</u> , 185	253
α-HCH-D₆ 	19.53	<u>197</u> , 212, 155	197

Linearity, within laboratory repeatability (WLr), specificity, LOQ, and stability experiments were conducted to confirm that results were reliable and consistent in accordance with EU Council Directive (2002/657/EC) (European Commission, 2002). To test method specificity 20 blank samples were processed with five mL of ultra pure water matrix plus 2.5 g of $\geq 99.5\%$ NaCl to make sure nothing present could interfere with the compounds of interest. WLr was assessed by a single analyst on three separate days. WLr studies test the precision and accuracy of a method under various conditions. The WLr study was carried out by analysing water samples fortified at five concentrations ($n=6$ at each level): 0.015, 0.03, 0.05, 0.1, and 0.15 $\mu\text{g/L}$. This allows results to be found for each compound with spikes at 0.5, 1.0, and 1.5 times the permitted limit of 0.1 $\mu\text{g/L}$ for lindane and 0.03 $\mu\text{g/L}$ for heptachlor, *exo*- and *endo*- heptachlor epoxide. The LOQ is the lowest concentration at which the analyte can be reliably detected and quantified (Armbruster and Pry, 2008). This was determined by testing 10 replicates fortified at the concentration 0.015 $\mu\text{g/L}$. The average and the SD was found for each compound and used to find the LOQ which is the number of replicates multiplied by the average SD. The calculated LOQ was then measured on the instrument in triplicate and the relative standard deviation (RSD) calculated. The RSD should be less than 20%. RSD was calculated by multiplying the average SD by 100 divided by the average concentration of five replicates spiked at each compounds calculated LOQ.

PA fibre longevity over time was determined by continually injecting spiked samples at 0.05 $\mu\text{g/L}$ until a consistent loss in concentration occurred which was taken as the number of injections a single PA SPME fibre could handle. The calculation of each analytes stability in prepared vials with sodium chloride (NaCl) over time was carried out by using the solution of the analyte freshly prepared at the time of analysis (C_o) and compared with the concentration found at each time point (C_i) to determine the percentage of analyte remaining in the vial (**Eqn. 6.2**). Samples were tested every two days until the analytes began to show a loss in concentration.

$$\text{Analyte remaining (\%)} = C_i \times 100 / C_o$$

[**Eqn. 6.2**].

6.5.2 Results and discussion

During initial method development four SPME fibres were tested to determine the ideal choice for the compounds of interest. The best recovery was achieved with a polyacrylate (PA) material for all the compounds (**Figure 6.4a**). It was observed that over time the actual concentration increased during the six replications with PDMS-DVB fibres. PDMS-DVB fibres should be avoided as they will not represent the true concentration in the sample. This carry over may be explained by PDMS-DVB fibres method of sorption. PDMS-DVB coatings sorb through adsorption which is more permanent than absorption (Pawliszyn and Alexandrou, 1989) resulting in carryover and subsequent cross contamination of samples. Salt saturation (0, 10, 30, 50, and 70%, w/v) experiments were conducted in triplicate using samples fortified at 0.05 µg/L. The ideal salt saturation for a PA fibre was found to be 50% (w/v) (**Figure 6.4b**). By increasing the salt content, the ionic strength of the water has been increased which allows the analytes to partition more effectively onto the SPME fibre (Pawliszyn, 2004).

The extraction temperature and time spent extracting at 250 rpm was optimized by testing spiked samples in duplicate at 30, 50, and 70°C (**Figure 6.5a**) and for extraction times 25, 35, 45, and 55 min (**Figure 6.5b**). Optimum extraction temperature was 50°C which also gave the best precision range (0.1 – 5.3%) and 45 min time extracting at 50°C suited all compounds best except lindane which prefers 55 min. Silinized vials were tested to help improve precision using a 10 % v/v silane solution in toluene. In six replicates fortified at 0.1 µg/L, lindane, heptachlor, and endo-heptachlor epoxide were not detected. Only exo-heptachlor epoxide was detected with an average concentration of 0.061 µg/L. Vials were not silanized for validation and application work.

Linearity is the ability to obtain results directly proportional to the sample concentration. A six point calibration curve from 0.015 – 5.0 µg/L was analysed in triplicate. EU Council Directive 2002/657/EC (SANCO/825/00, 2000) requires a minimum of five points across the calibration curve. Each of the four compounds of interest had a correlation coefficient of 0.9936 or greater when three sets of calibration curves were analysed and the average taken for each. Calibration curves were linear and not forced through the origin. Peak to peak signal-to-noise ratios revealed that all compounds can be seen with signal-to-noise ratios greater than 10 between the linear range. Signal-to-noise ratios should be greater than or equal to 10 for quantification or greater than or equal to three for qualitative

determination (SANCO/825/00, 2000). Fytianos *et al.* (2006) and Li *et al.* (2003) used signal-to-noise ratios of 3:1 to infer the LOD for heptachlor, lindane and heptachlor epoxide whereas this method uses quantitative peak to peak signal-to-noise ratios of 10:1. The retention times of each analyte gathered during the linearity and WLR study (n=33) did not change more than 2.5% in accordance with SANCO/825/00 (Ratola *et al.*, 2006) and selectivity tests carried out using 20 blank replicates revealed that no other interference peaks appeared at the analytes retention time. The deuterated internal standard was added to each sample to achieve the fortified concentration of 0.1 µg/L.

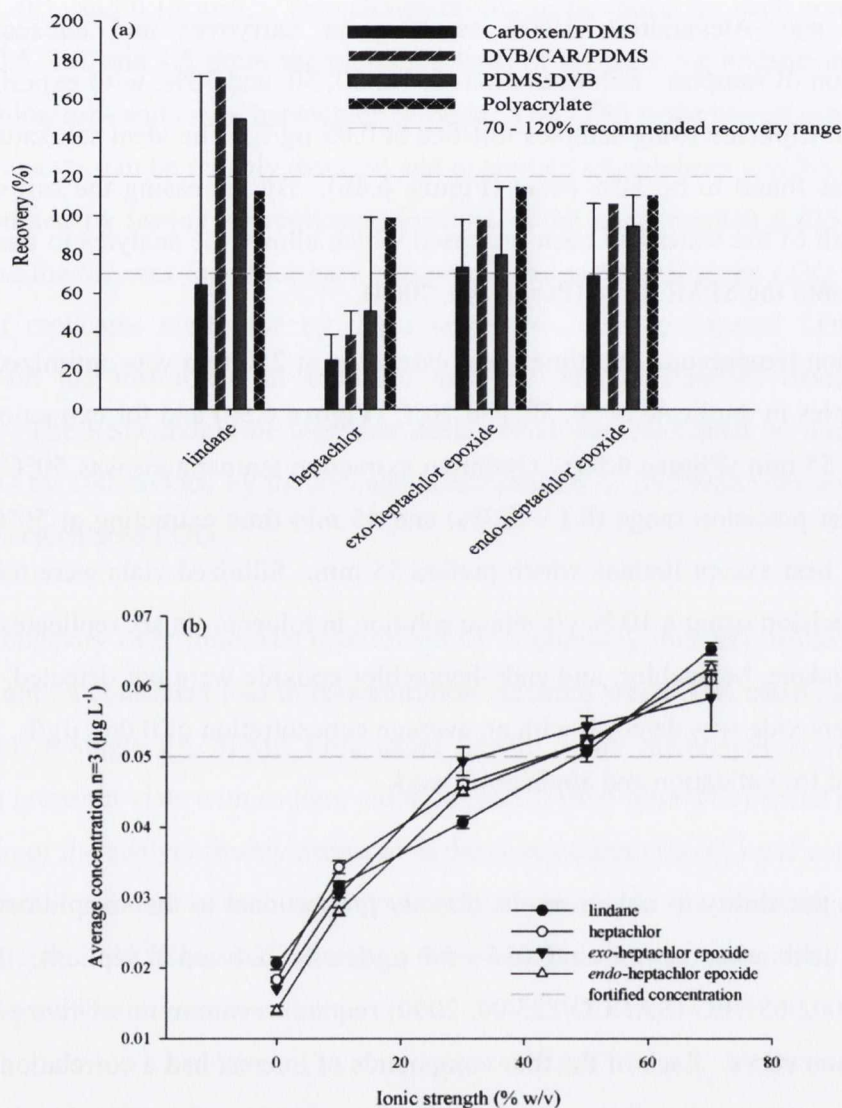


Figure 6.4 Optimisation of SPME conditions: (a) fibre choice and (b) ionic strength.

Error bars represent standard error of the sample mean.

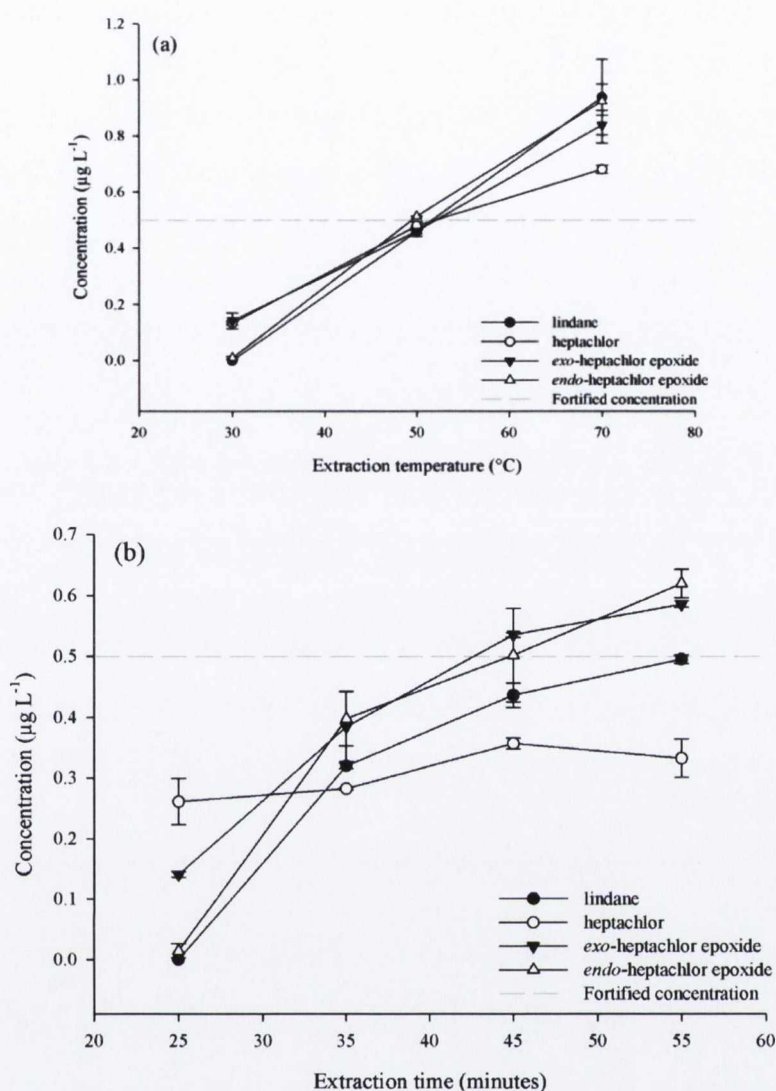


Figure 6.5 SPME optimization extraction experiments for (a) temperature and (b) time. Error bars represent standard error of the sample mean.

Recoveries from WLr studies (**Appendix 12**) indicate that lindane, heptachlor and *exo*- and *endo*-heptachlor epoxide all had good recoveries spanning the range (96 – 101%) over three concentration levels to within the 70 to 120% permitted limits set by SANCO/825/00 (SANCO/825/00, 2000). For WLr, the coefficient of variation (CV%) should be less than 35% (SANCO/825/00, 2000). CV% for lindane, *exo*- & *endo*-heptachlor epoxide and heptachlor were all less than 10.5% (**Appendix 12**). Relative recoveries of 81%, 79% and 86% in a study by Faraji and Helalizadeh (2010) were found for lindane, heptachlor and heptachlor epoxide, respectively. Precision for these recoveries were less than 7.3% but samples were spiked with uncharacteristically high concentrations of 2 and 10 µg/L.

Basheer *et al.* (2002) also spiked samples for validation at high concentrations of 40 $\mu\text{g/L}$ which is 400 times the EU DWS(i).

The LOQ for each compound was less than each individual compounds permitted limit (PL) in drinking water. Lindane has a drinking water standard of 0.1 $\mu\text{g/L}$, its LOQ was 0.023 $\mu\text{g/L}$ with a RSD of 3.8%. Heptachlor, *exo*-heptachlor epoxide, and *endo*-heptachlor epoxide had LOQ of 0.015, 0.017, and 0.017 $\mu\text{g/L}$, respectively with acceptable RSD all below 5.6% (**Appendix 12**).

Fibre longevity (**Figure 6.6**) to repeated injections fortified at 0.05 $\mu\text{g/L}$ showed a drop in sensitivity after 51 injections for lindane, 55 injections for *endo*-heptachlor epoxide, 56 injections for heptachlor and 87+ injections for *exo*-heptachlor epoxide. Thus a PA fibre for these compounds analysed together will only last 51 including a six-point calibration performed on each SPME PA fibre. However, QCs should be run every 10 injections to monitor fibre sensitivity especially in dirty samples with high concentrations as this will vary fibre deterioration.

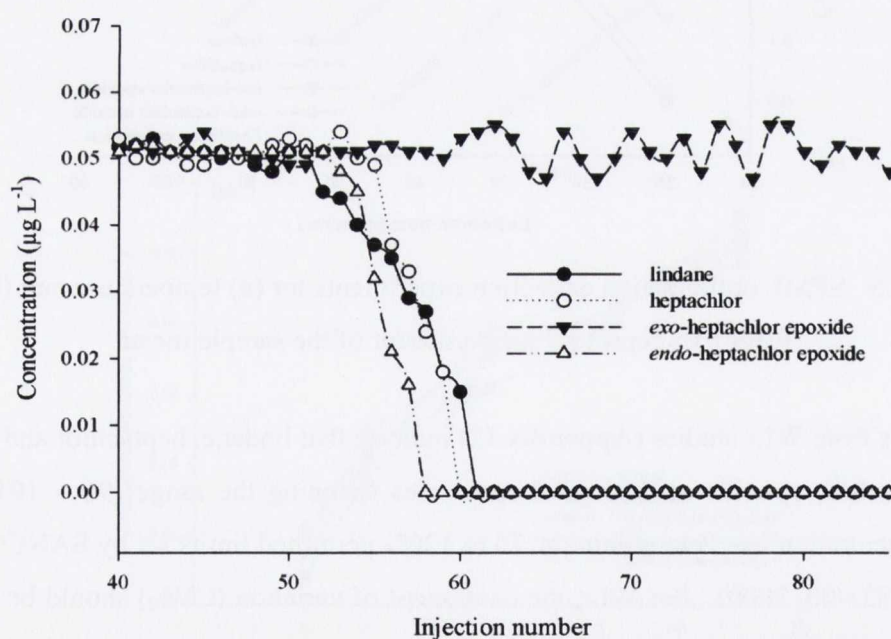


Figure 6.6 Fibre longevity following repeated injections of fortified samples at 0.05 $\mu\text{g/L}$.

6.5.3 Conclusions

A less labour intensive method using PA SPME fibres and GC-MS-SIS in EI mode was developed and validated in accordance with EU directives and protocols for the identification and quantification of two compounds now banned and two transformation products of heptachlor, which no other method until now has determined. Lindane, heptachlor, *exo*- and *endo*- heptachlor epoxide can be accurately identified and quantified at concentrations between 0.015 and 5.0 µg/L which will be able to detect concentrations in accordance with EU Council Directive 98/83/EC PLs allowed in groundwater of 0.1 µg/L for lindane and 0.03 µg/L for heptachlor and its two TPs. The 17 day stability study indicates that all prepared vials should be analysed within 24 h otherwise degradation of the sample will occur, especially in the case of heptachlor. PA fibres for these compounds will last up to 51 injections before fibre affinity losses occur. GC-MS with selective ion storage (SIS) was the technique adopted for quantification and identification. SPME coupled with GC-MS in SIS mode provides a powerful technique for the determination of several PPP covering a range of chemical groups with the ability to achieve LOQ below those set by the EU.

6.6 *Analysis of phenoxyacid herbicides and benzonitriles using liquid chromatography**

This method was developed to determine ten a.i. present in PPP and eight of their most common TP's in groundwater matrices to LOQ of 0.008 µg/L. This includes BAM and DBA both TP's of dichlobenil, a PPP now banned in Ireland and across several countries in the EU. This is the most comprehensive multi-residue method that has been developed for phenoxyacid herbicide residues in groundwater to date and further novelty lies in this methods ability to also detect benzonitrile compounds through polarity switching from negative to positive mode.

* This chapter section is the basis for a paper under internal review and will be submitted for publication to the Journal Water Research as: Sarah-Louise McManus, Mary Moloney, Catherine E. Coxon, Karl G. Richards and Martin Danaher 'Rapid determination & application of 10 pesticides and 8 transformation products in groundwater using SPE and UHPLC-MS/MS.'

6.6.1 Experimental

Formic acid (FA) and hydrochloric acid (HCl) were purchased from Sigma Aldrich (Arklow, Ireland). Ultra-pure water (18.2 MΩm) was produced in house using a Millipore water purification system (Cork, Ireland). Acetonitrile, acetone, chloroform, methyl tert-butyl ether (MTBE), and methanol used were all of HPLC grade and purchased from Lennox Laboratory Supplies Ltd. (Dublin, Ireland). Extracts were filtered using 1 mL sterile syringes from BD Plasticpak™ (Dublin, Ireland) coupled to PTFE filters 0.2 μm, 13 mm from VWR International Ltd. (Dublin, Ireland). Filtered extracts were stored in 1.5 mL clear screw cap neck vials with pre-slit caps purchased from Waters (Dublin, Ireland) with 200 μL cylindrical glass inserts purchased from Apex Scientific (Maynooth, Ireland). Bond Elut ENV 200 mg/6 mL cartridges from Agilent (Dublin, Ireland) were used for SPE clean up and Strata-X 200 mg/6 mL cartridges from Phenomenex (Cheshire, UK) were used in development. Borosilicate glass 14 mL glass disposable test tubes were obtained from VWR (Dublin, Ireland). High quality nitrogen gas (99% purity) was purchased from BOC gases (Dublin, Ireland) for use with sample concentration. Mobile phases were filtered through GH Polypro hydrophilic polypropylene membrane filters 0.2 μm, 47 mm from PAL-company (Ann Arbor, Michigan, U.S.A). Solvent reservoir caps and Teflon tubing with an I.D of 3 mm was purchased from Waters (Dublin, Ireland).

1 L amber Pyrex® glass bottles were obtained from Lennox (Dublin, Ireland) and polyethylene adaptor caps with luer tips were purchased from Phenomenex (Cheshire, UK). Samples were concentrated to near-dryness using a Techne DB-3 Dri-block® sample concentrator fitted with aluminium blocks, both from Lennox (Dublin, Ireland) and a vortex mixer from VWR (Dublin, Ireland) was used.

Analytical standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) including deuterated MCPA-D₆ for use as the internal standard. 3,5-dibromo-4-hydroxybenzoic acid (BrAc) was purchased from Wako Chemicals GmbH (Nuess, Germany). Primary stock standard solutions were prepared in HPLC grade methanol at concentrations of 100 μg/mL. Working solvent standards were prepared in HPLC grade methanol at concentration ranges of 20 (Std 1), 50 (Std 2), 100 (Std 3), 500 (Std 4), and 1000 (Std 5) μg/L. MCPA-D₆ was prepared at concentrations of 500 μg/L. Primary and working standards were stable for six months when stored at 4°C. Extracted matrix matched calibrations were prepared by fortifying 500 mL of ultra-pure water with 200 μL of working standard mixes (Std 1 – 5) prior to extraction to achieve a calibration curve

from 0.008 – 0.4 µg/L. Extracted matrix matched calibrants were stable for up to seven days at 4°C.

Validation fortification solutions were prepared in HPLC grade methanol to target the concentrations of 0.02, 0.04, and 0.06 µg/L. Recovery controls were prepared by fortifying samples post- and pre- extraction to monitor for loss of analytes during preparation. This technique combined with deuterated internal standards can help account for matrix effects. Blanks and QCs were extracted alongside samples in each batch to monitor for recovery and cross-contamination.

Water samples (500 mL) in amber glass Pyrex[®] bottles were acidified by addition of 2 mM HCl (2 mL). 200 µL of the working internal standard solution was then added. The sample was gently shaken and the bottle fitted with a reservoir cap and 40 cm of Teflon[®] tubing which was fed to pre-conditioned SPE cartridges fitted with polyethylene adaptor caps. Samples were loaded at 5 mL/min through Bond Elut ENV SPE cartridges (200 mg in a 6 mL tube). The cartridges were preconditioned using 10 mL of HPLC grade methanol and 10 mL of ultra pure water prior to loading. Once all sample was loaded onto the cartridge, adaptor caps and Teflon[®] tubing were removed. Cartridges were sequentially eluted by adding 2 × 3.5 mL volumes of HPLC grade acetone into a 14 mL glass test-tube. The acetone was concentrated from the extracts under nitrogen at 40°C to dryness. Concentrated extracts were re-suspended in 500 µL of acetonitrile:water (50:50, v/v), vortexed for 30 sec and filtered through 0.2 µm PTFE filters into 2 mL autosampler vials with glass inserts.

Separations were performed using a Waters (Milford, MA, U.S.A) Acquity UHPLC[®] system comprising of a stainless steel BEH analytical column (2.1 mm × 100 mm, particle size 1.7 µm) protected by an in-line stainless steel 2.1 mm × 10 mm guard column both maintained at 60°C and the pump was operated a flow rate of 0.6 ml min⁻¹. A binary gradient separation was used to separate analytes comprised of mobile phase A: 0.01% formic acid in ultra pure water and mobile phase B: 0.01% formic acid in acetonitrile. The gradient programme was as follows: [1] at 0.01 min is 99.9% A, [2] 2 min 85% of A, [3] at 7 min 40% of A, [4] 8.5 min 0.1% of A and [5] at 9.1 min 99.9% of A. Total run time was 11.9 min and injection volume was 20 µL. Weak and strong autosampler needle washes consisted of water:acetonitrile (50:50, v/v) and acetonitrile, respectively.

Detection and quantification occurred using a Waters Quattro Premier XE triple quadrupole instrument with electrospray ionisation (ESI) interface (Milford, MA, USA). Nitrogen (99.9%) was used for desolvation (1000 L/h) and cone gas (50 L/h). Argon (99.39%) was used as collision gas (0.013 L/h). The source temperature was set to 130°C and the desolvation gas temperature was 350°C. The ion spray voltage was set at 3000 eV for positive mode and 500 eV for negative mode. The UHPLC-MS/MS system was controlled using MassLynx™ software and data processed using TargetLynx™ software supplied by Waters.

MS conditions were optimised through tuning analyte-specific parameters. Individual standard solutions were prepared in methanol at 1,000 µg/L and injected directly into the MS detector at a flow rate of 10 µL/min and monitoring the two most abundant fragment ions produced from the molecular ion. MRM windows were time-sectored, and dwell time manipulated to get maximum response from the instrument. A summary of the monitored ions and optimised MS parameters obtained for each analyte is given in **Table 6.5**.

The method was validated with reference to EU legislation 2002/657/EC (European Commission, 2002) and SANCO/825/00 (SANCO/825/00, 2000). The following studies were undertaken: specificity, linearity, and within laboratory repeatability (WLR). WLR was achieved using samples fortified at 0.02, 0.04, and 0.06 µg/L. An accredited external laboratory was also employed to test blind four samples spiked at 0.2 µg/L (n=2) and 2.0 µg/L (n=2). This laboratory used SPE and GC-MS, details of which are unavailable outside of the laboratory.

Table 6.5 Specific compound settings applied during both electrospray ionisation (ESI) positive and negative mode with m/z ratios for the precursor and product ion transitions.

Compound	Cas. No.	ESI polarity	MRM window	Precursor (m/z)	Product (m/z)	Cone (V)	Collision energy (V)	Dwell time (s)
2,6-dichlorobenzamide (BAM)	2008-58-4	+	1	189.95	108.95	34	34	0.15
				189.95	144.96	34	27	0.15
				189.95	172.93	34	18	0.15
Phenoxyacetic acid (PAC)	122-59-8	-	2	151.9	94.06	23	14	0.07
				151.9	108.00	23	9	0.07
Dicamba	1918-00-0	-	2	219	175.02	15	8	0.07
				221.02	176.84	15	7	0.07
2,3,6-trichlorobenzoic acid (TBA)	50-31-7	-	2	222.95	178.9	14	7	0.07
				224.95	180.96	14	7	0.07
Bentazone	25057-89-0	-	3	239.19	132.01	26	27	0.07
				239.19	175.01	26	20	0.07
				239.19	196.99	26	21	0.07
Fluroxypyr	69377-81-7	-	3	253.02	194.59	22	13	0.07
				253.02	232.95	22	4	0.07
3,5-dibromo-4-hydroxybenzoic acid (BrAc)	3337-62-0	-	3	294.87	250.80	35	18	0.005
2,4-dichlorophenol (DCP)	120-83-2	-	4	160.82	125.03	36	16	0.02
				162.89	127.00	36	19	0.02
3,5,6-trichloro-2-pyridinol (T2P)	6515-38-4	-	4	195.99	195.99	28	1	0.02
				197.99	197.99	28	1	0.02
				199.99	199.99	28	1	0.02
MCPA acid	94-74-6	-	4	199.07	140.97	26	15	0.015
				201.08	143.04	26	15	0.015
MCPA D6 (methyl-D3, phenoxy-D3)	-	-	4	204.9	146.90	25	15	0.01
2,4-D	94-75-7	-	4	219	160.91	24	16	0.015
				220.94	162.98	24	15	0.015
Triclopyr	55335-06-3	-	4	254.03	195.86	19	14	0.015
				254.03	218.06	19	6	0.015
Bromoxynil	1689-84-5	-	4	275.98	78.92	38	26	0.015
				275.98	80.94	38	26	0.015
4-chloro-2-methylphenol (4C2MP)	1570-64-5	-	4	141.04	141.04	36	5	0.1
				143.04	143.04	36	5	0.1
3,5-dichlorobenzoic acid (DBA)	50-84-0	-	5	188.8	144.8	25	11	0.015
				190.8	147	25	11	0.015
2,4,5-trichlorophenol (TCP)	95-95-4	-	5	196.85	158.88	25	18	0.08
				196.85	160.88	25	18	0.08
Mecoprop	71526-69-7	-	5	213.13	140.94	25	16	0.1
Mecoprop-p	16484-77-8	-	5	213.13	140.94	25	16	0.1

6.6.2 Results and discussion

Strata-X and Bond Elut ENV cartridges were tested in a simple recovery study. A 200 mg sorbent bed size in a 6 mL cartridge were chosen since these sizes proved suitable for 500 mL sample volume as depicted from other studies (Marchese *et al.*, 2002; Jensen *et al.*, 2009; Sklivagou *et al.*, 2010). Ultra pure water samples (500 mL) were fortified with 200 μ L of 500 μ g/L working standard and loaded onto pre-conditioned cartridges drop wise. Cartridges were eluted using 6 mL of acetonitrile. Absolute recovery ranged from 15 – 86% for Strata-X and 20 – 124% for Bond Elut ENV (**Figure 6.7a**). Recovery should range between 70 – 120% for groundwater matrices (SANCO/825/00, 2000). Acetone, chloroform, acetonitrile:water (50:50, v/v), methanol, methanol:water (50:50, v/v) and MTBE:methanol (90:10, v/v) were tested as elution solvents. Consideration was given to the unresponsive compounds: PAC, TBA, BAM, fluroxypyr, dicamba, and BrAc (**Figure 6.7a**). Six mL of acetone for elution improved recovery for all compounds significantly (**Figure 6.7b**). Marked improvements were found for dicamba and BAM, but traded off for a decrease in recovery for TCP. Six, seven, and eight mL of acetone was tested alongside concentration temperature in a Techne evaporation Dri-block[®]: 30, 35, 40, and 45°C using samples fortified with 100 μ g/L. All elution solvents were delivered in 3, 3.5, and 4 mL aliquots with 7 mL found to be optimum with a 40°C temperature. All tests were carried out in duplicate.

A Waters Acquity UPLC[®] BEH and HSS column were tested at 0.6 mL/min with an operating temperature of 60°C. The BEH phase column gave the best peak shape for the 18 compounds. The BEH phase is especially suited to retaining polar compounds. A stainless steel 10 $\times$ 2.1 mm guard column was assembled to the BEH column to prevent residues contaminating the columns stationary phase without hampering chromatography or sensitivity.

The most abundant precursor ion and at least one product ion were monitored. Mecoprop and mecoprop-p have the same MRM transition of 213.1 > 140.9 (**Table 6.5**) thus this method can not differentiate between the two herbicide a.i. In modern PPP mecoprop-p is the dominant a.i. used. During this study a detection of either of these compounds will be referred to as mecoprop(s).

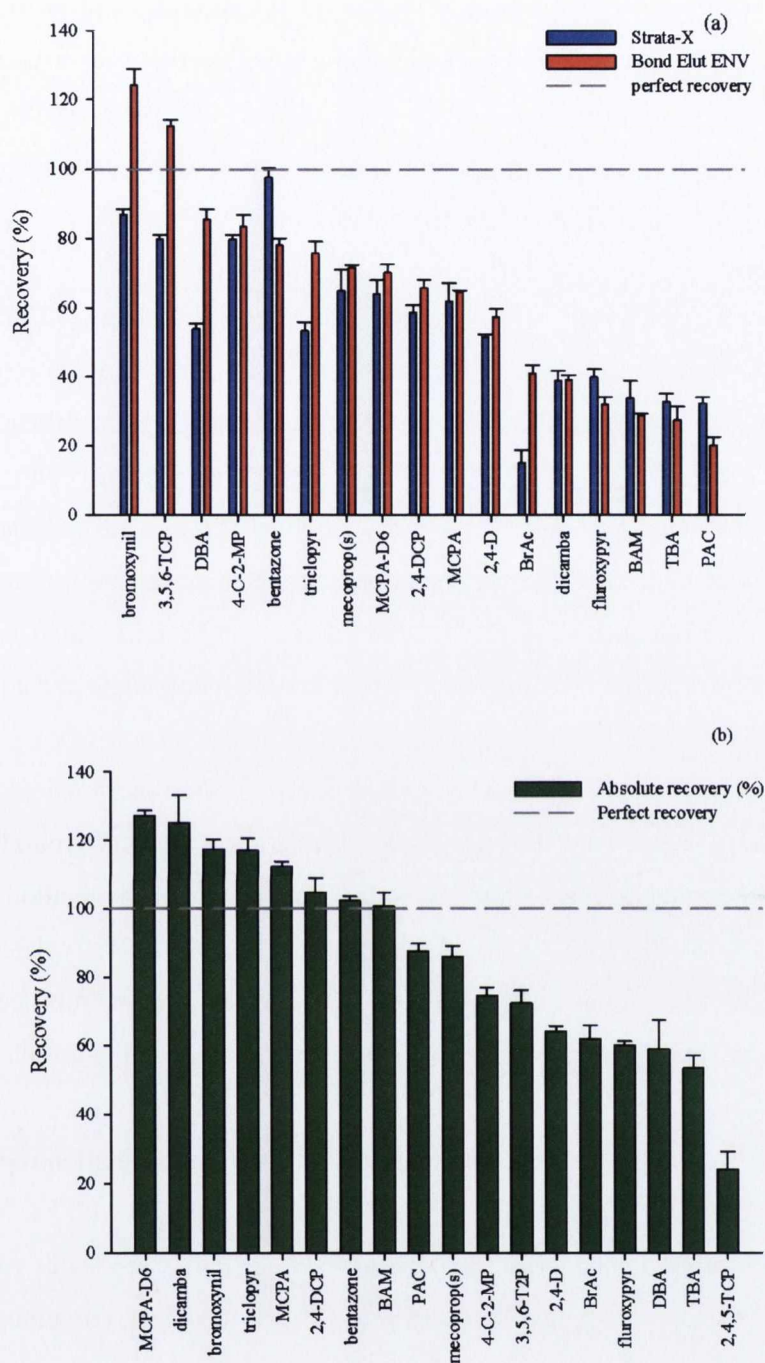


Figure 6.7 (a) Absolute recoveries for each compound using samples spiked at 100 µg/L from Strata-X and Bond Elut ENV (200mg in 6ml) SPE cartridges and (b) absolute recoveries for Bond Elut ENV cartridges using 6 mL of acetone as an elution solvent. Error bars represent standard error of the sample mean.

The following injection solvents were tested: 100% DMSO, 100% methanol, 100% acetonitrile, methanol:water (50:50,v/v), and acetonitrile:water (50:50, v/v).

Acetonitrile:water (50:50, v/v) was chosen as the injection solvent as it gave the best response for all compounds, with noticeable differences for the weaker compounds: PAC and DBA. The S:N ratio was an average of 543 for acetonitrile to 1,453 for acetonitrile:water (50:50, v/v). A column temperature of 60°C gave the best response. Matrix matching the injection solvent improved sensitivity.

Dicamba, triclopyr, TCP, and DBA initially had poor peak shape. The mobile phase additives: acetic acid, formic acid (FA), and ammonium formate were tested at 0.005 – 0.05%. All analytes preferred 0.01% FA. Cross-talking within the collision cell slightly interferes with mecoprop and 4C2MP, and 2,4-D, and DCP. Triclopyr and 3,5,6-T2P, and TBA and dicamba also cross-talk but they are resolved (**Figure 6.8**). Cross-talking is an artefact of collision cell in MS where ions occur at the same retention time (Vogeser and Seger, 2010). The quantifier ion for 4C2MP elutes at 5.31 min which is not the same retention time as mecoprop(s) eluting ions. 2,4-D and TCP both elute at 5.17 min.

Method specificity was tested using twenty blank samples. No interferences were revealed in a known blank groundwater matrix. Since validation, over 700 groundwater samples have been quantified using this robust method. The linearity of the method was evaluated over the range 0.008 – 0.4 µg/L. Curve linearity measured as r^2 were typically greater than 0.995. The regression parameters of the slope, intercept and correlation coefficient were calculated by weighted ($1/x$) linear regression and did not include the origin.

The WLR study was carried out by one analyst with the same validation repeated on three separate days. Each day 500 mL blank water matrix was fortified with 25, 50 and 75 µg/L to target the validation levels of 0.02, 0.04, and 0.06 µg/L. Six replicates were carried out for each level. Recoveries ranged between 88 – 118% for all 18 compounds (**Appendix 13**): within the range set out by SANCO/825/00 for groundwater of between 70 -120%. WLR precision was less than 32% for all compounds except 4C2MP at the 0.02 µg/L level: 46% coefficient of variation (CV). DBA also had high CV across all three concentration levels: from 45% CV at 0.02 µg/L to 41% at 0.06 µg/L levels.

External laboratory cross checks revealed that the method worked to the concentrations outlined with average concentrations from the external laboratory in general being slightly higher except for TBA which had lower averages for both fortified concentration levels (**Table 6.6**) implying that UHPLC-MS/MS is more sensitive for TBA than GCMS.

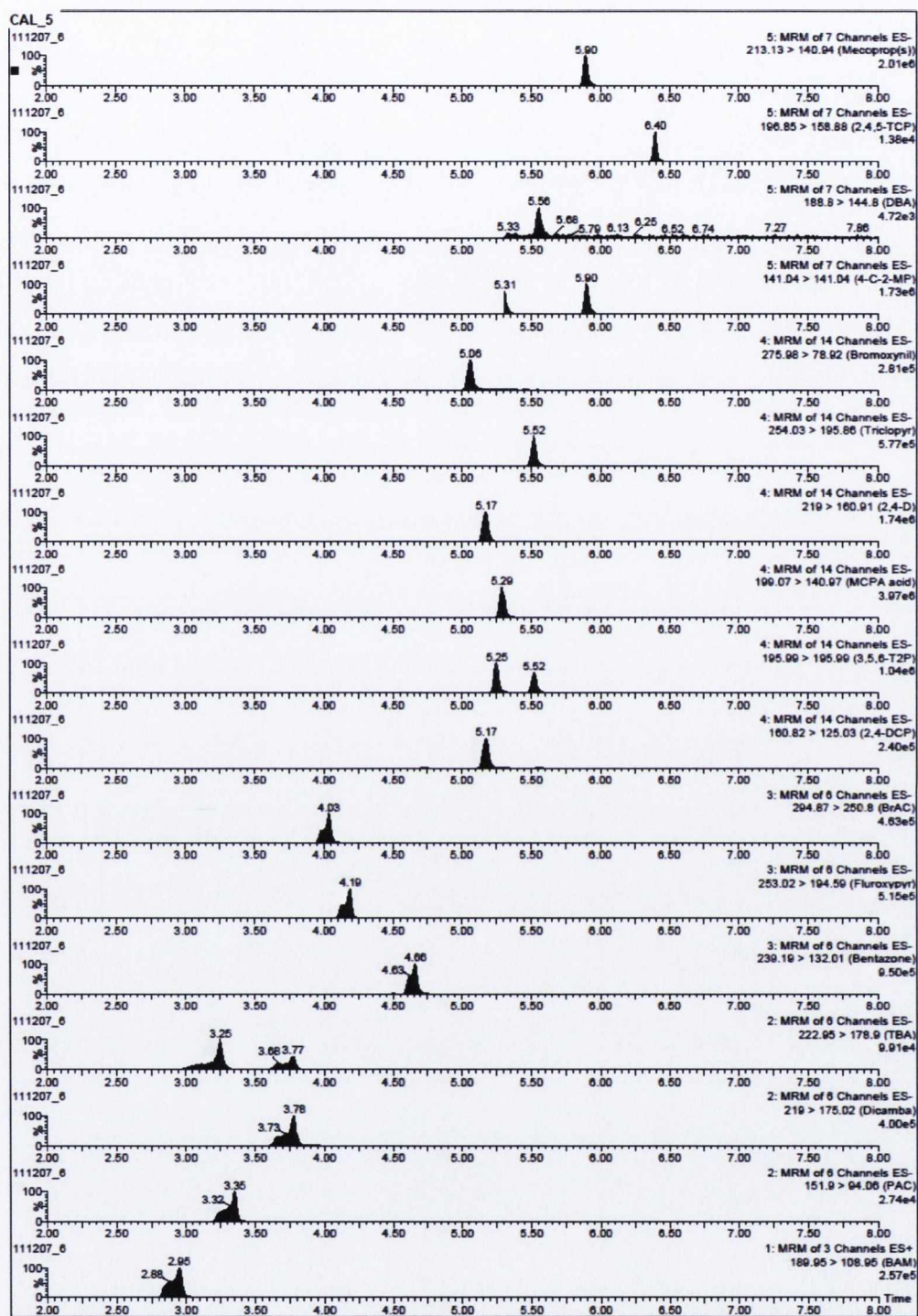


Figure 6.8 UHPLC-MS/MS trace for all 18 compounds at 0.4 µg/L after SPE clean up and re-suspension in acetonitrile:ultra pure water (50:50, v/v).

No other method until now has been able to determine both phenoxyacid herbicides alongside the benzonitrile herbicide TPs or as many of phenoxyacid herbicide TPs. **Table**

6.7 summarises the comparison of several methods which analyse for some of the same compounds presented here. Rodil *et al.* (2009) developed a method to quantify 53 compounds of which six were phenoxyacid herbicides. Similar compounds were mecoprop and 2,4-D with LOD of 0.0025 and 0.0006 µg/L, respectively during a 41 min run time. This method does not quantify for as many analytes across several chemical classes, but is able to detect the greatest number of phenoxyacid herbicides in comparison to other similar methods such as those by Marchese *et al.* (2002), Solymosné-Majzik *et al.* (2006), Marín *et al.* (2009), Rodil *et al.* (2009), and Sklivagou *et al.* (2010). The LOQ for this method is 0.008 µg/L and is low enough to be able to quantify below EU DWS(i) with a fast run time of 11.9 min.

Table 6.6 External laboratory results for blank matrices spiked at two fortification levels (n=2).

	Fortified at 0.2 µg/L		Fortified at 2.0 µg/L	
	Average concentration	CV %	Average concentration	CV %
2,3,6-TBA	0.18	4.04	1.80	7.86
2,4-D	0.26	5.44	2.35	15.04
bentazone	0.25	2.89	2.30	6.15
bromoxynil	0.25	2.89	2.45	2.89
DBA	0.24	21.06	2.35	9.03
fluroxypyr	0.26	5.44	2.40	5.89
MCPA	0.25	14.43	2.30	12.30
mecoprop	0.25	5.66	2.45	2.89

Table 6.7 Comparison between other methods on performance.

Author(s)	Separation	Detection	Extraction	Range of analytes	Number of phenoxyacid herbicides	Separation time (min)	Sample size (mL)	Recovery range (%)	LOQ (µg/L)
This method (Rodil <i>et al.</i> , 2009)	UHPLC	MS/MS	SPE	18	16	11.9	500	88-118	0.008
	LC	MS/MS	SPE	53	6	41	200	22-146	0.0006 (2,4-D)
									0.0025 (mecoprop)
	UHPLC	MS/MS	SPE	37	3	10	100	70-120	0.025
(Marín <i>et al.</i> , 2009)									
(Marchese <i>et al.</i> , 2002)	LC	MS/MS	Graphite cartridge	8	4	c.15	500	85-103	0.0001
(Solymosné-Majzik <i>et al.</i> , 2006)	LC	MS/MS	SPE	6	4	15	500	76-108	0.0011 (dicamba)
									0.0017 (2,4-D)
									0.0029 (MCPA)
									0.0015 (mecoprop)
(Sklivagou <i>et al.</i> , 2010)	LC	MS/MS	SPE	6	3	15	500	61-120	0.03 (2,4-D)
									0.003 (MCPA)
									0.003 (bentazone)

6.6.3 Conclusions

Using UHPLC-MS/MS with rapid polarity switching a quantitative multi residue method to determine nine a.i. present in PPP formulations, six phenoxyacid herbicide TPs, and two benzonitrile TPs was developed and validated in accordance with EU directive 2002/657/EC and SANCO/825/00 criteria. SPE was chosen as the clean up method. Using Bond Elut ENV 200 mg/6ml cartridges 500 mL of sample reached recoveries between 88 – 118%. LOQ were achieved for all compounds below the EU DWS(i) of 0.1 µg/L. The method was successfully applied to real groundwater samples and able to detect concentrations of 0.026 µg/L with a signal-to-noise ratio of 223.

6.7 Chapter 6 conclusions

For this project all groundwater sampled from piezometers, springs, drains, and streams has been collected in a representative manner to enable consistent results using low flow purging methods, chemically inert PTFE tubing, amber glass bottles, and measuring *in-situ* water chemistry variables. Stability tests on raw groundwater samples have shown that phenoxyacid and benzonitrile herbicides should be analysed within five days of collection and organochlorine herbicides within 24 hours of collection. A simple filtering experiment carried out was inconclusive in determining the effect of filtration on concentration but did suggest that the compounds DCP, 2,4-D, fluroxypyr, and PAC are susceptible to sorption onto sediment. To carry out the objectives of this study the two methods described above have been developed to quantify for phenoxyacid herbicides, organochlorine herbicides, and some benzonitrile herbicide TPs. The methods have also been validated to ensure that detections are true rather than anomalies and tested so any weaknesses are realised. This has enabled the majority of samples collected for the project to be quantified for 21 compounds. The LOD for each method used throughout catchment scale monitoring has been summarised in **Table 6.8**.

Table 6.8 Summary of limits of detection (LOD) for the compound classes used for catchment scale monitoring across the seven sites.

Method	Limit of detection	Units
Phenoxyacid and benzonitrile herbicide method (section 6.6)	0.008	µg/L
Organochlorine herbicide method (section 6.5)	0.015	µg/L
External analysis of phenoxyacid herbicides (section 6.4)	0.02	µg/L
External analysis of organophosphorous herbicides (section 6.4)	0.02	µg/L
<i>NIEA phenoxyacid herbicide method</i> (section 6.4.1)		
MCPA, mecoprop(s), 2,4-D, bentazone, and bromoxynil	0.025	µg/L
fluroxypyr and triclopyr	0.035	µg/L
phenoxyacetic acid (PAC)	0.45	µg/L

CHAPTER 7

CASE STUDY PESTICIDE RESULTS AND DISCUSSION

7.1 Introduction

This chapter aims to present and interpret results on the effect of site characteristics on groundwater pesticide occurrence. The groundwater samples were collected using methods detailed in section 6.2.1 and were then quantified for a range of pesticide compounds using external methods detailed in section 6.4 and also quantitative methods developed during this project which are detailed in section 6.5 for the organochlorine herbicides and section 6.6 for the phenoxyacid herbicides and benzonitrile TPs.

As highlighted in Chapter 1, the objectives of this chapter are to:

1. To determine which pesticide compounds are present in Irish groundwater.
2. To determine if pesticide a.i.s that are currently used within the EU can be detected in Irish groundwater and, if so, at what concentrations.
3. To determine if TPs are present in Irish groundwater and, if so, at what concentration.
4. To determine the physical characteristics of catchments that are associated with pesticide occurrence in groundwater.
5. To determine the influence of land use on the occurrence of pesticides in groundwater.
6. To describe any temporal patterns of pesticide in Irish groundwaters that can be discerned from the datasets in this study.

7.2 Groundwater pesticide frequency of occurrence

7.2.1 Percentage frequency calculation method

The percentage frequency of occurrence is a technique that has been adopted by many authors to describe the most frequently detected pesticide compounds in relation to the

number of samples collected and analysed for each particular compound (Kolpin *et al.*, 1997; Kolpin *et al.*, 1998a; Fytianos *et al.*, 2006; Guzzella *et al.*, 2006; Gonçalves *et al.*, 2007). Monthly groundwater pesticide results were summarised as the percentage frequency for each pesticide. Samples could not be taken on occasions when a MP was dry and unable to yield water, and these were recorded. To reduce bias frequency of occurrence was calculated by the number of detections divided by the number of samples processed for that particular compound. Alongside the number of samples analysed for each compound, the number of detections greater than or equal to the EU DWS(i) of 0.1 µg/L was recorded, the number of detections greater than the LOD but less than the EU DWS(i), and the number of non-detections. These categories were chosen with reference to the EU Drinking Water Directive (98/83/EC) (Council Directive, 1998). This parametric value of 0.1 µg/L is used in conjunction with the EU Water Framework Directive (WFD) (European Commission, 2000). Unadjusted detections of pesticides were used (see section 3.2.3). The LOD for each compound category is listed in **Table 6.8** (see sections 6.4.2 and 6.5.2).

7.2.2 Percentage frequency calculation results

A total of 61 compounds were quantified at several different sampling intervals during the two years of monitoring (**Appendix 10** and **11**). The number of samples analysed across all seven sites ranged from 59 for lindane, heptachlor, and endo-heptachlor epoxide to 740 samples for mecoprop(s), 2,4-D, and triclopyr.

The most frequently detected compounds at concentrations greater than the LOD were (**Figure 7.1**):

- 1) mecoprop(s)
- 2) phenoxyacetic acid (PAC)
- 3) 4-chloro-2-methylphenol (4C2MP)
- 4) 2,4-D and 2,6-dichlorobenzoic acid (DBA)
- 5) MCPA

The most frequently detected compounds at concentrations in breach of the EU DWS(i) were:

- 1) DBA
- 2) PAC
- 3) dieldrin
- 4) BAM (3,5-dichlorobenzamide)

The maximum observed concentration for any compound was 120 µg/L (TP DBA April 2010 at piezometer 7b, site FvPDa). The EU DWS(i) was exceeded on at least one occasion for 11 of the compounds analysed for throughout the project (**Table 7.1**). Six of the 11 exceedances were the TPs PAC, 4C2MP, DBA, T2P, TCP, and BAM. The parent a.i. mecoprop(s), 2,4-D, MCPA, dicamba, and TBA all exceeded the EU DWS(i) on at least one occasion (**Table 7.1**). The average breached the EU DWS(i) for the following TPs: PAC, DBA and BAM (**Table 7.1**). The mean, median or 90th percentile were less than the EU DWS(i) for parent a.i.'s. The mean and median in **Table 7.1** were calculated for samples only containing detections.

A number of samples were also sent to external laboratories for analysis of pesticides. Samples collected in March and April 2010 had no detections greater than the LOD and some of these compounds were not analysed in subsequent months (see section 6.4.1) included: chloramben; 2,4,5-TP; 2,4-DB; ioxynil; 2,4-DB; dalapon; 2,4,5-T; MCPB; acifluorfan; imazapyr; dinoseb; and picloram. In addition organophosphorous herbicides were analysed on a single sampling date (March 2012) and no detections greater than the LOD were observed (see section 6.4.2 and **Appendix 11**).

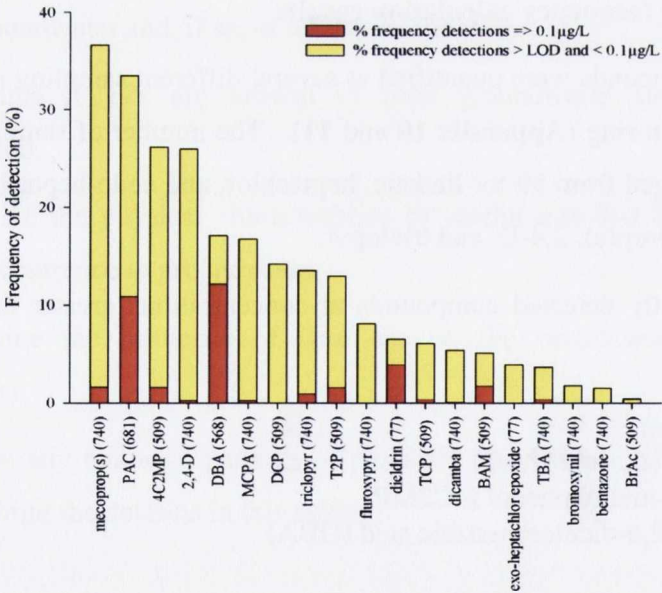


Figure 7.1 Percentage frequency of detection for all seven sites sampled monthly from March 2010 to March 2012. The total number of samples analysed for each compound is stated in brackets.

Table 7.1 Compound frequency of occurrence, the maximum, mean, median, and 90th percentile observed concentration monitored monthly throughout the catchment scale study for all seven sites. Compounds are listed in order of decreasing frequency of occurrence.

Compound	Frequency of occurrence (%)	Maximum observed concentration (µg/L)	Mean (µg/L)	Median (µg/L)	90 th percentile
mecoprop(s)	36.62	1.461	0.026	0.007	0.047
PAC [‡]	33.48	4.148	0.209	0.044	0.458
4C2MP [‡]	26.13	1.364	0.035	0.007	0.058
2,4-D	25.95	0.237	0.01	0.005	0.023
DBA [‡]	17.08	120	3.222	0.22	5.527
MCPA	16.76	1.047	0.019	0.006	0.021
DCP [‡]	14.15	0.049	0.009	0.009	0.014
triclopyr	13.51	0.071	0.026	0.008	0.071
T2P [‡]	12.97	0.341	0.046	0.031	0.1
fluroxypyr	8.11	0.075	0.007	0.004	0.018
dieldrin	6.49	0.078	0.078	0.078	0.0978
TCP [‡]	6.09	0.15	0.033	0.017	0.0941
dicamba	5.41	0.126	0.014	0.006	0.038
BAM [‡]	5.11	0.1354	0.178	0.041	0.639
<i>exo</i> -heptachlor epoxide [‡]	3.90	0.04	0.021	0.019	0.076
TBA	3.65	0.79	0.057	0.02	0.099
bromoxynil	1.76	0.08	0.026	0.017	0.056
bentazone	1.49	0.05	0.015	0.009	0.023
BrAc [‡]	0.39	0.005	0.004	0.004	0.005

[‡] indicates compounds that are transformation products (TP)

Concentrations which exceeded the EU DWS(i) of 0.1 µg/L are highlighted in bold

Karst well-drained grassland (KWDg)

Of all the seven sites, KWDg had the lowest percentage frequency of pesticide occurrence. Over the two year monitoring period, seven samples had detections. Of all the compounds detected, only DBA exceeded the EU DWS(i) ($0.25 \mu\text{g/L}$ in March 2010). *Exo*-heptachlor epoxide and dieldrin were the most frequently detected compounds in terms of % frequency, although this is attribute to the low number of samples (three samples, each with one detection) actually analysed for these organochlorine compounds (**Figure 7.2**). At KWDg 2,4-D had the highest number of samples with a detection (four detections out of 20) (**Appendix 15**). BrAc (3,5-dibromo-hydroxybenzoic acid), PAC, mecoprop(s), and MCPA were also detected. Although BrAc was detected in KWDg the parent compound bromoxynil was not. Holtze *et al.* (2008) states BrAc is a TP of bromoxynil.

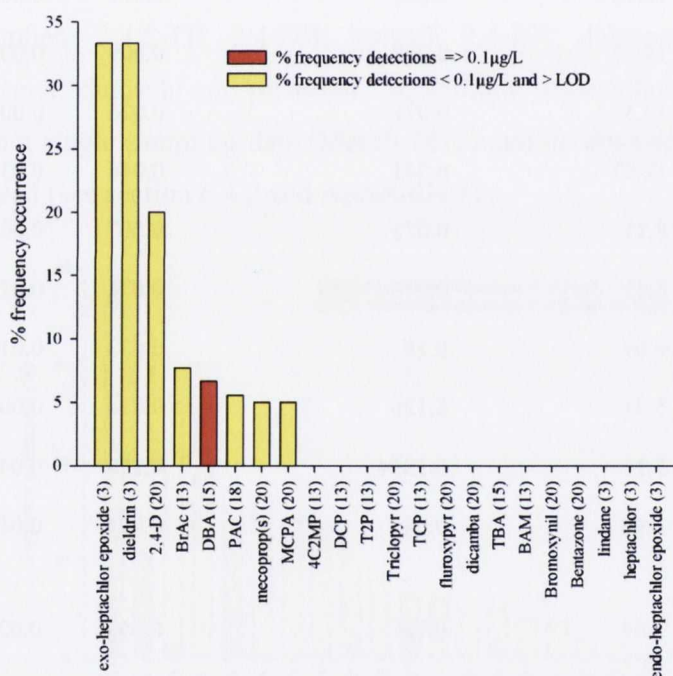


Figure 7.2 Percentage frequency of detection for samples collected at karst well-drained grassland (KWDg) between March 2010 to March 2012. The total number of samples analysed for each compound is stated in brackets.

Karst well-drained arable (KWDa)

From the Boiling Spring at KWDa, ten compounds were detected throughout monitoring. Five of these were the parent compounds: mecoprop(s), 2,4-D, triclopyr, dicamba, and bromoxynil, while the TPs PAC, 4C2MP, DBA, PAC, and BAM were the other five compounds detected (**Figure 7.3**). It was only the TPs that exceeded the EU DWS(i) (PAC, DBA, and BAM). At KWDa the highest number of non-detects were for the herbicides MCPA, fluroxypyr, and bentazone, of which 29 samples from separate sampling dates were analysed for each (**Appendix 15**). Bromoxynil was rarely detected across the seven sites but was detected at KWDa in one sample out of 29 samples which was analysed for the bromoxynil at KWDa.

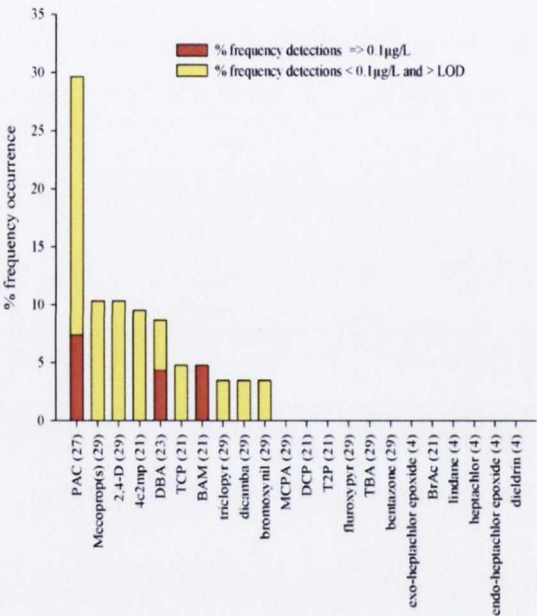


Figure 7.3 Percentage frequency of detection for samples collected at the Boiling Spring at karst well-drained arable (KWDa) between March 2010 to March 2012. The total number of sampling dates for each compound that was analysed is stated in brackets.

Intergranular/karst well-drained arable (I/KWDa)

At I/KWDa, 16 compounds were detected throughout the course of monitoring (**Figure 7.4**). This is in contrast to the number of compounds detected at KWDg and KWDa, with eight and ten compounds, respectively. Half of the compounds detected in I/KWDa were TPs and the other half parent a.i. Eight of the compounds detected were found at concentrations in breach of the EU DWS(i), the most notable of these were PAC and DBA with 15.2% and 12.5% of samples collected on separate sampling dates exceeding the EU DWS(i) (**Appendix 15**). The two most commonly detected compounds from all samples collected at I/KWDa were mecoprop(s) and 2,4-D, with 48.4% and 45.2% of total detections, respectively. These detections also included those exceeding the EU DWS(i) (**Appendix 15**). As regards the percentage frequency of occurrence of pesticides across all MPs at every site sampled during this catchment scale study, overall I/KWDa had the most detections taking into consideration that each site had different numbers of MPs and different numbers of samples quantified for pesticides. I/KWDa had the second highest detection of mecoprop(s) at 48% (**Appendix 15**) out of all seven sites.

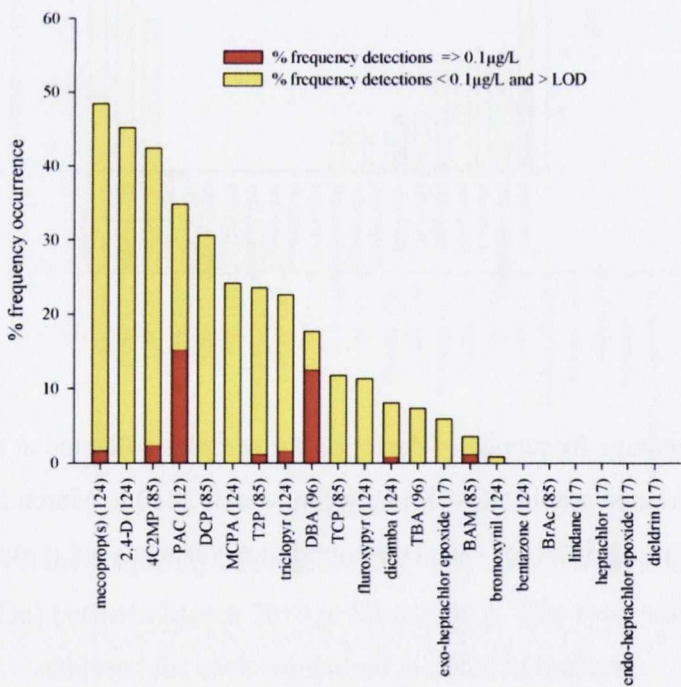


Figure 7.4 Percentage frequency of detection for samples collected at all MPs at I/KWDa between March 2010 to March 2012. The total number of sample dates analysed for each compound is stated in brackets.

Fractured-volcanic well-drained arable (FvWDa)

At FvWDa the total number of compounds detected throughout the course of monitoring was 16 (**Figure 7.5**). Nine of these compounds were TPs, and the most commonly detected compound was also the TP PAC. Five compounds at FvWDa were in breach of the EU DWS(i). These were, in descending order of frequency of exceeding the EU DWS(i): DBA, PAC, BAM, 4C2MP, and mecoprop(s) (**Appendix 15**).

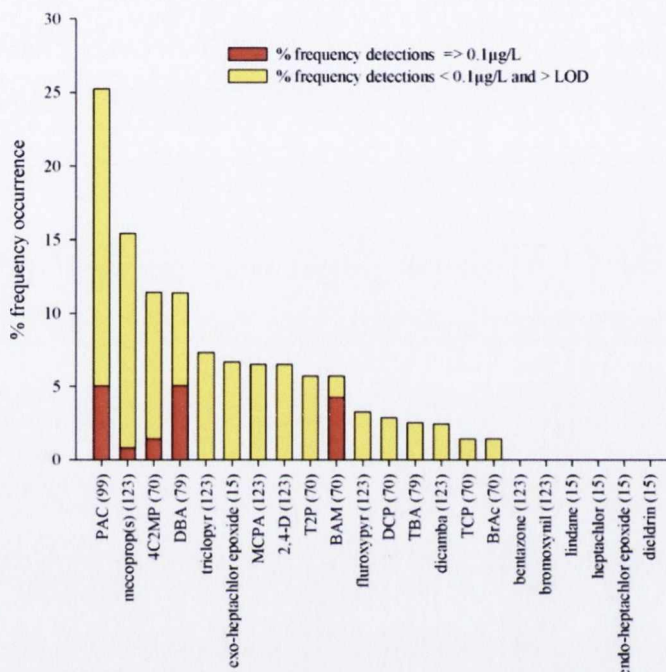


Figure 7.5 Percentage frequency of detection for samples collected at all MPs at FvWDa between March 2010 to March 2012. The total number of samples analysed for each compound on separate sampling occasions is stated in brackets.

Fractured-volcanic poorly-drained arable (FvPDa)

At FvPDa 16 compounds were detected during monitoring and 11 of these exceeded the EU DWS(i) for individual pesticides on at least one sampling occasion (**Figure 7.6; Appendix 15**). In all groundwater samples collected at FvPDa the compounds mecoprop(s), PAC, 2,4-D, 4C2MP, MCPA, and DCP were detected in 30% or more of samples (**Appendix 15**). PAC and DBA exceeded the EU DWS(i) in 22% and 13% of samples, respectively (**Appendix 15**). Of all the 16 compounds detected, nine were TPs. Of the 11 compounds which exceeded the EU DWS(i) on at least one occasion, six were TPs. FvPDa had the highest occurrence of mecoprop(s) out of all seven sites with 51% of samples having a detection.

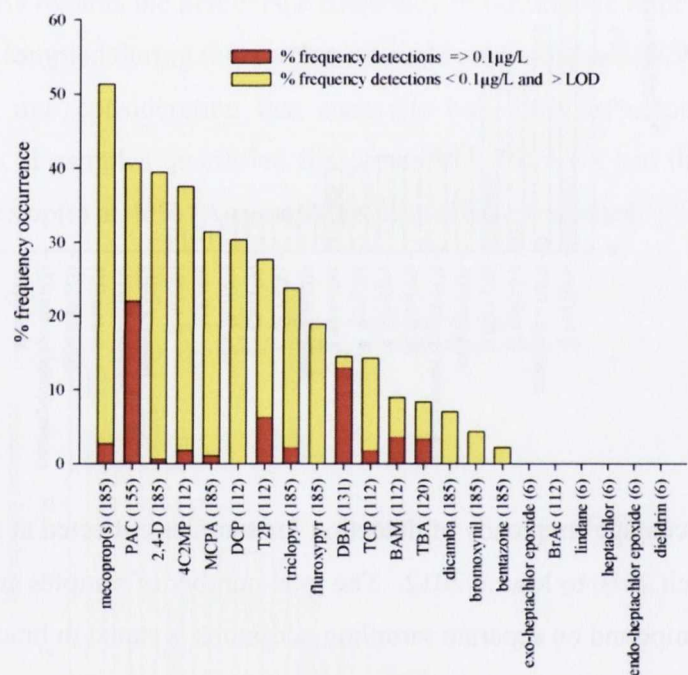


Figure 7.6 Percentage frequency of detection for samples collected at all MPs for groundwater at FvPDa between March 2010 and March 2012. The total number of samples analysed on separate sampling occasions for each compound is stated in brackets. Surface water samples collected at FvPDa have not been included for the percentage frequency of occurrence.

Fractured-metasediments well-drained arable 1 (FmWDa₁)

At FmWDa₁, 18 compounds were detected throughout the course of monitoring (**Figure 7.7**). Half were parent compounds and half were TPs. The EU DWS(i) was only breached by TPs. The compounds were: DBA (11.3%), PAC (5.9%) and 4C2MP (0.8%) (**Appendix 15**). The most commonly detected compound at FmWDa₁ was PAC as it was present in 27.5% of samples analysed for on separate occasions.

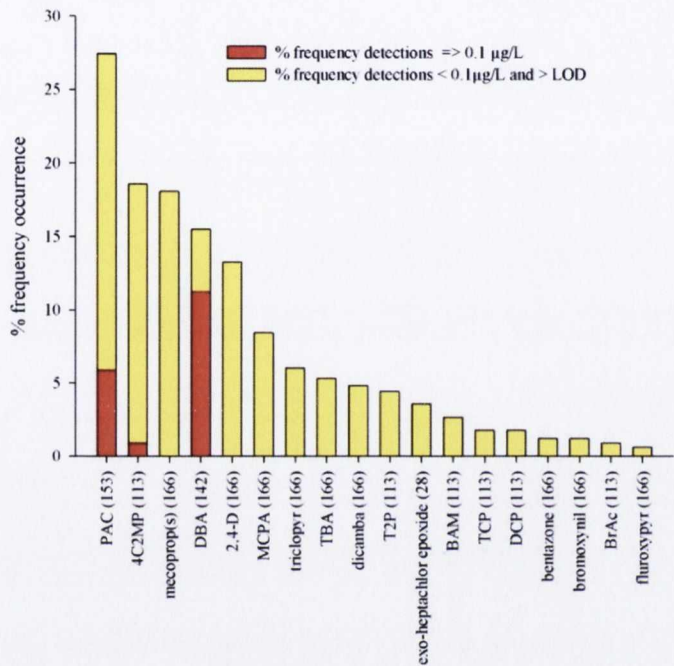


Figure 7.7 Percentage frequency of detection for all groundwater samples collected at MPs at FmWDa₁ from March 2010 to March 2012. The total number of samples analysed for each compound is stated in brackets. Surface water samples have not been included for the percentage frequency of occurrence.

Fractured-metasediments well-drained arable 2 (FmWDA₂)

At FmWDA₂, 16 compounds were detected throughout the course of monitoring (**Figure 7.8**). Half were TPs and half were parent compounds. Four compounds exceeded the EU DWS(i). The TP DBA had 16 detections in breach of the EU DWS(i) out of 135 samples analysed for this compound. PAC had five detections in breach of the EU DWS(i) (**Appendix 15**). The other two compounds to exceed the EU DWS(i) were the parent compounds triclopyr and mecoprop(s). Triclopyr and mecoprop(s) were detected in concentrations in breach of the EU DWS(i) in 0.6% and 1.3% of samples, respectively (**Appendix 15**). The four most commonly detected compounds ranged in detection frequency from 30.4% to 17% (**Appendix 15**). PAC was detected in nearly 30.4% of the groundwater samples analysed for this compound.

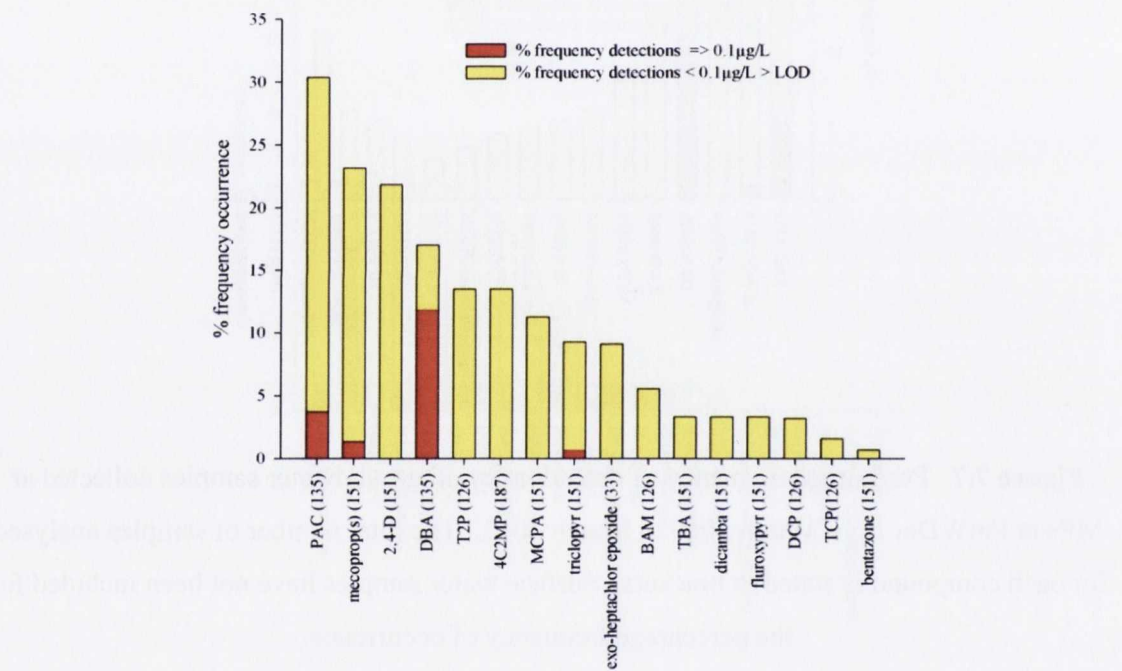


Figure 7.8 Percentage frequency of detection for samples collected at all MPs at FmWDA₂ between March 2010 and March 2012. The total number of samples analysed for each compound is stated in brackets. Surface water samples have not been included for the percentage frequency of occurrence.

7.3 Within site variation of pesticide occurrence

7.3.1 Within site variation at Intergranular/karst well-drained arable (I/KWDa)

As described in 5.3.1, two boreholes were constructed at either end of the site, each with three piezometers to target the shallow groundwater (4-5m b.g.l), interface groundwater (9-12 m b.g.l), and the bedrock aquifer (22-28 m b.g.l). However the shallow piezometer at MP2 was installed using a Giddings Rig rather than using air rotary drilling as for the other MPs to sample shallow groundwater between 2.8 – 4.8 m b.g.l (see section 5.3.1). Borehole 2 (MP2) is located downgradient of MP1 (see section 5.6.3). Monthly samples gathered over two years had total pesticide concentrations up to 14.8 µg/L. This 14.8 µg/L detection occurred in a single sample in March 2012. DBA contributed the most to this total concentration at 14.2 µg/L, with PAC also present, and in breach of the EU DWS(i) with 0.4 µg/L. The other TPs 4C2MP, TCP, and DCP were also detected in this sample from the shallow piezometer at MP2 but not at concentrations exceeding the EU DWS(i). Parent a.i. were also detected in this sample totalling a concentration of 0.108 µg/L. These were 2,4-D, fluroxypyr, triclopyr, MCPA, and mecoprop(s). This sample collected in March 2012 was the most pesticide laden sample ever collected at I/KWDa as regards the concentrations detected and the range of compounds.

In comparison to MP1, the three piezometers at MP2 had more detections in samples (**Table 7.2**). The interface piezometer at MP2 had the most detections out of all six MPs at I/KWDa. This piezometer targets groundwater in the sand and gravel aquifer at this site. Lapworth *et al.* (2006) found that pesticides in groundwater were more common at sites with sand and gravel deposits and with high transmissivities rendering the aquifer vulnerable. And the higher occurrence of pesticides in sand and gravel groundwater may also be attributed to the smaller effective porosity in these porous systems which will have a slower flow velocity than a fractured rock (Alley *et al.*, 2002). The shallow piezometer would be influenced by local conditions and the deep piezometer was installed to target the Rkd (regionally productive karstified diffuse) aquifer. The Rkd aquifer will have a contributing area much greater than the localised MP2 shallow piezometer, with pesticide applications elsewhere across the aquifer potentially able to contribute pesticides to the groundwater at this MP. Pesticide records were unavailable for the wider area over the Rkd aquifer at I/KWDa.

Table 7.2 Summary of detections at each piezometer at the Sawmills Field at Intergranular/karst well-drained arable (I/KWDa).

Piezometer and sample depth	Number of samples collected at MP	Number of samples with a detection $\geq$ EU DWS(i) on at least one occasion	Number of samples with a detection $>$ LOD but $<$ EU DWS(i) on at least one occasion	Percentage of samples with pesticide detections in piezometer throughout monitoring (%)
MP1 shallow (4-6 m b.g.l)	13	3	6	69.2
MP1 interface (8-10.5 m b.g.l)	23	4	7	47.8
MP1 deep (22-28 m b.g.l)	23	2	11	56.5
MP2 shallow (2.8-4.8 m b.g.l)	18	9	5	77.8
MP2 interface (7.5-10.5 m b.g.l)	23	5	16	91
MP2 deep (18-24 m b.g.l)	23	5	12	73.9

* the number of samples does not include duplicates.

7.3.2 Within site variation at fractured-volcanic well-drained arable (FvWDa)

Both BHs and springs were sampled at FvWDa. Comparing pesticide detections in the two types of MP at this site, boreholes (BHs) had more detections in groundwater than springs (**Figure 7.9**). The Upper BH had detections exceeding the detection limit in 68.2% of samples collected at the site over the monitoring period and the Lower BH had 65.2%. The three springs had similar detection frequencies with the Lower Sp. having the most detections out of all the samples collected here throughout monitoring at 50%. The Upper Sp. had detections in 44.4% of samples, and finally the House Sp. had 42.1% of samples with a pesticide detection.

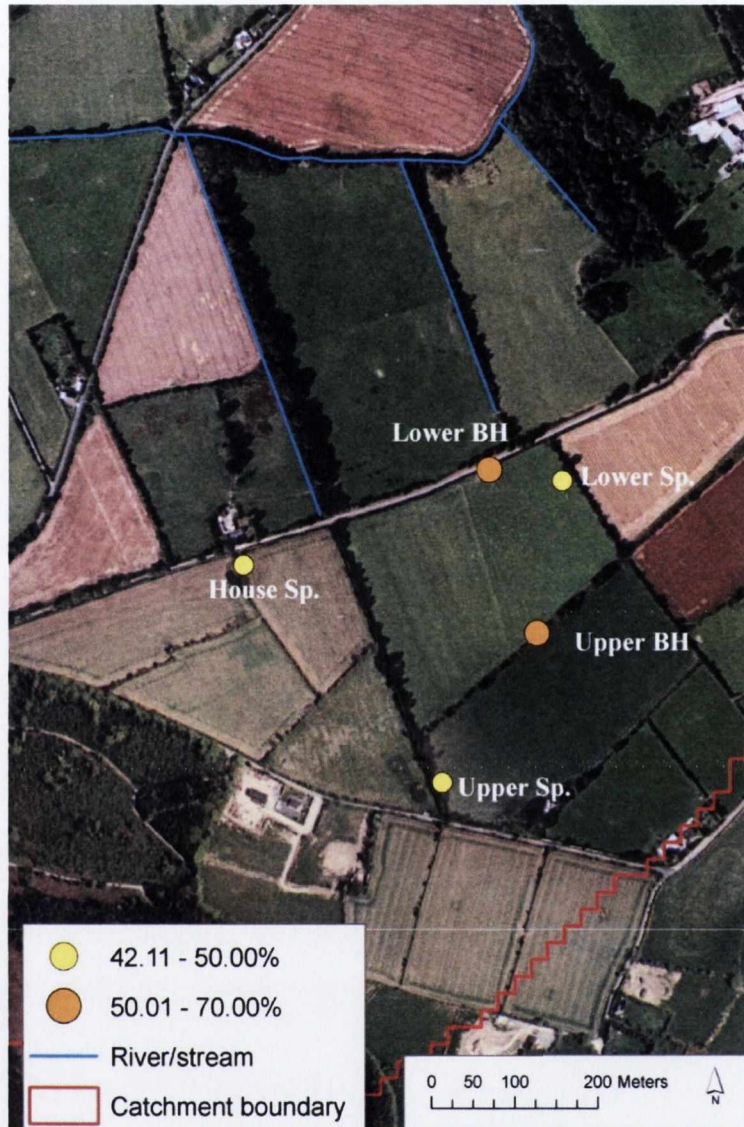


Figure 7.9 Within site distribution of the percentage frequency of pesticide occurrence at FvWDa using graduated symbols based on the number of detections recorded at each MP as a function of the number of samples collected throughout monitoring. Printed under licence No. 6155 from the Ordnance Survey of Ireland.

7.3.3 Within site variation at Fractured-volcanic poorly-drained arable (FvPDa)

At FvPDa pesticide occurrence varied spatially across the MPs surveyed at the site. The MPs which had the greatest percentage of pesticide detections are shown in **Figure 7.10**. In descending order the MPs with the greatest percentage of detections were $7b > 8b > 5b > 1b > 9b > 2b > 4b$. The lowest pesticide occurrences occurred in the drain with 26.3% and the artesian borehole at 34.8% of all samples collected throughout monitoring having

at least one detection. **Figure 7.10** shows the percentage frequency of detections for each MP at FvPDa and Ortho-photography from 2000. The land use in the three fields with MPs has since changed. The most northerly field (MPs: 7b, 8b, 9b, and the stream) has been in grassland since 2006, while the fields with the other MPs (which in **Figure 7.10** are in grassland) were converted to tillage in 2006. The grassland field up to 2006 had spring wheat sown since 2000 but the wet conditions at this field made harvesting difficult therefore it was converted to grassland and tillage sown on the two field which are shown as grassland from **Figure 7.10** with Ortho photography from 2000. These fields were converted to spring barley in 2006. Piezometers in the most northerly field (which was in grassland throughout monitoring) (**Figure 7.10**) had the most detections in its MPs compared to the MPs located in the other two tillage fields south of this grassland field. The grassland field had on average 84.5% of all samples collected in the piezometers here containing a pesticide detection. The top tillage field (MPs 1b and 2b) had an average of 77.2% of samples with a pesticide detection, while the middle field (MPs: artesian, 4b, and 5b) had 78.6% of samples with a detection. The grassland field is down groundwater gradient of the upper two tillage fields (see section 5.6.5 and **Figure 5.27**).

Piezometers 1b and 5b from EM31 ground conductivity geophysics in **Appendix 5** intersect gravelly deposits embedded within the low permeability Irish sea till subsoil. These higher permeability gravel deposits may enhance the movement of water and pesticides through this site which is dominated by low permeability material. Transport may be especially efficient for soluble compounds such as the phenoxyacid herbicides quantified during this study. Over the monitoring period, pesticide detections observed were lower in the artesian well with 34.8% of samples having at least one detection, 4b (60%), and 2b (72.7%). Fewer pesticide detections at 2b may be because this is the deepest piezometer drilled at the site which has mild flowing artesian conditions (**Figure 5.5**). The upwelling of water may contribute to diluting pesticides in piezometer 2b (see section 5.9.5).

The gravel deposits represent areas of higher risk to groundwater contamination within low permeability material and will allow for a different potential for transport of pesticides. The gravel deposits at this site complicate the FvPDa site which is further complicated through artesian conditions across the site. At MP 2b, the deepest piezometer drilled after the artesian BH, had a potentiometric head above ground level, inferring upwelling water from below. At FvPDa with depth towards the volcanic aquifer beneath, the pressure

causes the upwelling of deeper groundwater towards the surface and this appears to be preventing pesticides leaching deeper to the aquifer beneath. The artesian aquifer 11.5 m b.g.l. (**Appendix 3**) had 34.8% of samples with a pesticide detection. 23 samples were collected from the artesian MP on separate sampling occasions, six samples had pesticides in detectable concentrations which did not exceed the EU DWS(i). The EU DWS(i) was breached in August 2010 (0.158 $\mu\text{g/L}$ of PAC) and in October 2011 (0.326 $\mu\text{g/L}$ of PAC) in the artesian MP.

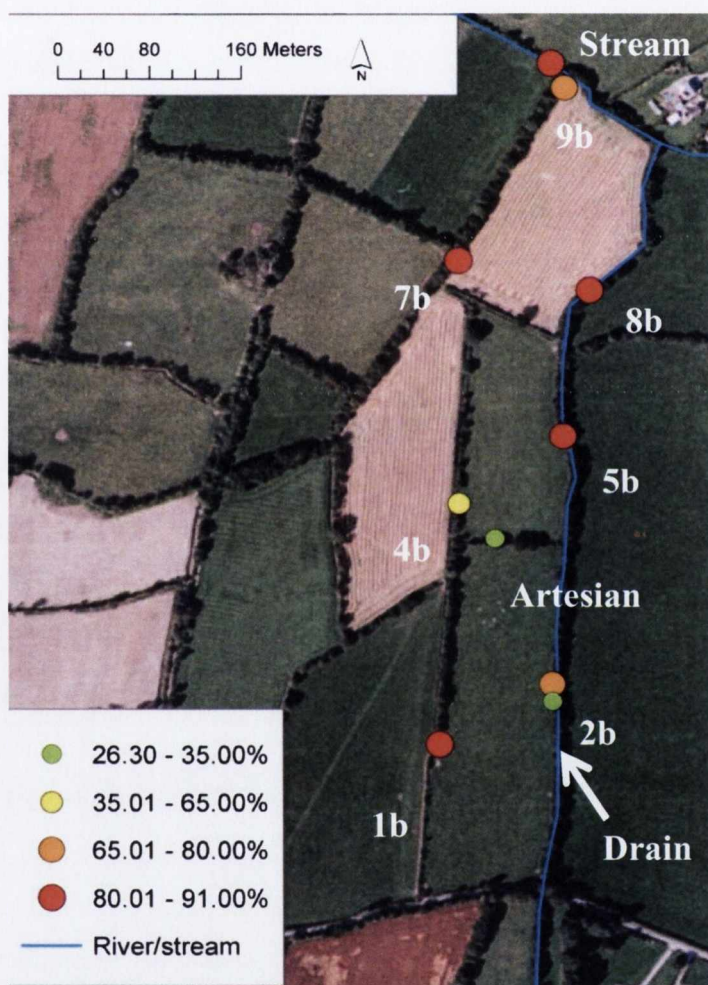


Figure 7.10 Within site distribution of the percentage frequency of pesticide occurrence at FvPDa using graduated symbols based on the number of detections recorded at each MP as a function of the number of samples collected throughout monitoring. Printed under licence No. 6155 from the Ordnance Survey of Ireland.

The spatial distribution of the pesticides suggests that they are transported through higher permeability pathways such as gravel lenses rather than the heavy textured gley soils and

low permeability Irish Sea Till deposits (**Appendix 5**) which cover and ultimately protect the aquifer beneath since it had very few detections in comparison to other MPs at the site.

7.3.4 Within site variation at Fractured-metasediments well-drained arable 1 (FmWDa₁)

At the three BHs at FmWDa₁ it is the Upper and Middle BHs (encompassing all three piezometers) which had the highest percentage frequency of detection from all samples collected from the three piezometers at this BH (**Table 7.3** and **Figure 7.12**). From all samples collected at all piezometers in the Upper BH, 57.5% of samples had at least one detection. From all samples collected at all piezometers in the Middle BH, 59.5% of samples had at least one detection. In the Lower BH 30.2% of samples had at least one detection. The highest detections were found in the deep piezometers across all three boreholes. The Lower BH had the most uniform spread of detections with the opposite occurring in the Upper BH (more contrast between the three piezometers in the Upper BH compared to the Lower BH). Geophysical results at this site near the Lower BH (**Appendix 5**) indicate saturated and clay-rich deposits becoming thinner and more gravelly with distance uphill towards the Upper BH. In the Lower BH there is hydrological evidence to suggest that groundwater is unable to recharge as successfully as in Upper and Middle BHs since this near-stream BH is under the influence of discharge mechanisms from the stream to the aquifer (**Figure 5.15**). When pesticides reach the base of the slope and the Lower BH they are under the influence of near-stream discharge processes, conceptually illustrated in **Figure 7.11** and hydrologically in **Figure 5.15**. The discharge of stream water to shallow and interface piezometers located in the Lower BH may be diluting water in these zones and reducing the concentration of pesticide as found in **Table 7.3**. **Figures 5.16** and **5.17** show the hydrological groundwater table for the Middle and Upper BHs, respectively. Both of which, as detailed in section 5.5.3.2, show evidence of recharge processes as opposed to discharge occurring at the Lower BH (**Figure 5.15**). The stream at FmWDa₁ had detections in four of the ten samples collected at the one stream MP sampled at FmWDa₁. In absolute numbers four of these samples contained detectable quantities of pesticides with the EU DWS(i) exceeded in two samples: July 2011 for PAC and October 2011 for DBA.

Table 7.3 Breakdown of detections at fractured-metasediments well-drained arable (FmWDa₁).

Borehole	Piezometer depth	Number of samples collected at MP	Number of samples with a detection $\geq$ EU DWS(i) on at least one occasion	Number of samples with a detection $>$ LOD but $<$ EU DWS(i) on at least one occasion	Percentage of samples with pesticide detections in piezometer throughout monitoring (%)
<i>Lower BH</i>	shallow	6	0	1	16.7
	interface	12	1	1	16.7
	deep	21	5	7	57.1
<i>Middle BH</i>	shallow	13	5	3	61.5
	interface	18	1	7	44.4
	deep	22	6	10	72.7
<i>Upper BH</i>	shallow	22	2	10	54.5
	interface	22	1	11	54.5
	deep	22	3	11	63.6

Mean detections in Lower BH = 30.2%

Mean detections in Middle BH = 59.5%

Mean detections in Upper BH = 57.5%

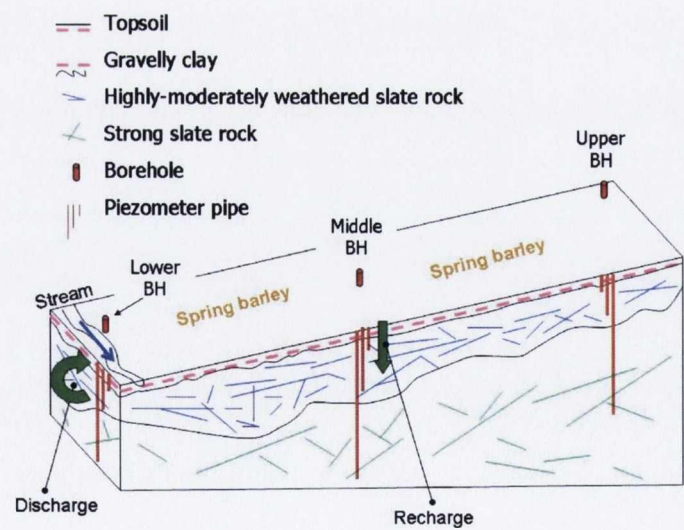


Figure 7.11 Conceptual model showing borehole installations and piezometers to target the shallow, interface, and deep groundwater with areas under the influence of discharge and recharge highlighted.

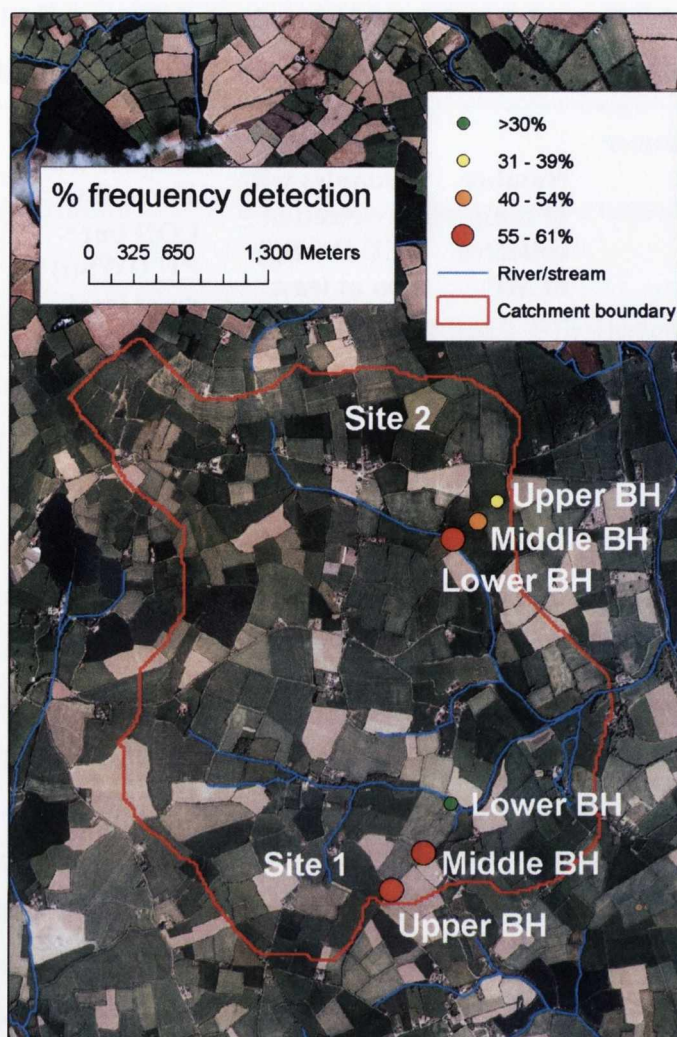


Figure 7.12 Within site distribution of the percentage frequency of pesticide occurrence at FmWDA₁ and FmWDA₂ using graduated symbols based on the number of detections recorded at each MP as a function of the number of samples collected throughout monitoring. Printed under licence No. 6155 from the Ordnance Survey of Ireland.

7.3.5 Within site variation at fractured-metasediments well-drained arable 2 (FmWDA₂)

At FmWDA₂ the Lower BH had the fewest pesticide detections in comparison to the Middle and Upper BHs at the site (**Figure 7.12**). In the Lower BH 60.8% of samples collected had at least one detection, in the Middle BH 54.4% of samples had at least one detection, and in the Upper BH 38.5% of samples collected had at least one detection (**Table 7.4**). In the FmWDA catchment, pesticide movement at site 2 is different to that at

site 1. Both sites have clay-rich material at their lower near-stream BHs. At Site 2 it is the Lower BH which has most of the pesticides in comparison to Site 1 (**Table 7.3**). The stream at FmWDa₂ had detections in five of the ten samples collected at the one stream MP sampled since June 2011, but none of these detections exceeded the EU DWS(i).

Table 7.4 Breakdown of detections at fractured-metasediments well-drained arable 2 (FmWDa₂).

Borehole	Piezometer depth	Number of samples collected at MP	Number of samples with a detection $\geq$ EU DWS(i) on at least one occasion	Number of samples with a detection $>$ LOD but $<$ EU DWS(i) on at least one occasion	Percentage of samples with pesticide detections in piezometer throughout monitoring (%)
<i>Lower BH</i>	shallow	11	2	4	54.5
	interface	19	8	3	57.9
	deep	20	5	9	70
<i>Middle BH</i>	shallow	12	1	6	58.3
	interface	20	2	9	55
	deep	20	2	8	50
<i>Upper BH</i>	shallow	6	1	2	50
	interface	18	3	5	44.4
	deep	19	2	2	21.1

Mean detections in Lower BH = 60.8%

Mean detections in Middle BH = 54.4%

Mean detections in Upper BH = 38.5%

7.4 Temporal variation of pesticide occurrence at each site

7.4.1 Temporal variation at karst well-drained grassland (KWDg)

Discharge results are presented from the 10th May 2010 to the 21st March 2011 (**Figure 5.12**). From samples collected every month between these dates no pesticide detections occurred in any of the samples. From **Figure 5.12** of effective rainfall and discharge (Q) from the KWDg Risings Spring, Q responds within a day to effective rainfall. Although no Q data is available, effective rainfall was plotted against pesticide occurrence to explore

if it could be related to pesticide occurrence at the site (**Figure 7.13**). Temporal patterns at KWDg for pesticides in groundwater discharging from the KWDg Risings Spring indicate that pesticide detections occur in their highest concentrations when effective rainfall did not occur e.g. March 2010 and May 2011. In samples collected at this spring every month there were very few pesticide detections so it is difficult to draw any conclusions from pesticide occurrence with effective rainfall. However, the reason why high pesticide detections occurred during times of low effective rainfall may be because of the dilution factor. That is when there is no effective rainfall, pesticide detections are more common since they are not diluted.

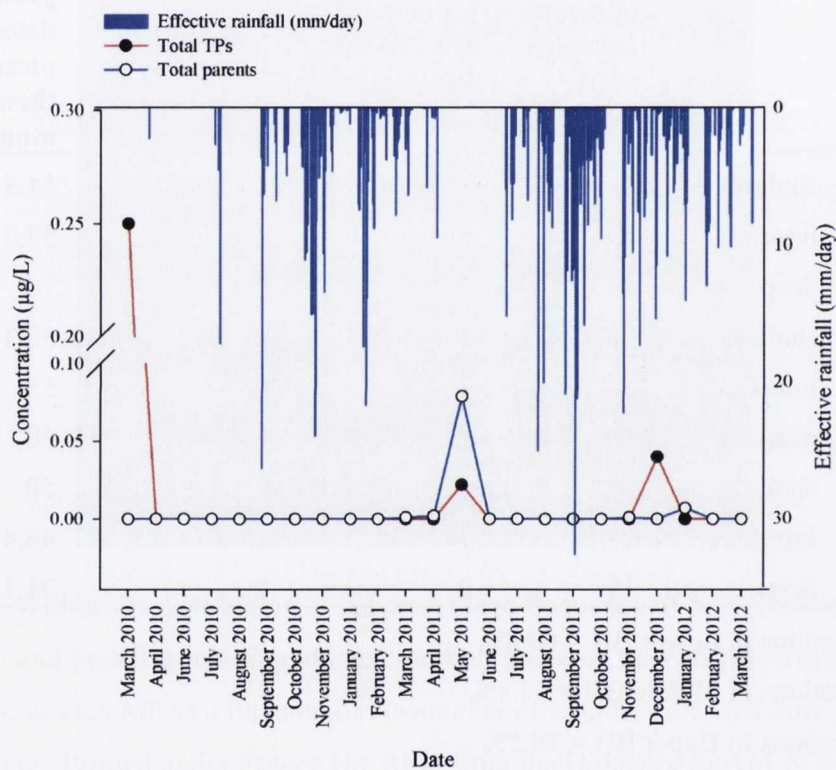


Figure 7.13 Temporal variation between total parent pesticide compounds at the karst well-drained grassland (KWDg) Risings Spring in Co. Mayo.

7.4.2 Temporal variation at karst well-drained arable (KWDa)

Monthly sampling

Monthly samples collected from the Boiling Sp. and the Sp. under the bridge indicate that only TPs exceeded the EU DWS(i) and that samples from the Boiling Sp. had higher pesticide concentrations than groundwater collected from the Sp. under the bridge (**Figure**

7.14). The spring under the bridge up gradient of the Boiling Sp. periodically had water flow during wet periods. The Sp. under the bridge may be an overflow Sp. of the Boiling Sp. but that would mean pesticide detections would be similar concentrations when they occurred and this was not the case from **Figure 7.14**: the Sp. under the bridge does not mimic pesticide detections occurring on the same sampling occasion. The hydrochemistry of the two springs also differs (see section 5.8.3.2) in relation to NPOC, turbidity, NO_3^- , bicarbonate fractions, and conductivity.

No effective rainfall data was available from the KWDa catchment but total rainfall was available from a rain gauge in the catchment to compare the occurrence of pesticides temporally. From **Figure 7.14** pesticide detections were highest in 2011 and 2012 with the highest total pesticide concentration occurring between September 2011 and December 2011. For the months when Q responds to total rainfall (**Figure 7.14**), pesticide detections occur on three of those occasions but detections at the Boiling Sp. also occur in the summer when rainfall does not instigate a response in Q (see section 5.5.2.2) therefore as with KWDg, periods of higher Q do not necessarily mean that a pesticide detection will occur.

Event based sampling

At the Boiling Spring in May 2012 a rainfall event based sampling programme took place in association with the EPA Pathways Project, where one sample was collected every day from both the Boiling Sp. and also the R. Nuenna approximately 10 m downstream of where the Boiling Sp. joins the R. Nuenna. Overall surface water contained more pesticides than groundwater discharging from the Boiling Sp. (**Figure 7.15**). In samples collected from surface water every day for six days, MCPA and 2,4-D were detected each day, 4C2MP was detected on four occasions, and mecoprop once.

In groundwater 4C2MP had 100% frequency of occurrence and mecoprop(s) had 83% frequency of occurrence (i.e. five days out of six with a detection). Concentrations never exceeded the EU DWS(i) during the event with concentrations ranging from 0.004-0.016 $\mu\text{g/L}$ for surface water and between 0.004-0.007 $\mu\text{g/L}$ for groundwater.

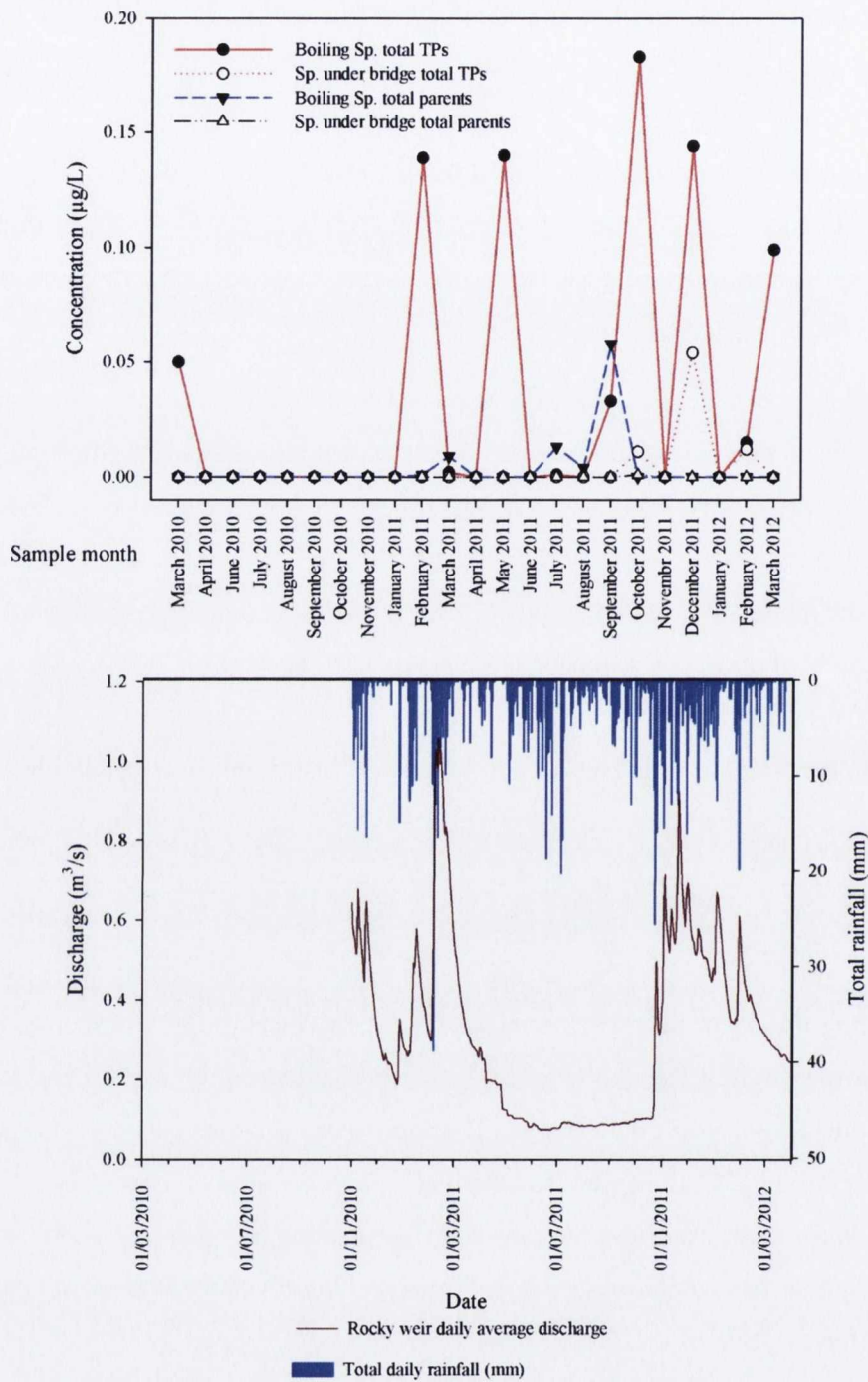


Figure 7.14 Temporal variation between total parent active ingredient (a.i) and total transformation products (TPs) from monthly samples collected at KWDa with daily average discharge from Rocky weir and total rainfall.

Figure 7.15 shows the response of Q at Rocky Weir to total rainfall. In the preceding days before the first sample was collected for the event on the 6th May 2012, Q at Rocky Weir was responsive to rainfall. The dashed green box in **Figure 7.15** indicates the days when an event sample was taken. This has been magnified in **Figure 7.16**. More compounds were detected in the R. Nuenna and of a higher concentration in comparison to detections at the Boiling Sp. At the Boiling Sp. mecoprop(s) had an elevated concentration on 7th May 2012 (day 2 of event) which coincided with the highest amount of total rainfall during the event. An elevated concentration of mecoprop(s) also occurred in the R. Nuenna on the 7th May 2012. The Boiling Sp. contributes 35% of discharge to the R. Nuenna (see section 5.5.2.2) and will therefore influence pesticides detected and their concentrations in surface water downstream of where the Boiling Sp. joins the R. Nuenna. Only 2,4-D and MCPA acid were detected in the R. Nuenna, these compounds were not detected in the Boiling Sp. indicating the source of these two a.i. is from up-stream of the Boiling Springs entry into the R. Nuenna.

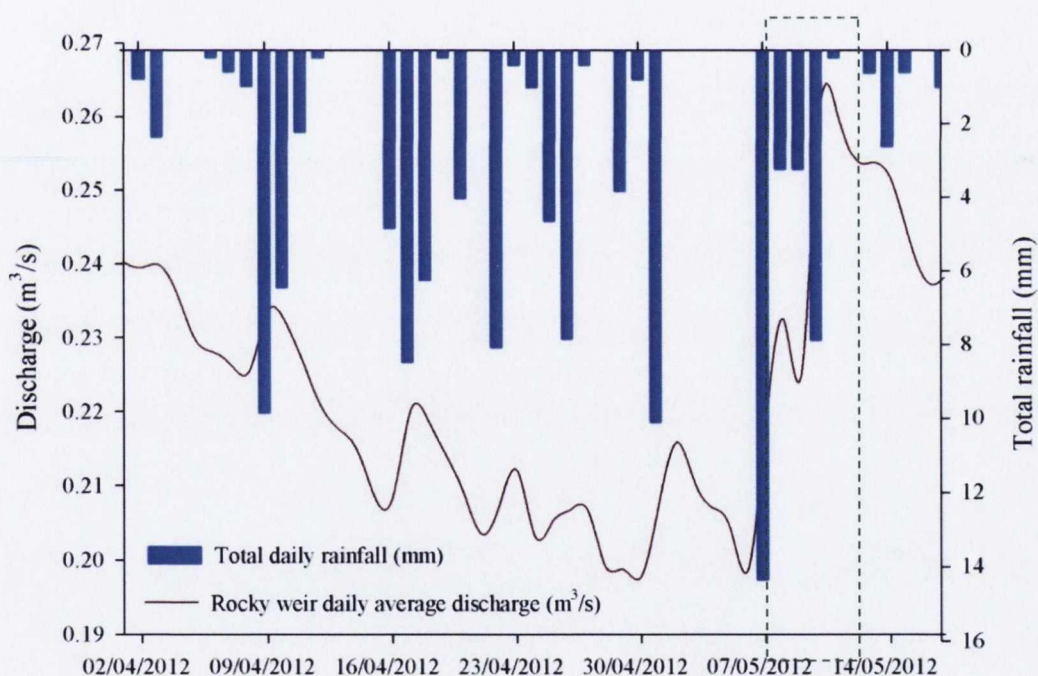


Figure 7.15 Total rainfall and stream discharge at the Rocky Weir located approximately 200 m downstream of where the Boiling Spring enters the R. Nuenna at karst well-drained arable site (KWDa) before and after event-based sampling which occurred in May 2012.

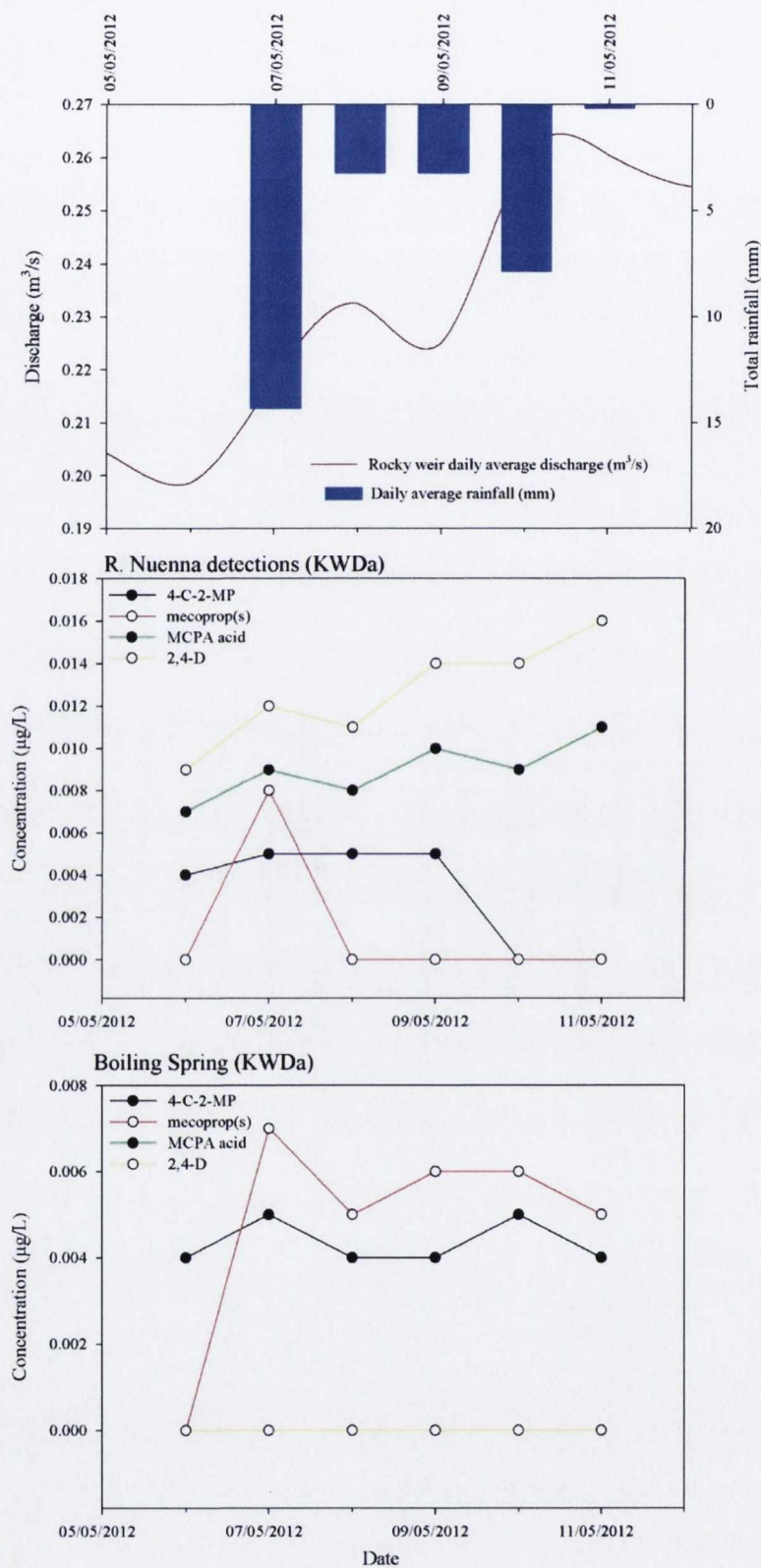


Figure 7.16
Temporal variation between total parent active ingredient (a.i) and total transformation products (TPs) from event-based samples collected at karst well-drained arable (KWDa) with daily average discharge at Rocky weir and total rainfall.

7.4.3 Temporal variation at intergranular/karst well-drained arable (I/KWDa)

High concentrations of pesticides were found in both BHs at I/KWDa but overall MP2 had higher concentrations of pesticides than MP1 (**Figure 7.17**). Detections at MP2 in March and April 2011 may have arisen because of the incidence of considerable effective rainfall in late February 2011. However, at MP1 this effective rainfall did not instigate a response in groundwater pesticide detections. In January, February, and March 2012 pesticide detections increased at both BHs. These increased pesticide detections also occurred in March 2011 and March 2010 but concentrations were not as high (**Figure 7.17**). Effective rainfall in the autumn months preceding these detections will have recharged the groundwater system beneath. Recharge months at I/KWDa were: October 2010 to February 2011 and September 2011 to January 2012 (**Figure 5.14**).

Detections not only occurred in the winter (January and February) and the spring (March and April), but also June, July, August, and September. In June 2011 considerable detections of both parent a.i. and TPs were observed in MP1 yet in the same month in MP2 no pesticides were detected. However, in July and August 2011 pesticides, especially TPs were observed at only MP2, rather than MP1. Groundwater flow direction travels from MP1 to MP2 (**Figure 5.23**) so the occurrence of pesticides in June 2011 up gradient of MP2 and then detections in the following two months down gradient may indicate movement of the compounds. Also at MP1 in June 2011 parent a.i. were detected and TPs but in MP2 in July and August 2011 less parent a.i. were detected but considerably more TPs were observed in MP2 (**Figure 7.17**).

The compounds detected in June 2011 at MP1 were PAC, mecoprop(s), triclopyr, fluroxypyr, 2,4-D, 3,5,6-T2P, 2,4,5-TCP, 2,4-DCP, and 4C2MP. These three were detected in all piezometers (shallow, interface, and deep). The next month at MP1 (July 2011) a considerably lower number of pesticides were detected. Yet down groundwater gradient many pesticides were observed in July 2011. These included 4C2MP, 2,4,5-TCP, 3,5,6-T2P, 2,4-DCP, 2,4-D, DBA, dicamba, fluroxypyr, triclopyr, MCPA, mecoprop(s), PAC, and BAM. Some of these compounds may have relocated from up gradient to MP2 between sampling months moving through the sand and gravel aquifer and karstified diffuse aquifers at the site. Also the Rkd aquifer at I/KWDa has a considerably larger contributing area than the Rg aquifer which may allow pesticides to travel from outside the Sawmills Field, even though they were not applied in the immediate vicinity of the MPs.

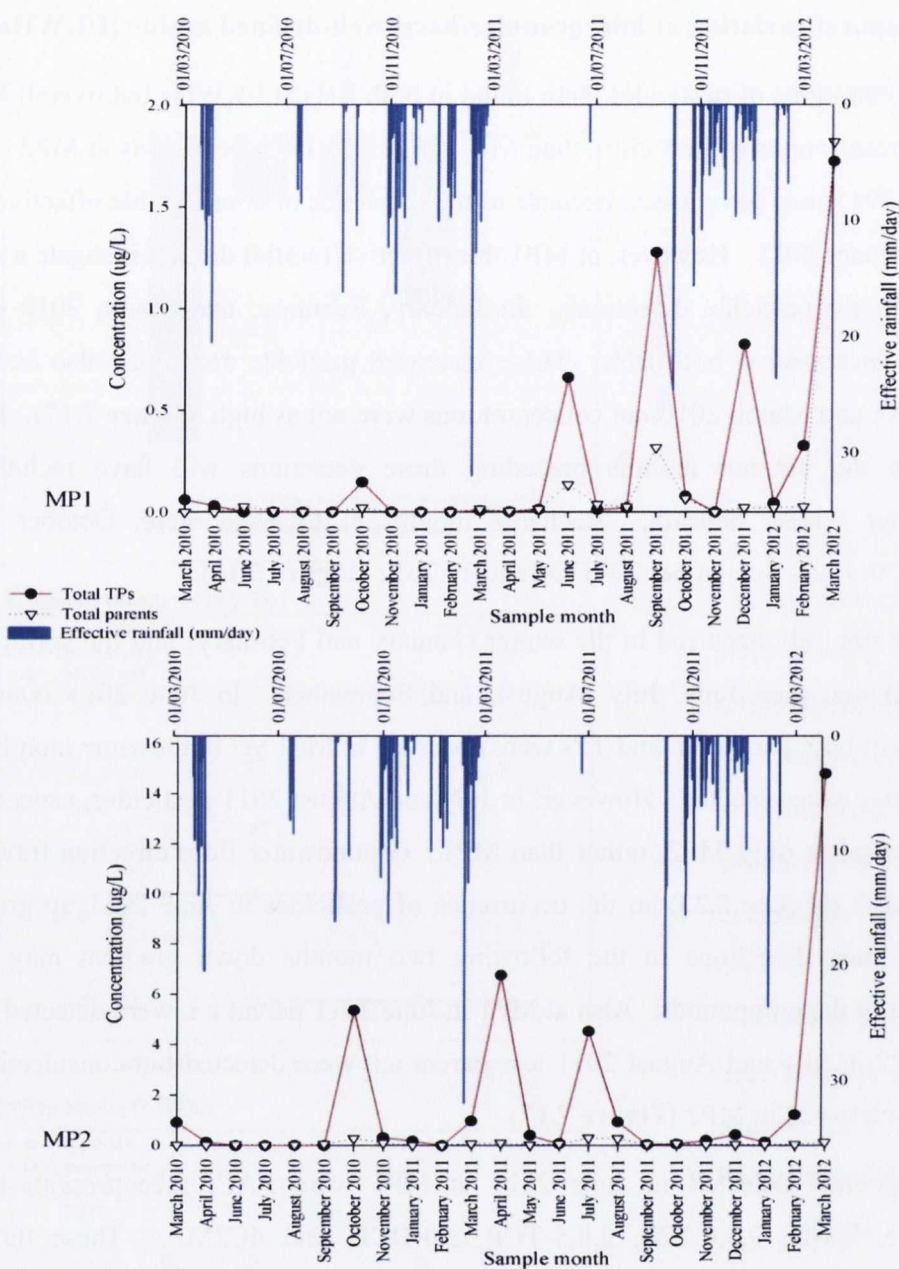


Figure 7.17 Temporal variation between total parent pesticide compounds and TPs from MP1 and MP1 at I/KWDa. Note differences in the y-axis scale between MP1 and MP2.

7.4.4 Temporal variation at fractured-volcanic well-drained arable (FvWDa)

The Upper BH had the highest total amount of TPs or parent a.i. over the monitoring period of up to 2.522 µg/L in May 2011 (**Figure 7.18**). Between the two BHs and the three springs, the temporal trends in pesticide occurrence do not always align on every occasion when there was a pesticide detection. Although in Winter 2011/2012 pesticide concentrations do align, especially for TPs, between all BHs and some springs at FvWDa. More specifically the sample dates: October 2011, November 2011, December 2011, and February 2012 all have detections of pesticides in both springs and BHs. July 2011 is another sample date when both BHs and the House Sp. all had a detection. At both BHs in September 2011 there were detections of parent compounds. Then in October and November 2011 both BHs had increasing concentrations of TPs, especially the Lower BH where the TP concentration peaked in December 2011. The TPs detected here may have either moved downslope from the Upper BH through the aquifer or these TPs may have degraded from other a.i. which were not analysed for. The TP compounds detected in the Lower BH in December 2011 were PAC (0.065 µg/L) and BAM (0.167 µg/L).

Recorded pesticide applications occurred between April and June each year. These are marked with an asterisk (*) in **Figure 7.18** and **7.19**. At the Lower BH in June 2010 the a.i.s 2,4-D, triclopyr, MCPA, and mecoprop(s) were detected. MCPA was applied in April 2010 and detected two months later in June 2010. Fluroxypyr was again applied but not detected (**Appendix 2**). In 2011 at the Lower BH, fluroxypyr was applied in April 2011 and was detected (0.002 µg/L) in May 2011 along with mecoprop(s). Detections of TPs were found in the Lower BH during applications, but more detections of TPs occurred in the Upper BH between April to July 2011, which may have then moved through the saturated zone within the highly weathered Ordovician volcanics from the Upper BH to the Lower BH, which were then detected later in 2011 after September (**Figure 7.18**).

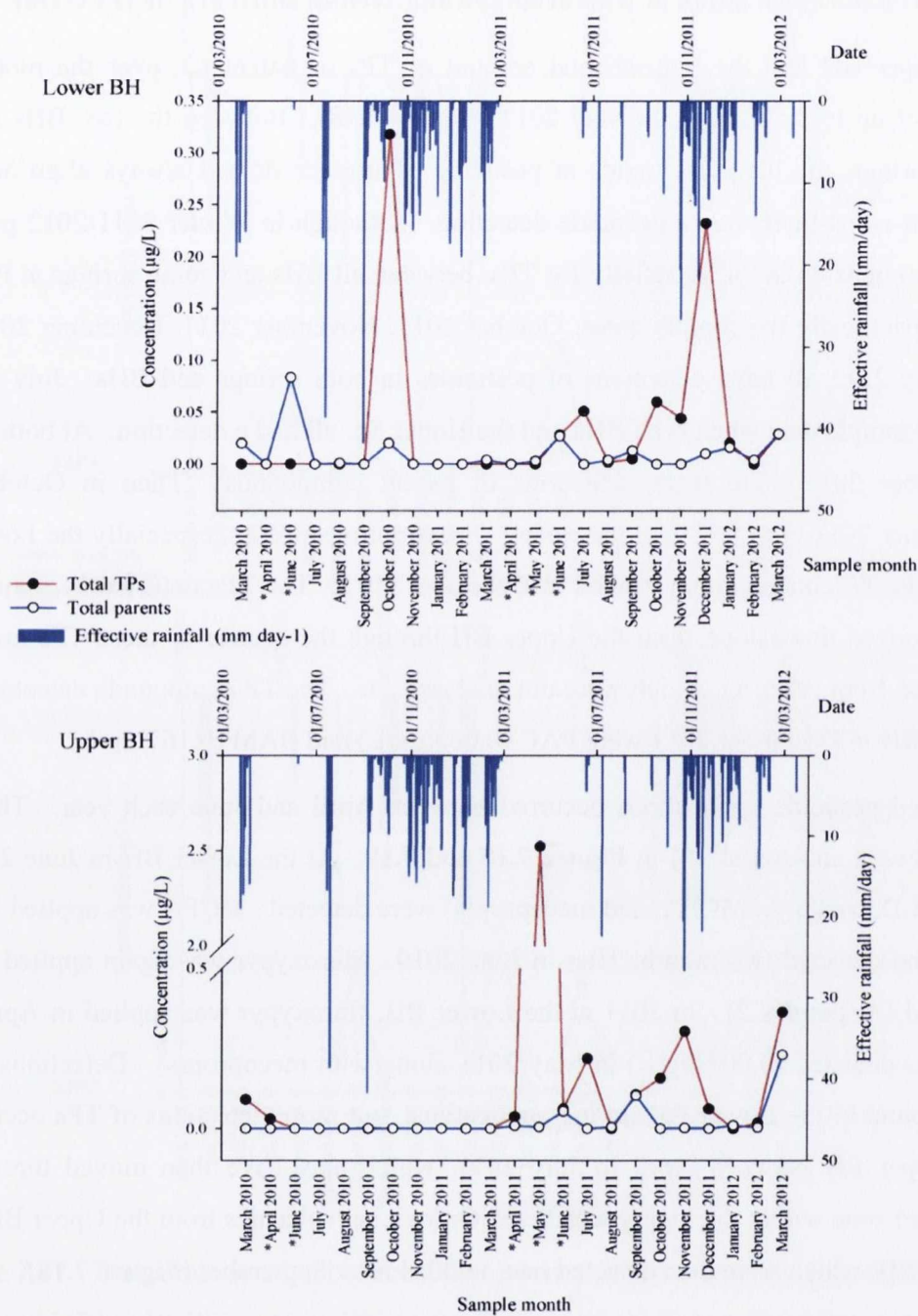


Figure 7.18 Temporal variation between total parent pesticide compounds and TPs from the upper and lower boreholes (BHs) and effective rainfall at FvWda. Note differences in the y-axis scale. Months marked with an asterisk (*) indicates months when pesticides were applied.

Comparing pesticide detections in springs (**Figure 7.19**) and BHs (**Figure 7.18**), the BHs had more detections in samples collected at the Lower and Upper BH (**Figure 7.9** and section 7.3.2). For springs, the average percent of samples with detections was 45.5%. From groundwater sampled at the springs at FvWDa, TPs were the more commonly found than parent a.i., notably at the Upper Sp. in October 2011 and the House Sp. in July, August, and October 2010. In groundwater collected from the House Sp. on two occasions effective rainfall which occurred prior to sampling caused detections of TPs in groundwater. In August 2010 intense effective rainfall occurred prior to the detections, while in October 2010 more prolonged and less intense rainfall may have flushed TPs into the groundwater system.

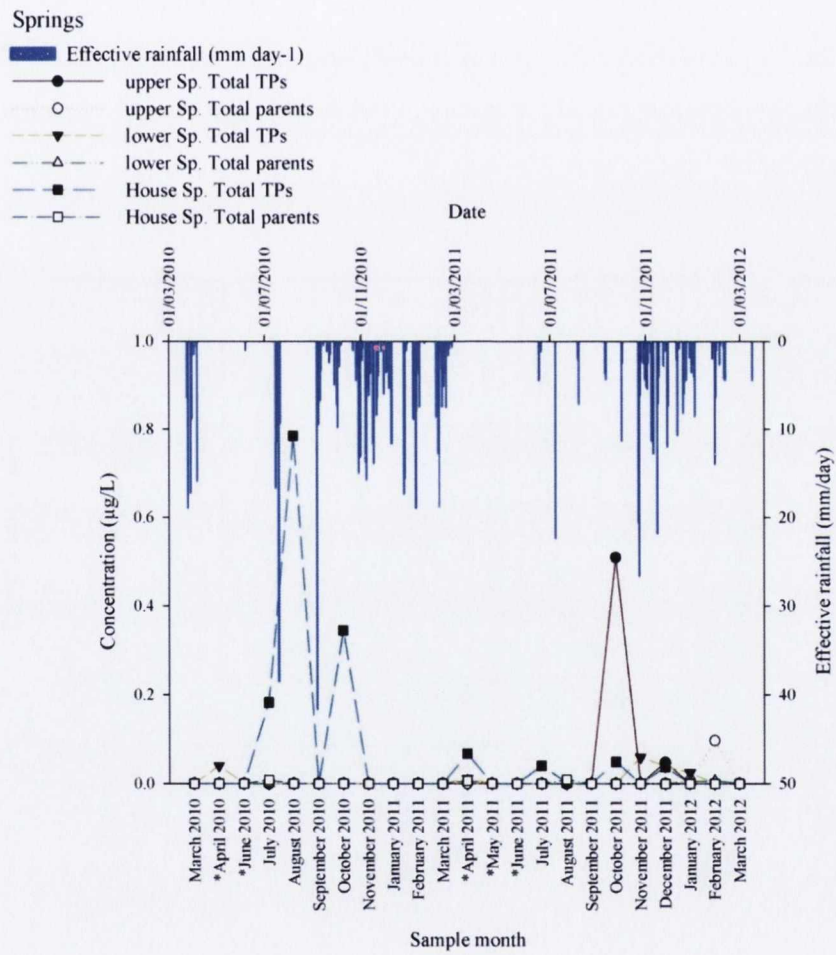


Figure 7.19 Temporal variation between total parent pesticide active ingredients (a.i.) and transformation products (TPs) from the three springs (Sp.) and effective rainfall calculated for FvWDa. Months marked with an asterisk (*) indicates the months pesticides were applied. The location of these springs can be found in **Figure 4.7** and **5.3**.

7.4.5 Temporal variation at fractured-volcanic poorly-drained arable (FvPDa)

Most detections at FvPDa occur in July 2011 and September 2011 and do not coincide directly with the highest rates of effective rainfall (**Figure 7.20**). However, the lack of effective rainfall between March and October 2011 may reduce the amount of water present at the site to dilute pesticides. This coinciding with pesticide application in May and June 2011 (**Appendix 2**) will have contributed to the elevated pesticide detections in July 2011 at piezometers 1b and 5b. Piezometers 1b and 5b are located in higher permeability deposits which will allow the quicker translocation of pesticides to deeper groundwater compared to the surrounding low permeability Irish sea till deposits as explained in section 7.3.3. In October 2011 total pesticide detections were high in 1b and 5b but high pesticide detections were not found at 7b or 9b until the following month: November 2011. This infers that travel times through the deposits encompassing these MPs are different. In gravel deposits the length of time is less than for pesticide travelling through low permeability subsoil.

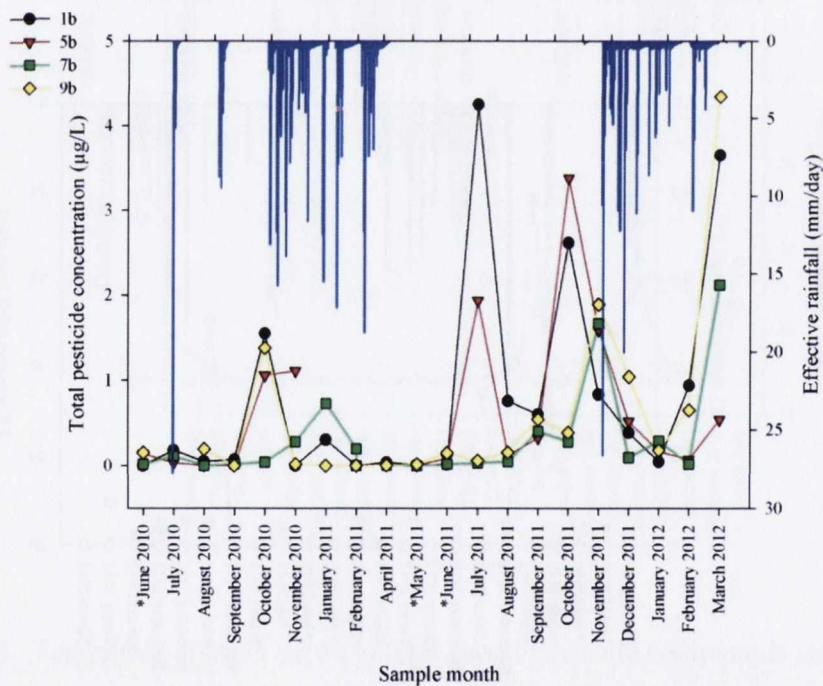


Figure 7.20 Temporal variation between total parent pesticide compounds at fractured-volcanic poorly-drained arable (FvPDa) and effective rainfall. Months marked with an asterisk (*) indicates that pesticides were applied.

7.4.6 Temporal variation at fractured-metasediments well-drained arable site 1 (FmWDa₁)

At FmWDa₁, the months March 2010, October 2010, March 2011, June 2011, and February 2012 all had pesticide detections in each BH. It was also frequently the deep piezometer across the three piezometers which had the most detections, followed by the shallow piezometer. The deep piezometer in October 2011 in the Middle BH and in February 2012 in the Upper BH (**Figure 7.21**) had the two highest total pesticide concentrations found in any one sample at FmWDa₁. The total concentrations were 36.1 µg/L in October 2011 and 6.1 µg/L in February 2012 in the Middle and Lower BHs, respectively. Detections were common in the Middle and Lower BHs between October to December 2011. These are recharge months as indicated by the amount of effective rainfall (**Figure 7.21**).

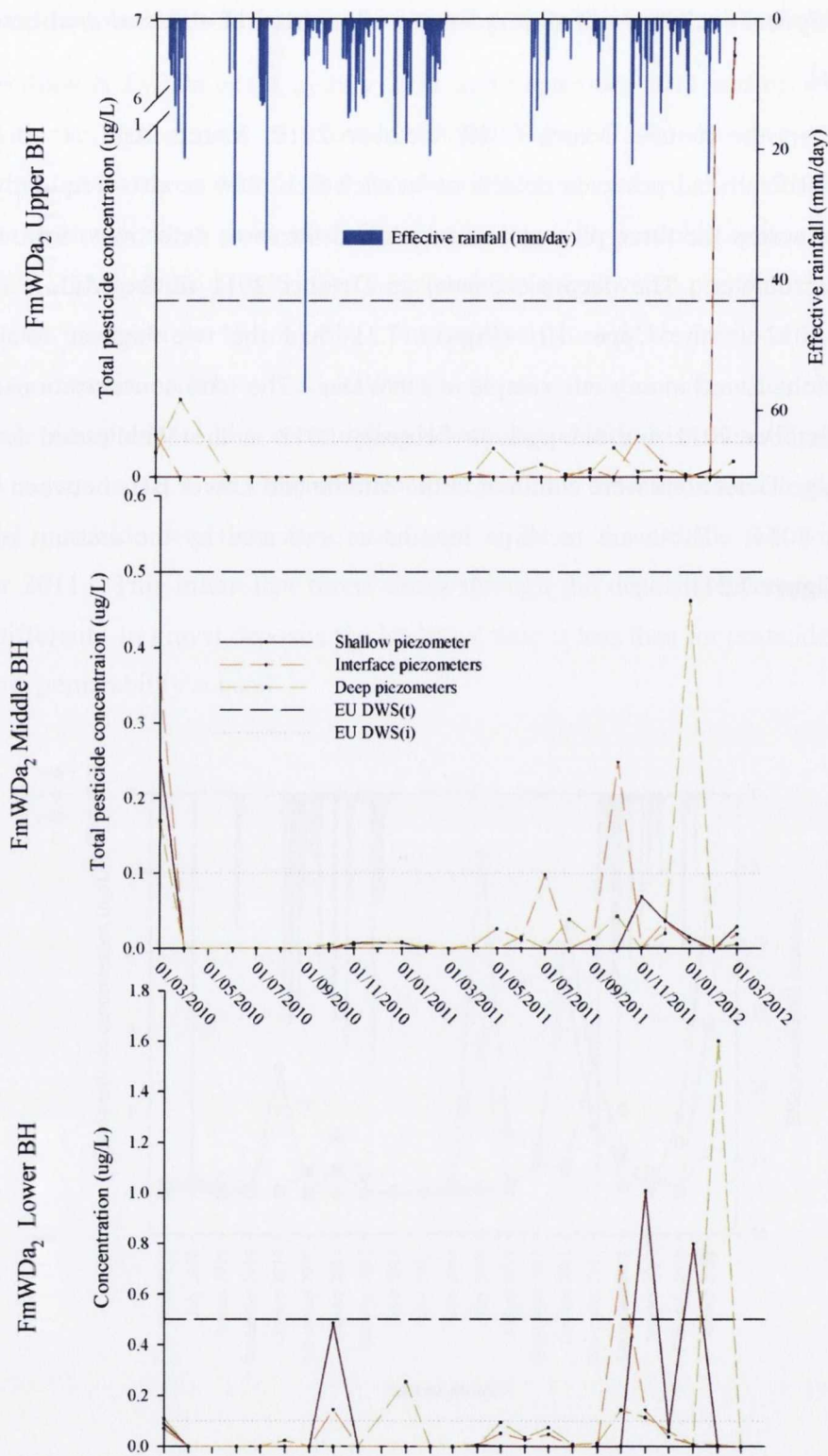


Figure 7.21 Temporal variation between total pesticide compounds at fractured-metasediments well-drained arable site 1 (FmWDA₁) and effective rainfall.

7.4.7 Temporal variation at fractured-metasediments well-drained arable 2 (FmWDa₂)

At FmWDa₂, the months of March 2010, May 2011, July 2011, October 2011, and November 2011 all have pesticide detections in each of the BHs (Lower, Middle, and Upper) with considerably more detections occurring in late 2011 and 2012 (**Figure 7.22**). At FmWDa₂ pesticides were equally distributed across depth (shallow, interface, or deep).

The piezometers with the highest total pesticide concentrations were the shallow and interface piezometers in the Upper BH in March 2012 which had 6.8 µg/L and 6.5 µg/L, respectively. These were the highest total concentrations recorded at any one piezometer at FmWDa₂. At the Middle BH in the interface piezometer in July and October 2011, concentrations were high and pesticides here may have moved within the saturated zone over time to eventually reach the deep piezometer in the Middle BH where detections were higher several months later in January 2012, and in breach of the EU DWS(i).

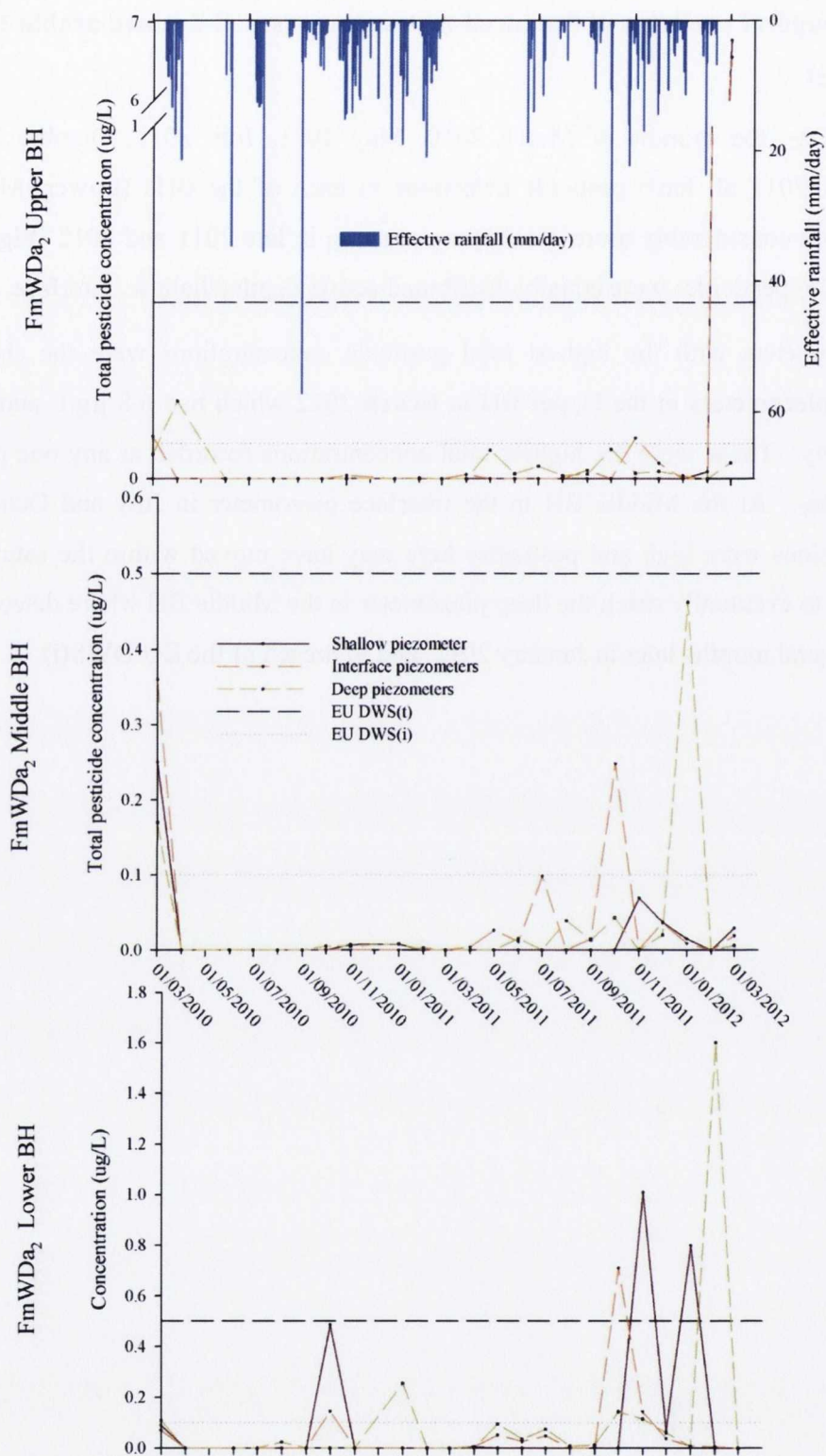


Figure 7.22 Temporal variation between total pesticide compounds at fractured-metasediments well-drained arable site 2 (FmWDA₂) and effective rainfall.

7.5 *Statistical correlations of variables with pesticide detections*

7.5.1 Introduction to statistical analysis

The main objective of this chapter was to establish which site characteristics contribute to pesticide occurrence in groundwater. The pesticide occurrence data across all seven sites between March 2010 and March 2012 were statistically analysed to explore the data to see which physical characteristics were more associated with pesticide detections in groundwater and if any chemical variables were associated with pesticide occurrence in groundwater.

7.5.2 Sample pre-treatment and statistical materials and methods

The monthly dataset collected by this project has a non-random sampling nature since each site and MP was selected to instigate a response (see section 4.1). Therefore, statistical tests employed cannot be taken as indicating cause and effect relationships but as indicating relationships that may be of use in the planning of more detailed observations on a national basis. The results of the analysis have to be interpreted strictly as indicative associations to explore the data for outcomes which may be associated with pesticide occurrence in groundwater.

The complete dataset was pre-treated before statistical analysis to investigate if any chemical or physical variables had an association with either total pesticide occurrence, parent a.i. occurrence, or TP occurrence in groundwater. For each sample collected (an observation) a spreadsheet column was assigned to sum up the total pesticide concentration which included both TPs and a.i. Then for each compound where a detection occurred, no matter whether the concentration was in breach of the EU DWS(i) or not, the cell was given a binary outcome of '1' for a detection and '0' for a non-detection. Chemical variables were analysed separately from physical characteristics to (a) aid comparisons between the national scale dataset analysed in Chapter 3 and the catchment scale monitoring achieved by this project and (b) so physical characteristics did not control the outcome of the chemical variable associations with pesticide occurrence.

Table 7.5 lists all the variables input into SAS for statistical analysis. The pesticides were grouped into the following categories with each one analysed against chemical and physical variables:

- (A) sum of pesticides (sum of concentration of both TPs and a.i. in any one sample)
- (B) total pesticides (binary data)
- (C) total parent a.i. (binary data)
- (D) total TPs (binary data)

In total 18 physical catchment characteristic variables and 27 water quality variables (chemical variables) were included in the analysis (**Table 7.5**) using the four categories (A)-(D) listed above. Section 5.8.2.3 summarises the chemical variables relating to hydrochemistry of the sites.

A mixed model approach using the GLIMMIX procedure in SAS[®] 9.3 was used so that correlations, due to repeated sampling of the same sites, could be taken into account. The analysis was also used to determine which site would have a higher probability of a pesticide detection in groundwater. Automatic variable selection procedures were used to isolate a set of variables for further testing in the mixed models. The procedure was repeated and hypotheses tested four times using categories (A)-(D).

Data was not structured to suit statistical analysis as has been done by other authors for example by substituting a value less than the LOD as half the LOD value (Worrall *et al.*, 2002; Hildebrandt *et al.*, 2008; Finizio *et al.*, 2011). Helsel (1987; 1990; 2006) state that data with non-detects should not have non-detect values substituted for another value because potentially severe bias can occur in the statistics (see section 3.2.3).

SAS[®] 9.3 (Statistical Analysis Software, Dublin, Ireland) was employed for statistical analysis. Under a statistician's guidance (Dr. J. Grant, Teagasc), a generalized linear mixed model (GLMM) was used for the detect/non-detect binary responses and a normal-based linear mixed model sufficed for counts of total pesticide occurrence. In the first instance, site name was used as a random effect, which induces a correlation within each site but was later used as a fixed effect to more easily estimate approximate site probabilities. Fixed effects in each model were the MP I.D and the factors in **Table 7.5** are the response variables.

GLMM models provide a flexible approach for analysing non-normal data when random effects are present and allow models to be fitted to non-normal data with correlations (Bolker *et al.*, 2009). Correlation structures within each site were accounted for in the GLMM by using random effects. The GLMM procedure in SAS[®] 9.3 is referred to as the GLIMMIX procedure and effects can be treated as non-random or random effects (SAS Institute, 2004). The random effects term in GLMM is used to adjust for the lack of independence of repeated measures on the same MP over time (Bradman *et al.*, 2011) as well as providing inference on a broader basis than a fixed effects model (insofar as the wells in the study represent the range of values that would be encountered in a random sample). The GLMM used each physical characteristic as an independent variable to measure a significant bivariate (marginal) relationship with pesticide occurrence in groundwater. Only binary categories (B)-(D) were used for physical characteristics.

Table 7.5 Variables tested statistically against the pesticide categories (A)-(D).

Variable	Example/units/cross-reference
<i>Physical characteristics</i>	
Monitoring point (MP) type	Borehole (see section 5.9)
Soil association	Acid brown earth (Table 4.9)
Soil texture	Loam (see section 4.4)
Soil CEC	17.7 m.eq/100g (see section 4.4)
Soil OM	5.5 % (see section 4.4)
Subsoil type/genesis	Gravels derived from Limestones (Table 4.9)
Subsoil acid/base	Acidic (Table 3.2)
Bedrock geology	Dinantian pure bedded limestones (see section 4.4)
Aquifer type	L1 (Table 4.9)
Aquifer importance classified by GSI	Regionally important (Table 4.9)
Aquifer flow regime used for WFD	Intergranular (Table 4.9)
Sample depth (categorical)	Interface (Appendix 3)
Depth of sample point (continuous)	7 m (Appendix 3)
Groundwater vulnerability classification	High (H) (Table 2.2)
Subsoil thickness	11.9 m (Appendix 3)
Unsaturated zone depth for sand and gravel aquifers	0.5-3 (Appendix 3)
Subsoil permeability	Low (GSI, 2011)
Soil drainage class	Deep well drained mineral (Table 4.9)
<i>Chemical variables</i>	
Water pH	6.3 [‡]
ORP	198 mV [‡]
RDO	6.1 mg/L [‡]
Conductivity	402.9 [‡]

Table 7.5 Variables tested statistically against the pesticide categories (A)-(D) contd.

Variable	Example/units/cross-reference
Turbidity	88.93 NTU [‡]
Temperature	8.4 °C [‡]
Ca	97 mg/L [‡]
Cu	0.16 µg/L [‡]
Fe	284 µg/L [‡]
K	0.26 mg/L [‡]
Mg	2.65 mg/L [‡]
Mn	6.28 µg/L [‡]
Na	13.1 mg/L [‡]
Zn	0.12 µg/L [‡]
NPOC	2.17 mg/L [‡]
Total nitrogen	3.17 mg/L [‡]
Chloride	10.4 mg/L [‡]
Ammonium-N	0.1 mg/L [‡]
Total oxidisable nitrogen	7.8 mg/L [‡]
Nitrate-N	3.97 mg/L [‡]
Nitrite-N	0.03 mg/L [‡]
Total reactive phosphorous	0.008 mg/L [‡]
Total carbon	15.2 mg/L [‡]
Bicarbonate alkalinity as CaCO ₃	290 mg/L [‡]
Bicarbonate alkalinity as HCO ₃ ⁻	354 mg/L [‡]
Bicarbonate alkalinity as CO ₃ ²⁻	174 mg/L [‡]
Season	Autumn

[‡]See **Table 5.12** for hydrochemical variables for each site.

The months included for season were Spring: February, March, and April; Summer: May, June, and July; Autumn: August, September, and October; Winter: November, December, and January.

7.5.3 Results of statistical analysis

Results of statistics which are significant to $p \leq 0.05$ or $p \leq 0.1$ are given below for the physical characteristics, chemical variables, and each site which have been determined as more associated with pesticide occurrence in groundwater.

7.5.3.1 Physical characteristics

The GLMM procedure detailed whether or not a physical characteristic had an association with pesticide detections from binary categories (B)-(D). From those physical characteristics listed as significant in **Table 7.5**, odds ratios and their interpretation are given below. An odds ratio shows the strength of association between the predictor and the response. Only odds ratios between significant characteristics have been given

therefore not every category within each physical characteristic will have an odds ratio to compare because the statistical output was insignificant.

Table 7.6 Association (P value) of site physical characteristics in groundwater total pesticides, parent active ingredients (a.i.), and transformation products (TPs) using a generalized linear mixed model (GLMM).

Physical characteristic	Total pesticides (B)	Parent a.i. (C)	TPs (D)
Monitoring point (MP) type	0.0001*	0.0001*	0.0001*
Soil association	0.0001*	0.0001*	0.0005*
Soil texture	0.0001*	0.0016*	0.0034*
Soil CEC	0.0232*	0.1098	0.0138*
Soil OM	0.6087	0.7314	0.1235
Subsoil type/genesis	0.0017*	0.0001*	0.1991
Subsoil acid/base	0.4483	0.5326	0.4640
Bedrock geology	0.6567	0.7670	0.7377
Aquifer type	0.0078*	0.0089*	0.0124*
Aquifer importance classified by GSI	0.9182	0.9528	0.9483
Aquifer flow regime used for WFD	0.4817	0.4193	0.8239
Sample depth (categorical)	0.0001*	0.0001*	0.0002*
Depth of sample point (continuous)	0.1535	0.2672	0.0840
Groundwater vulnerability classification	0.0003*	0.0001*	0.0711**
Subsoil thickness	0.0004*	0.0001*	0.0879**
Unsaturated zone depth for sand and gravel aquifers	0.0957	0.3457	0.5742
Subsoil permeability	0.0001*	0.0191*	0.0230*
Soil drainage class	0.0001*	0.0012*	0.0006*

Values in bold are significant (* $p \leq 0.05$ and ** $p \leq 0.1$).

Odds Ratio Estimate Interpretation

- MP type

○ Parent a.i. are 1.4 times more likely in a drain than a spring, and 4.1 times more likely in a drain than a stream.

○ TPs are 1.2 times more likely in a BH than a stream and 3.7 times more likely in a drain than a spring.
- Soil association

○ Total pesticides are 2 times as likely to be in association with a minimal grey grown podzolic (mGBP) than a typical acid brown earth, 2 times as likely to be in association with a mGBP than a typical

	groundwater gley, and five times more likely to be in association with a typical acid brown earth than a grey brown podzolic.
	○ Parent a.i. are 1.4 times more likely to be in association with a mGBP than a shallow brown earth and rendzina, are 2.2 times more likely to be in association with a shallow brown earth and rendzina than a typical brown earth, are 2.2 times more likely to be in association with a shallow brown earth and rendzina than a typical groundwater gley, and 1.2 times more likely to be in association with a typical surface water gley than a grey brown podzolic. ○ TPs are 1.4 times more likely in association with a mGBP than a typical brown earth, are 4 times more likely to be in association with a shallow brown earth and rendzina than a typical groundwater gley, 3 times more likely in association with a shallow brown earth than an acid brown earth, and 3 times more likely to be in association with an acid brown earth than a grey brown podzolic.
Soil texture	○ Parent a.i. are 1.2 times more likely to be in association with a clay loam than a sandy loam. ○ TPs are 1.2 times more likely to be in association with a clay loam than a sandy loam.
Subsoil type/genesis	○ Total pesticides are 1.5 times more likely to be in association with bedrock at or near the surface than till derived from lower Palaeozoic sandstones and shales. ○ Parent a.i. are 1.7 times more likely to be in association with bedrock at or near the surface than till derived from lower Palaeozoic sandstones and shales and are 1.2 times more likely to be in association with gravels derived from limestones than Irish sea till derived from limestones.
Aquifer type	○ Total pesticides are 1.5 times more likely in an Rf aquifer than a Ll aquifer, are twice as likely in an Rg & Rkd aquifer than an Ll aquifer, and 1.4 times more likely in a Rg & Rkd aquifer than an Rf aquifer. ○ Parent a.i. are 1.5 times more likely in an Rf aquifer than a Ll aquifer,

	are 2.7 times as likely in an Rg & Rkd aquifer than an Ll aquifer, and 1.8 times more likely in a Rg & Rkd aquifer than an Rf aquifer.
Sample depth (categorical)	○ Total pesticides are 1.5 times more likely in a deep piezometer than a shallow piezometer, are 2.5 times more likely in a drain than a Sp., and are twice as likely in a stream than a Sp. ○ Parent a.i. are 2 times as likely in a drain than a stream and 2 times as likely in a Sp. than a stream. ○ TPs are 2 times as likely in a drain than a Sp. and 2.4 times as likely in a Sp. than a stream.
Groundwater vulnerability classification	○ Total pesticides are 1.2 times more likely to be in association with an extreme groundwater vulnerability category than a high category. ○ Parent a.i. are 1.2 times more likely to be in association with an extreme groundwater vulnerability category than a high category.
Subsoil permeability	○ Total pesticides are 1.2 times more likely to be in association with a high permeability subsoil than a low permeability subsoil.
Soil drainage class	○ Total pesticides, parent a.i., and TPs are all 1.2 times more likely to be in association with a deep poorly drained mineral soil than a shallow well drained mineral soil.

Odds ratio estimate summary

There are ten physical characteristics associated with pesticide occurrence in groundwater (Table 7.6). The interpretation of odds ratios reveals that BHs used as MPs are more associated with pesticide occurrence in groundwater. Minimal grey brown podzolic soil associations are more likely to be present when total pesticides, parent a.i., and TPs are detected in groundwater. A clay loam soil texture is more likely to be present when total pesticides, parent a.i., and TPs are detected. When bedrock is at or near the surface as opposed to Irish sea till derived from limestone, total pesticides and parent a.i. are more likely to be detected in groundwater. Total pesticides and parent a.i. are more likely to occur in groundwater when Rg & Rkd aquifers are present, followed by Rf aquifer types. Extreme groundwater vulnerability classifications are more associated with total pesticides and parent a.i. occurrence in groundwater than high groundwater vulnerabilities. High

subsoil permeability was more associated with total pesticide occurrence in groundwater compared to low permeability subsoil. Deep poorly-drained mineral soils are more associated with detections of total pesticides, parent a.i., and TPs in groundwater than shallow well-drained mineral soils.

7.5.3.2 Chemical variables

The chemical variables listed in **Table 7.5** were analysed using a mixed model in SAS[®] 9.3. Those chemical variables associated with pesticide occurrence in groundwater are listed in **Table 7.7**, with each significant variable corresponding p-value and a trend scenario of whether the association is positive or negative. For example a positive trend (+) indicates a significant positive relationship between the chemical and pesticides.

Table 7.7 The chemical variables which are associated with pesticide occurrence from the mixed model in SAS[®] 9.3 with their significance level and trend.

Category	Chemical variable in association	p-value	Trend
Total pesticides (A)	Ca	0.0001	+
	Mn	0.0496	+
	Na	0.0001	+
Total pesticides (B)	pH	0.0332	-
	ORP	0.0001	-
	Ca	0.0028	+
	Mg	0.0001	+
Parent a.i. (C)	ORP	0.0108	-
	Ca	0.0002	+
	Na	0.0001	+
TPs (D)	Mg	0.0001	+
	Total nitrogen	0.0497	+
	Turbidity	0.0312	-

A higher concentration of Ca in groundwater was associated with total pesticides and parent a.i. in groundwater. A higher concentration of Mn, Na, and Mg were also

associated with total pesticides in groundwater. Na had a positive association with parent a.i. in groundwater. Low pH and low ORP was associated with total pesticide and parent a.i. occurrence in groundwater. Total nitrogen and Mg were positively associated with TP occurrence in groundwater while turbidity was negatively associated with TP occurrence in groundwater.

7.5.3.3 Sites most associated with pesticide occurrence in groundwater

Using the mixed procedure in SAS[®] 9.3 with site name used as a fixed effect, the site which had the highest probability of having either a total pesticide detection, parent a.i. detection, or TP detection in groundwater was found along with a p-value. The most significant output was found for total pesticides with I/KWDa having the highest probability of a pesticide detection (**Table 7.8**). This was followed by FvPDa which was also found in **Table 7.8**. The estimate value from **Table 7.8** and **7.9** given to each site is the pesticide concentration likely to be detected in groundwater at this site. The accompanying p-value provides the significance of this estimate.

Table 7.8 Site estimates for total pesticides in groundwater from a mixed model.

Rank	Site name	Estimate value	p-value
1	I/KWDa	2.65	0.0001
2	FvPDa	2.39	0.0001
3	FvWDa	1.72	0.0001
4	FmWDa ₁	1.8	0.0001
5	FmWDa ₂	1.7	0.0001
6	KWDa	0.86	0.0430
7	KWDg	0.20	0.8088

The sites with the lowest probability of a pesticide detection or parent a.i. detection were KWDa and KWDg (**Table 7.8**). There was not a significant effect for site on TP occurrence in groundwater using the mixed model in SAS[®] 9.3.

Table 7.9 Sites which are more likely to have higher detections of parent active ingredients (a.i.) in groundwater.

Rank	Site	Estimate value	p-value
1	FvPDa	0.62	0.0533
2	FvWDa	0.59	0.1941
3	FmWDa ₁	0.57	0.2168
4	FmWDa ₂	0.55	0.2149
5	I/KWDa	0.43	0.3941
6	KWDa	0.14	0.0015
7	KWDg	0.09	0.0407

7.6 Discussion

7.6.1 Discussion of parent compounds and transformation products detected in the study

Ten parent compounds and nine TPs were detected in groundwater throughout the course of monitoring but no comparable published data from other studies exists because this suite of TPs and parent a.i.s have not been included in any other groundwater monitoring programme until now. The literature contains many publications on the methodological analysis for many of these compounds using different techniques (Lancas *et al.*, 2007; Olujimi *et al.*, 2011) but few studies have attempted to quantify and interpret their occurrence in groundwater. From monthly monitoring over the two years across all seven sites the most frequently detected pesticide compounds were mecoprop(s), PAC (phenoxyacetic acid), 4C2MP (4-chloro-2-methylphenol), 2,4-D, DBA (2,6-dichlorobenzoic acid), and MCPA (**Figure 7.1**). At concentrations greater than or equal to the LOD each of these compounds had a frequency of detection greater than 15% (**Table 7.1**). Compounds which exceeded the EU DWS(i) (DBA and PAC) were present in over 10% of samples. In addition 13 compounds were detected greater than or equal to the EU DWS(i) on at least one occasion throughout the course of monitoring and six of these compounds were TPs. DBA and PAC breached the EU DWS(i) most often out of all the TPs (**Table 7.1**). In April 2010 the highest concentration (120 µg/L) of any compound was observed at FvPDa in piezometer 7b. The EU DWS (Council Directive, 1998) states that

metabolites, degradation, and reaction products of pesticides (TPs) must also adhere to the parametric value of 0.1 µg/L in drinking water.

The occurrence of PAC and DBA in groundwater has never until now been investigated either in Ireland or internationally. Fava *et al.* (2005) and Hotlze *et al.* (2008) indicate that DBA is a TP of dichlobenil and BAM (3,5-dichlorobenzamide) with DBA formed in the environment from the hydrolysis of the nitrile group of the parent herbicide dichlobenil and then subsequent hydroxylation at the three-position of the phenyl ring (Roberts, 1999). But the occurrence of DBA in surface water or groundwaters has not been reviewed before nor has the persistence or toxicity of DBA been looked at. The source of BAM was most likely from dichlobenil, which was applied to surface water courses in Ireland by Waterways Ireland (Horgan *Pers. Comm.* 2011). The application of dichlobenil has since ceased following its removal from the Irish market in 2007 (Conroy *Pers. Comm.* 2011). Even less is known about PAC: its origin, degradation pathway, occurrence in surface waters and groundwater, nor its toxicity or persistence. It could be that PAC and DBA are harmless or they could be harmful both to the ecological environment and if ingested by humans and other fauna. The toxicity of both PAC and DBA requires further research, since these compounds have been found in groundwater across Ireland at mean concentrations of 0.2 µg/L for PAC and 3.2 µg/L for DBA, they should not be ignored unless they are proven as harmless in the environment.

The parent a.i. mecoprop(s) during this study was the most frequently detected compound in concentrations greater than the LOD while not taking into consideration the EU DWS(i) (**Figure 7.1**). Mecoprop(s) referred to in this study includes mecoprop (MCP) and mecoprop-p (MCP-P) because analytical techniques developed during this project were unable to distinguish between the two as both have the same parent to daughter transitions (see section 6.5 and **Table 6.5**). Mecoprop contains an asymmetric (chiral) carbon atom on the aliphatic side chain of the benzene ring which results in two optically active isomers: the R-isomer and S-isomer which are referred to as enantiomers (Buss *et al.*, 2006). Mecoprop as a herbicide is a racemate mixture of 50% of each isomer (Heron and Christensen, 1992). A racemate mixture is a combination of equal amounts of both isomers with the S-isomer orientated to the left of the carbon atom and the R-isomer orientated right around the carbon atom (Zipper *et al.*, 1998). The high incidence of mecoprop(s) in groundwater at these seven catchment-scale sites and from national groundwater monitoring discussed in Chapter 3 (**Figure 3.3**) may also be accounting for

the presence of chlorophenol TPs which were also found in groundwater (**Table 7.2**). The detection of the chlorophenols 4C2MP, DCP, T2P, TCP, and PAC may be either from (1) the metabolism of the phenoxyacid herbicide parent a.i. or (2) from the impurities in these herbicides due to incomplete synthesis reactions and insufficient clean up procedures during their production (Reitzel *et al.*, 2004). In the case of mecoprop (not mecoprop-p) which has both isomers, only the R-isomer is herbicidally active (Zipper *et al.*, 1998). The R-isomer is only present in mecoprop-p. Since the 1980s the synthesis of mecoprop has become obsolete and production has been improved to synthesise a.i. with fewer impurities which may be mistaken as TPs (Reitzel *et al.*, 2004). Mecoprop-p has thus taken over from mecoprop regarding the quantities produced and applied since this a.i., with its herbicidally active R-isomer, is all that is required for it to have an impact as a herbicide. Mecoprop-p is a purer a.i. containing 1-2% chlorophenols in comparison to mecoprop which will contain more chlorophenols as impurities which when present in the environment are often assumed to be TPs when in fact they may be artefacts of the herbicides synthesis (Reitzel *et al.*, 2004). The reason for mecoprop(s) relatively ubiquitous nature in Irish groundwater may be explained in a comprehensive review by Buss *et al.* (2006) who stated that mecoprop was subject to little sorption or retardation in the topsoil, because it is water soluble especially when applied as a salt, which is common practice in the UK. Agertved *et al.* (1992) also stated mecoprop in aquifer material was subject to little retardation. Once present in the aquifer mecoprop(s) appears to be recalcitrant and may travel long distances within the aquifer (Buss *et al.*, 2006). The high incidence of mecoprop(s) at the seven sites may be partly explained by reoccurring applications of mecoprop containing PPP, its varied sorption to soil, and its ability to travel long distances in aquifers once leached there.

TPs were associated with the physical characteristics; MP type, soil association, soil texture, soil CEC, sample depth, aquifer type, groundwater vulnerability, subsoil thickness, subsoil permeability, and soil drainage class (**Table 7.6**). TP occurrence in groundwater was also significantly associated with Mg, total nitrogen, and turbidity (**Table 7.7**). Turbidity was not associated with total pesticides or parent a.i., only TPs and the relationship was negative. This outcome indicates that the TPs monitored during this study may be transported through the same mechanisms as parent a.i. The compounds mecoprop(s), 2,4-D, MCPA, triclopyr, fluroxypyr, dicamba, bromoxynil, and bentazone are referred to as the phenoxyacid herbicides and one of the reasons for their popularity in

agriculture is their high solubility in water (Bucheli *et al.*, 1998) and their low cost. Turbidity was measured *in-situ* and can indicate the amount of material present in a sample which may thus aid colloidal transport. Colloids are particulates which certain pesticides may sorb onto and tend to be less than 0.2 μm in size. Phenoxyacid herbicides are highly soluble so colloidal transport is not a dominant mechanism in their transport to groundwater however, the TPs were statistically negatively associated with turbidity (**Table 7.7**) indicating these TPs are not associated with colloidal matter.

Statistical analysis was not able to determine if any particular site had a higher probability of TP occurrence, but the percentage frequency of occurrence at each site is given in **Table 7.10**. The sites which had the highest detections of TP occurrences expressed as a percentage of the number of samples were I/KWDa and FvPDa.

The high incidence of TPs at I/KWDa compared to the other sites may be attribute to:

1. The porosity of the sandy soil, quaternary deposits, and aquifer material with higher transmissivities rendering the aquifer vulnerable (Lapworth *et al.*, 2006) and smaller effective porosity in these porous systems which will have a slower flow velocity than a fractured rock (Alley *et al.*, 2002).
2. The high RDO and conductivity at I/KWDa (**Table 5.11**) may explain why TPs were detected in 23.4% of samples. However, high RDO and conductivity averages were also found for KWDa and KWDg. KWDg had the least percentage of samples with TPs but KWDa had the third highest occurrence of TPs (**Table 7.10**). The differences between KWDg and I/KWDa, FvPDa, and KWDa is land use. KWDg is dominated by grassland, the others arable land use. It is arable land use which is contributing pesticides, and to the presence of TPs at these diffuse agricultural sites.
3. Average turbidity at I/KWDa was high except at MP1 deep which had the lowest average turbidity and highest RDO (**Table 5.11**). MP1 deep had the second lowest percentage of samples with detections from the site, and was the third lowest MP at I/KWDa with TPs, verifying from statistics that a low turbidity was more associated with TP presence in groundwater. The MP with the most TPs found at I/KWDa was MP2 shallow. This piezometer samples groundwater above a layer of silt and clay (**Appendix 3**) which is one of the discontinuous clay lenses found at I/KWDa (Jahangir, 2012; Premrov *et al.*, 2012). MP2 shallow had higher turbidity than the site average at I/KWDa and the hydrochemical composition of water at this MP was

dominated by turbidity (**Figure 5.32**). Although turbidity was negatively associated with TP occurrence statistically, turbidity at MP2 shallow and the location of the MP being above a discontinuous clay lens may be the reason for elevated TPs here.

The high incidence of TPs at FvPDa compared to the other sites may be attribute to:

1. Longer residence times at the site allowing pesticides to remain at FvPDa and which are then unable to leach to deeper groundwater below because of upwelling artesian conditions. Discontinuous gravel lenses running laterally across the site and the limitations of recharging water to move water already within the system may allow for the increased formation of TPs which are then trapped in the system and unable to degrade as quick as they would in an aerobic system.
2. Anaerobic conditions at FvPDa (**Table 5.12**) may be encouraging the higher occurrence of TPs at this site compared to the other sites (**Table 7.10**) since in anaerobic conditions pesticide compounds such as 2,4-D or BAM may be used as electron acceptors during microbial processes (Holtze *et al.*, 2007) which may potentially lead to the formation of TPs such as DBA, PAC, or 4C2MP for example. Reducing conditions also favour the dehalogenation of chlorinated compounds (Larsen and Aamand, 2001). In anaerobic soils microbes gain energy by transferring electrons from electron donors to different electron acceptors such as NO_3^- , Mn(IV) , Fe(III) , SO_4^{2-} , and CO_2 . Sulfate reductase microbial processes are in operation at piezometer 1b at FvPDa indicated by the smell of $\text{H}_2\text{S}_{(\text{g})}$ during sampling. **Table 7.7** details that more negative ORP values in groundwater will be associated with the occurrence of total pesticides and parent a.i. No statistically significant association with ORP and TP was found. This may be because TPs were commonly detected in both aerobic sites e.g. I/KWDa and the anaerobic site FvPDa.

The existence of confining layers at FvPDa and MP2 shallow at I/KWDa coupled with the high input of pesticides to both these arable areas and the higher turbidity of water at these sites (**Table 5.12**) appears to be associated with TP presence in shallow groundwater.

The presence of PAC may be from the metabolism of MCPA or 2,4-D which contain PAC within their chemical structure (Onneby *et al.*, 2010) or PAC may be an impurity within MCPA or 2,4-D formulation products as highlighted above for the presence of chlorophenols such as TCP, T2P, and DCP from the phenoxyacid herbicide mecoprop. Although the degradation pathway has not been proven, it is highly likely that when

MCPA or 2,4-D degrade, they will degrade to PAC. Vroumsia *et al.* (2005) states that PAC is the non-chlorinated version of 2,4-D so should the chlorines present in 2,4-D get degraded in the environment, the end product will be PAC. **Figure 7.23** proposes a degradation pathway for 2,4-D to PAC drawn using ChemSketch version 12.01. The chlorophenol 4C2MP has been proven by Zertal *et al.* (2001; 2005) as a higher toxicity TP than the parent a.i. it was derived from: MCPA. Vione *et al.* (2010) states 4C2MP can form in surface waters following direct photolysis of MCPA. Mecoprop (both mecoprop and mecoprop-p) can degrade to 4C2MP (Buss *et al.*, 2006) in laboratory cultures (Tett *et al.*, 1994), soils (Klint *et al.*, 1993), and groundwater (Agertved *et al.*, 1992; Harrison *et al.*, 2003). From **Figure 7.7** and **Appendix 15** the frequency of occurrence of both mecoprop(s) and 4C2MP are 36.6% and 26.1%, respectively, so perhaps the high amount of 4C2MP may be attribute to mecoprop(s) presence.

Table 7.10 The number of transformation products (TPs) detected at each site from samples collected from monthly monitoring between March 2010 to March 2012 and the percentage frequency of occurrence of TPs at each site.

Site	Number of TPs detected at site	Number of TPs analysed for in samples	Percentage frequency of occurrence of TPs at each site
I/KWDa	152	650	23.4%
FvPDa	215	958	22.4%
KWDa	14	113	12.4%
FmWDa ₂	114	933	12.2%
FvWDa	55	613	8.9%
FmWDa ₁	99	1,114	8.8%
KWDg	4	49	8.2%

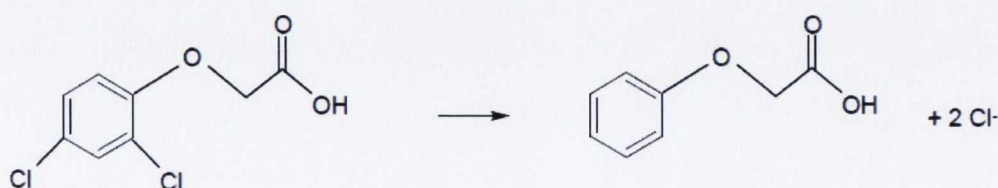


Figure 7.23 A proposed degradation pathway for 2,4-dichlorophenoxyacetic acid (2,4-D) to degrade to phenoxyacetic acid (PAC).

Other phenoxyacid herbicides which have been proven to degrade to their respective TPs also included for monitoring in this study include 2,4-D, which can degrade to 2,4-DCP (Fontmorin *et al.*, 2012) through photocatalytic oxidation, photolysis, and chlorination (Bedoux *et al.*, 2012). 2,4-DCP is a stable by-product in the environment (Bedoux *et al.*, 2012) which will make it more persistent. Padkel (1994) state that DCP is formed in the soil from the oxidation of the side chain of 2,4-D. 2,4-D does not persist in the environment for very long because its readily susceptible to microbial degradation (Vroumsia *et al.*, 2005) although 2,4-D was the fourth most frequently detected compound from monitoring with 25.9% of samples having a detection greater than or equal to the detection limit (**Appendix 14**).

Trichloro-2-pyridinol (T2P) can be a TP of triclopyr or chlorpyrifos (FOOTPRINT, 2006; Sinclair *et al.*, 2006). Chlorpyrifos was not quantified in groundwater during this monitoring programme. Both triclopyr and T2P were detected in groundwater samples from the seven sites. Triclopyr was present in 13.5% of samples and T2P in 13% of samples (**Appendix 14**). The presence of T2P in groundwater is of concern since it has been identified as a potential health hazard because of its high affinity to DNA through groove-binding onto the molecule (Kashanian *et al.*, 2012). Sinclair *et al.* (2006) developed a prioritization scheme of pesticide TPs from agriculture to help focus future research and monitoring. For Great Britain, which has a similar temperate maritime climate to Ireland, T2P was ranked the highest TP to reach drinking water and which also had the most adverse effect to human health. T2P during this catchment scale study was the fifth most frequently found TP out of ten TPs which were detected in Irish groundwaters. Eight detections of T2P were in breach of the EU DWS(i). Petty *et al.* (2003) state that in field studies triclopyr dissipated from water with a half life range of 0.5 to 7.5 days while T2P was more persistent with a half-life range of 4.2 to 10 days. The same review (Petty *et al.*, 2003) shows that triclopyr and T2P have little affinity for sediments except those with high organic matter contents. This poor affinity for sediment will warrant triclopyr and its TP T2P a concern for leachability which has been confirmed with their presence in groundwater across Ireland.

7.6.2 Discussion of temporal variations in pesticide occurrence

The temporal occurrence of pesticides in groundwater did not always coincide with effective or total rainfall at a site nor did pesticide occurrence coincide with groundwater

level response to effective rainfall or a springs discharge in response to rainfall. At the two sites with only springs used as MPs (KWDg and KWDa). **Figure 7.13** and **Figure 7.14** show that detections occurred not only when discharge responds to rainfall but also during the summer when the dilution factor was not so dominant. In a study by Nasrabadie *et al.* (2011) water samples taken from a surface water stream during high flow periods in December and low flow periods in May found pesticide detections during both seasons with detections during low flow periods in May a result of less river water dilution because of lower precipitation rates. However, during a higher resolution monitoring period at KWDa in May 2012 (see section 7.4.2), the concentration of mecoprop(s) peaked during the highest amount of total rainfall during the event (**Figure 7.16**) indicating that some compounds will get flushed through the system assisted by effective rainfall.

The combined effect of pesticide application and lack of effective rainfall to dilute pesticides preceding detection at FvPDa (**Figure 7.19**) (see section 7.4.5) may have contributed to elevated pesticide detections in July 2011 at piezometers 1b and 5b. Piezometers 1b and 5b are located in higher permeability gravelly clay lenses and are also the MPs with the highest percentage frequency of occurrence at FvPDa (**Figure 7.10**).

At the two sites with Rkd aquifer types (KWDa and I/KWDa) both sites have recession periods during the summer months (**Figure 5.13** and **Figure 5.14**, respectively) where discharge or groundwater level does not respond to rainfall however, pesticides were still detected in groundwater.

The Lower BH at FmWDa₁ in comparison to the other two BHs at FmWDa₁ had a uniform spread of detections in the shallow and interface piezometers which may infer that discharge processes may be diluting pesticides in shallow and interface depths in near stream areas. Hancock *et al.* (2008) observed in the U.S.A. that parent a.i. and TPs present in the stream water may be transported downward through the streambed into the unsaturated zone beneath or adjacent to the stream through bank filtration mechanisms during high stream flow events (**Figure 7.12** and **Table 7.3**).

In the artesian BH and piezometer 2b at FvPDa in **Figure 7.9** these two MPs had some of the lowest percentage frequency of detection than the other MPs across the site. The hydrology of FvPDa (see section 5.6.5) indicates that in these two MPs mild artesian conditions may indicate the recharging of water from south west of the ZOC at Boley Hill (**Figure 5.28**). The dominant land use in this upland area is devoted to woodland, scrub and arable land. Pesticide applications would be negligible to woodland and scrub but the

arable land would receive pesticide applications. However, the distance recharging water from Boley Hill and the environs to travel to the MPs at FvPDa can be assumed to be a long time considering the low permeability material recharging water would have to travel through. **Figure 5.28** shows the estimated ZOC for FvPDa. No residence times or tracer studies were carried out at FvPDa. This increased time in the ground at FvPDa will allow the pesticides to degrade more than in a system such as KWDg and KWDa where effective rainfall causes a faster response in discharge and groundwater levels, flushing pesticides into groundwater. The thick, low permeability deposits at FvPDa combined with upwelling water from the Rf aquifer beneath in the artesian BH and piezometer 2b are protecting the aquifer beneath while the gravel lenses act as reservoirs and pathways for pesticides. The high incidence of pesticides across the other MPs at FvPDa (**Figure 7.10**), notably 1b and 5b which intersect the gravelly deposits (**Appendix 5**), has allowed for the recharging water from above ground at the fields where MPs are located to leach to these gravel lenses and carry with it, pesticides.

7.6.3 Discussion of the relationship between pesticide occurrence and site characteristics

Site characteristics were found to have significant effects on groundwater pesticide occurrence (**Table 7.6**). Groundwater vulnerability was a physical characteristic associated with pesticide occurrence for the three categories (B)-(D). Odds ratio interpretation of this physical characteristic reveals that extreme vulnerability areas are 1.2 times more likely to be associated with total pesticides and parent a.i. occurrence in groundwater than a high vulnerability area. No other significant comparisons can be made between other groundwater vulnerability categories such as low or moderate from exploratory analysis of this dataset. The Irish approach to determining groundwater vulnerability to anthropogenic activities has been detailed in section 2.1.5. The approach delivered by the DELG/EPA/GSI (1999) refers to a range of potential contaminants from nitrate and phosphorus to pesticides. This approach has been successfully applied to a pesticide catchment scale dataset to reveal that extreme and high vulnerability areas are more at risk to total pesticide and parent a.i. pesticide compounds. Moe (2008) found through a modelling study in Ireland that the GSI (2009) national map of groundwater vulnerability was able to identify exposed (X), extreme (E), and high (H) vulnerability areas where pesticide occurrence in groundwater was more likely (see section 2.1.4). **Table**

2.3 lists the features these locations possess. The majority of sites used in this catchment scale study had extreme or high groundwater vulnerabilities, only the following MPs had moderate or low vulnerability: artesian BH (low), 2b, and 9b at FvPDa (both moderate). Future monitoring studies wishing to verify the accuracy of the groundwater vulnerability assessment in identifying areas more prone to pesticide occurrence should include equal proportions of the four possible vulnerability categories currently in use in Ireland. Also a further limitation of this result was that the site KWDg was classified as extreme, yet this site actually had the fewest pesticide occurrences (**Table 7.11**). This grassland site may not have a great enough source of pesticides applied to warrant their inclusion as groundwater more prone to pesticide contamination.

Subsoil permeability was another physical characteristic associated with all three categories (B)-(D) and their occurrence in groundwater (**Table 7.6**). Subsoil permeability is a characteristic used to help identify groundwater vulnerability (**Table 2.3**) thus both should have similar outcomes. This catchment scale study found that high permeability subsoils were 1.2 times more likely to have an association of total pesticides compared to a low permeability subsoil. An example of a high permeability subsoil is a sand/gravel e.g. I/KWDa and a low permeability would be a clayey subsoil e.g. FvPDa (DELG/EPA/GSI, 1999). Although statistical analysis indicates that a low permeability subsoil would have fewer detections, it does not imply that no detections would occur as at FvPDa, with a clayey subsoil, pesticide detections were high (**Appendix 15; Table 7.10**). Caution should be exercised when assessing an area's vulnerability to groundwater contamination from pesticides using physical characteristics as sites are complex in their ability to transport pesticides to groundwater and the FvPDa site has been identified as a reservoir of pesticides and TPs where their longevity in the environment is unknown.

Subsoil type was another physical characteristic associated with total pesticide and parent a.i. occurrence in groundwater. Odds ratio interpretation states that both total pesticides and parent a.i. are more likely to be in association with bedrock at or near the surface than till derived from lower Palaeozoic sandstones and shales. This is an expected outcome since the shallower the depth of material a pesticide has to travel through, the more easily a pesticide can be transported to groundwater. Odds ratio interpretation of subsoil type also states that a pesticide detection in groundwater is more associated in areas with subsoil as gravels derived from limestones than if the subsoil was Irish sea till derived from limestones. This statistical outcome highlights that pesticide occurrence in groundwater

with gravelly subsoils is more common than in Irish sea till. This statistical outcome mirrors findings of the sites which are more likely to have a pesticide detection (**Table 7.8, 7.9, and 7.11**) with I/KWDa having slightly more pesticides detected in groundwater than FvPDa, including TPs (**Table 7.10**). Irish sea till has a much lower porosity and is more water logged (**Figure 5.9**) compared to gravels derived from limestone. The ability of water to travel through both materials will be different with transit times potentially slower in Irish sea till subsoils compared to gravels. The sites with these subsoils were I/KWDa with gravels derived from limestones and FvPDa with Irish sea till derived from limestones (see section 4.5.3 and 4.5.5, respectively). At the interface piezometer, MP2 at I/KWDa, which targets the gravel aquifer 7.5-10.5 m b.g.l., 91% of samples collected at this site throughout monthly monitoring had a pesticide detection. This was the highest percentage of samples with detection at any of the six MPs at I/KWDa.

Aquifer type was a characteristic with an association of pesticides in groundwater (total pesticides and parent a.i.) (**Table 7.6**). From odds ratio interpretation, regionally productive aquifers (Rg, Rkd, and Rf) were more associated with pesticide occurrence in groundwater than locally productive aquifer types (Ll). This result was also found during analysis of the national-scale monitoring dataset in Chapter 3. Section 3.4.3 discusses the relationship between aquifer type and pesticide occurrence.

The significant effect of soil type on pesticide occurrence (categories (B)-(D)) in groundwater has been observed previously in the literature (Holman *et al.*, 2004; Andrade *et al.*, 2009). From **Table 7.6** soil association, soil texture, and soil drainage class were the physical characteristics related to soil which were associated with pesticide occurrence in groundwater for parent a.i., TPs, and total pesticides. Soil texture and soil drainage class indicate the particle size and capacity of soil based on its porosity to accommodate draining water. More porous soils with a higher drainage capacity were expected to allow pesticides to leach more easily to groundwater. Odds ratio interpretation of these two physical characteristics revealed the opposite expectation with clay loams more likely to be associated with pesticide occurrence in groundwater than sandy loams, and deep poorly drained mineral soils more likely to be in association with pesticide occurrence in groundwater compared to a shallow well drained mineral soil. The likelihood is small at 1.2 times more associated for each characteristic (see section 7.5.3.1). The results relate to numerous pesticide detections in the shallow piezometers at the FvPDa site. Although these shallow piezometers are not deep groundwater which is potable, they represent a

reservoir of pesticides which may be capable of contaminating surrounding areas especially surface water if upwelling artesian conditions prevent downward transport. These physical characteristics can be used in the future to gain further insight into the soils which could be more associated with pesticide occurrence in groundwater. These characteristics were only for seven sites which renders the results as exploratory and indicate areas which require further investigation.

Statistical analysis on the effect of MP type on pesticide occurrence at the catchment scale revealed that all three categories were (B), (C), and (D) were associated with the type of MP sampled (**Table 7.6**). Odds ratio interpretation found that parent a.i. were more associated in a drain than a spring or stream. TPs were more associated in a BH than a stream and a drain than a spring. Statistical analysis was unable to determine if a spring was more associated with pesticide detections than a BH which was the outcome from the national scale dataset (see section 3.4.3 and **Figure 3.6**). This may be because only five springs were used as MPs during this catchment scale study and the pesticide loading to each was variable because of land use differences and due to the low resolution sampling carried out at springs.

Land use has an affect on pesticide occurrence in groundwater since the only grassland site used for catchment scale monitoring, KWDg, had the fewest detections compared to the other six sites. All the other arable land use sites had detections of pesticides in their groundwater. These arable fields receive annual applications of pesticides which will “top-up” pesticide concentrations already in the system and contribute to their occurrence in groundwater.

Land use in neighbouring areas also affected the occurrence of pesticides as seen at I/KWDa. The parent a.i.s detected at I/KWDa had detections of compounds which were not recorded as being applied in the Sawmills Field (records where the MPs were located). This outcome indicates that the ZOC influencing the hydrology of the deep piezometers (which target the Rkd aquifer), have a ZOC much greater than the field scale as indicated in **Figure 5.24**. The compounds detected thus have the capacity to remain in the environment for longer than their half-lives would state. The compounds detected which were not recorded as being applied to the Sawmills Field were MCPA, triclopyr, 2,4-D, fluroxypyr, TBA, and bromoxynil.

Table 7.11 Pesticide frequency of occurrence, absolute numbers greater than the analytical detection limit (LOD), absolute numbers greater than the European Union Drinking Water Standard for individual pesticides EU DWS(i), and the total number of samples processed at each site.

Total number of groundwater samples processed for site	Number of samples with at least one detection $\geq$ DWS	Number of samples with at least one detection $<$ DWS and $>$ LOD	% frequency of samples $\geq$ DWS (%)		% frequency of samples $<$ DWS (%)		Total detections in samples collected at the site (%)
I/KWDa	28	63	21	47.4			68.4
FvPDa	58	52	33.9	30.4			64.3
FmWDa ₂	22	63	14.6	41.7			56.3
FmWDa ₁	25	63	15.1	37.9			53
FvWDa	12	39	12.1	39.4			51.5
KWDa	4	11	9.7	26.8			36.6
KWDg	1	6	4.3	26.1			30.4

7.7 Chapter 7 conclusions

This study is the first to be carried out on several phenoxyacid herbicide parent a.i. and some of their associated T.Ps in groundwater and has revealed that more TPs are present in Irish groundwaters than parent a.i.s; this finding is of concern since TPs are not routinely monitored for and their toxicity and persistence is relatively unknown for the majority of the TPs detected here. The TPs of concern are PAC, DBA, 4C2MP because of their widespread occurrence in groundwater, and the presence of T2P which was identified by Kashanian *et al.* (2012) as a DNA groove binding molecule. The site which had the highest percentage frequency of occurrence for TPs in groundwater was I/KWDa which is a site dominated by sand and gravel deposits above a karstified diffuse aquifer. The percentage frequency of occurrence was also high at FvPDa, a site dominated by anaerobic conditions. TP presence was high at both I/KWDa and FvPDa which had both aerobic and anaerobic conditions. Statistically, ORP was found to be associated with total pesticide occurrence with a decrease in ORP causing an increase in total pesticides. Statistically, TPs were negatively associated with turbidity which indirectly may indicate that TP will not leach through colloidal transport. These compounds are derived from highly water soluble phenoxyacid herbicides which would have limited capacity for colloidal transport due to their low affinity for colloidal matter.

Pesticide occurrence does not coincide with the onset of rainfall as detections occurred during both summer recession periods and during high precipitation events. However, the combined effect of rainfall following application can lead to more frequent pesticide occurrences. Although, the dilution factor during rainfall events may warrant non-detections as analytical LODs were not low enough.

CHAPTER 8

OVERALL DISCUSSION AND CONCLUSIONS

8.1 Main findings

During this study, the occurrence of pesticides in groundwater was investigated at seven sites across Ireland under pressure from diffuse agricultural sources. This was achieved by selecting sites across Ireland representative of varying hydrogeology with agricultural pressures. A groundwater monitoring network was established to reflect pathways where pesticides may be transported to groundwater.

This study developed two new quantitative methods: one to quantify for organochlorine herbicides (McManus *et al.*, 2013) and the other for phenoxyacid herbicides (under internal review). Catchment scale results were used to determine the frequency of occurrence of 61 compounds (parent a.i. (a.i.) and transformation products (TPs)), and to investigate temporal and spatial variation within each site. Statistical relationships between pesticide data and both site physical characteristics and other water quality variables such as nitrate and pH were also investigated. A national scale dataset from the EPA on groundwater pesticide occurrence was summarised and pesticide occurrence was related to several physical characteristics of a monitoring points (MPs) zone of contribution (ZOC). National scale groundwater pesticide occurrence data and higher resolution temporal catchment scale data was compared to assess pesticide occurrence and the physical characteristics associated with this pesticide occurrence in groundwater.

In Chapter 1, section 1.2, the aims and objectives of this doctoral thesis are stated, and below the main findings from this study are outlined and then discussed further in section 8.2:

Compounds detected

- The TPs, 4-chloro-2-methylphenol (4C2MP), phenoxyacetic acid (PAC), and dichlorobenzoic acid (DBA) were found frequently in groundwater during catchment scale monitoring and frequently exceeded the European Union drinking water standard (EU DWS(i)) for individual pesticides. However, little information exists in the

literature about the toxicity or persistence of these compounds except for Zertal *et al.* (2001; 2005) who states 4C2MP is more toxic than MCPA from which it is derived. The other frequently detected TPs may be harmless or harmful in the environment.

- The sources of the two most commonly detected TPs, DBA and PAC in groundwater are unknown, they may be natural, TPs of PPP, or from another contaminant. More information is available on DBA; Fava *et al.* (2005) and Hotlze *et al.* (2008) have stated that DBA is a degradation product of dichlobenil and BAM. Even less is known about PAC in the environment, although it is suggested that PAC is a TP of 2,4-D or MCPA as it forms part of their chemical structure (Onneby *et al.*, 2010).
- Mecoprop(s), 2,4-D, and MCPA were the most frequently detected a.i.s from the catchment scale monitoring programme and although they exceeded the EU DWS(i) more in comparison to other a.i.s such as bromoxynil, they did not exceed the EU DWS(i) as often as the TPs. MCPA and mecoprop were commonly detected in groundwater during both the national scale study and the catchment scale study.
- Detections from the catchment scale study breached the EU DWS(i) in 18% of samples and during the national scale study only 3% of samples breached the EU DWS(i) (**Table 8.1**).
- National scale monitoring by the EPA (Chapter 3) revealed that mecoprop and MCPA were the two most frequently detected compounds out of the 13 compounds analysed for. None of the compounds analysed on a national scale level were TPs. These two a.i.s were also the most frequently detected parent a.i. at the catchment scale.

Physical characteristics and pesticide occurrence

- At the national scale several site physical characteristics within the ZOC were associated with pesticide occurrence in groundwaters. These were regionally important aquifers as categorised by the DELG/EPA/GSI (1999), aquifers with a karstic flow regime, Quaternary deposits (subsoils) of an alkaline nature which overly karst aquifer types, and lastly springs used as monitoring points.
- In addition, at the catchment scale groundwater pesticide occurrence was significantly associated with the following physical characteristics; sample type, sample depth, soil association, soil texture, soil drainage class, subsoil type, subsoil thickness, subsoil permeability, aquifer type, and groundwater vulnerability.

- At the catchment scale groundwater pesticide occurrence was mainly associated with soil factors. The association with groundwater vulnerability suggests an integrated effect of soil, subsoil, and aquifer characteristics. This is also supported by the relationship between pesticide occurrence and aquifer characteristics at the national scale.
- In the catchment scale study, sites more likely to have total pesticide detections in groundwater were I/KWDa and FvPDa which is supported through percentage frequency of occurrence information in section 7.2 and **Table 7.10** and **7.11**.
- Artesian conditions present at FvPDa are a result of the confining layer of Irish sea till which ‘protects’ the groundwater in the flowing artesian well which had low detections compared to the other MPs targeting shallow groundwater. Pesticides were observed in 35% of samples (**Figure 7.10**) taken from the flowing artesian MP, highlighting the potential for lateral pesticide transport from the aquifer recharge area in comparison to the higher detections found in the shallow piezometers (c.60 – 91%).
- At the two sites with MPs located within 2 m of a stream (FmWDa site 1 and 2), these Lower BHs were under the influence of near-stream discharge processes. This discharge may prevent pesticides leaching to deeper groundwater which may cause less of a risk to deeper potable groundwater but more of a risk to surface water and receptors downstream.
- Evidence of groundwater pesticide transport from adjoining fields was observed. Some pesticide compounds were observed in the groundwater when there was no evidence that they were applied to the site within the last six years. This indicates not just vertical leaching but also horizontal transport across field boundaries. For example at the I/KWDa site, application records for the Sawmills Field since 2003 showed no application of MCPA, triclopyr, 2,4-D, fluroxypyr, TBA, and bromoxynil even though they were detected in groundwater between 2010-2012. The presence of the Rkd aquifer with a large zone of contribution (ZOC) means there is potential for pesticide transport to groundwater through lateral groundwater movement, if these compounds are applied off-site and then conveyed with groundwater flow to a MP located downgradient.
- There was no clear temporal pattern of groundwater pesticide occurrence observed in the catchment scale study. Pesticide detections were observed to be related to rainfall

events and non-rainfall periods. Detections also occurred in the summer months when groundwater levels were lower and there was less dilution. However, pesticides in groundwater were observed to coincide with pesticide application before effective rainfall in some sites: FmWDa₁ (fractured-metasediments well-drained arable site 1) and FvPDa.

Chemical characteristics and pesticide occurrence

- The catchment scale study revealed that groundwater pesticide occurrence was also correlated with physico-chemical characteristics. Calcium (Ca), manganese (Mn), sodium (Na), magnesium (Mg), and total nitrogen (TN) were positively associated with pesticide occurrence in groundwater. pH, oxidation-reduction potential (ORP), and turbidity were negatively associated with pesticide occurrence in groundwater.
- TPs were associated with a decreasing turbidity in groundwater whereas parent a.i. and total pesticides did not show either a positive or negative association with turbidity (**Table 7.7**). This indicates that the TPs quantified during this study may be more mobile and less influenced by colloidal transport since turbidity can indicate the potential for colloidal material (Goppert and Goldscheider, 2007).
- TPs were commonly detected at FvPDa, which may be because of (1) longer residence times in lower permeability subsoil materials and less movement resulting in longer pesticide persistence which in turn increases time for pesticide degradation. In addition, anaerobic conditions in these materials may force microbes to use pesticides as electron donors resulting in the formation of TPs (Larsen and Aamand, 2001; Holtze *et al.*, 2007). At I/KWDa TPs were also commonly detected, especially in MP2 shallow. This MP is above a discontinuous clay lens at the site. The confining layers at I/KWDa and FvPDa are characteristics with more TPs. This may be because degradation processes in these areas and the microbial population already in existence to degrade a.i. and TPs are established. Janniche *et al.* (2012) state that degradation is more common in already polluted aquifers than pristine aquifers. The confining layers at these two sites may be hot spots of microbial activity capable of degrading parent a.i. to TPs.

8.2 Discussion

Before this catchment scale monitoring study no one project had undertaken quantifying these pesticide compounds in groundwater in a range of scenarios which were compared in terms of their physical characteristics either in Ireland or internationally. The role of physical site properties had been stated in the literature as affecting pesticide leaching to groundwater (Burkart *et al.*, 2001; Worrall *et al.*, 2002; Lindsey *et al.*, 2006) and this study attempts to explore the physical characteristics which may be more associated with pesticide occurrence in groundwater. Through determining as many pesticide compounds and their derivatives in groundwater as possible, the quality of groundwater can be more comprehensively assessed and managed in the future.

8.2.1 Comparison between national scale and catchment scale monitoring

The physical characteristics associated with pesticide occurrence in groundwater were determined using an existing national scale dataset from the EPA and using catchment scale data. The physical characteristics associated with pesticide occurrence were tested at both scales using similar statistical techniques (logistic regression). Comparing the physical characteristics from both studies which were significantly associated with pesticide occurrence in groundwater, the same four characteristics were also associated with pesticide occurrence in groundwater at the catchment scale as they are at the national scale (**Table 8.2**). However, the national scale study did not show an association between pesticide occurrence and soil association, groundwater vulnerability, or subsoil permeability. The differences in resolution may be causing this difference, since during catchment scale monitoring, an average of 35 MPs were sampled throughout the 23 months of this project, while 158 MPs were sampled during the national scale study. Although there were more MPs to sample, the temporal sampling resolution was lower in comparison to the catchment scale study. The national scale study was good for spatial coverage, while the catchment scale had better temporal variability because of more sampling occasions. Results from both studies would have been more comparable if the same compounds had been quantified. An attempt at this comparison has been made in **Table 8.1** by only showing percentage frequency of occurrence for the same compounds quantified in both studies. These were: MCPA, mecoprop, lindane, 2,4-D, and bentazone. More frequent groundwater sampling in tillage areas at the catchment scale highlighted

that detections of pesticides in groundwater are more widespread than was revealed by national scale monitoring. At the national scale, non-detections were 73% compared to 41% at the catchment scale. Thus there were more detections found using higher temporal resolution catchment scale monitoring.

During the national scale study abstraction wells were sampled as opposed to monitoring wells in the catchment scale study. Abstraction wells are high yielding public supply boreholes pumped more often than monitoring wells during the catchment scale study. Monitoring wells were only pumped once a month using low-flow purging. This difference may account for the differences in detection in **Table 8.1** between the two studies. There may be potential in public supply wells for increased pesticide dilution. Jørgensen and Stockmarr (2009) found groundwater quality assessed from abstraction wells to be better than groundwater quality from monitoring wells because screens are longer in abstraction wells and they tap major aquifers. At national scale there were no pesticide detections greater than or equal to the EU DWS(t) of 0.5 µg/L, whereas 8% of samples from the catchment scale breached the EU DWS(t).

Table 8.1 Differences in sample detection frequency between national- and catchment-scale monitoring. LOD = limit of detection.

Concentration category	National scale	Catchment scale
Number of samples analysed for pesticides	845	835*
Detections $\geq$ EU DWS(t)	0%	8%
Detections $\geq$ EU DWS(i)	3%	18%
Detections $<$ EU DWS(i) and $>$ LOD	24%	41%
Non-detections	73%	41%

*maximum number of samples for any one compound.

EU DWS(t) = 0.5 µg/L

EU DWS(i) = 0.1 µg/L

Table 8.2 Comparison of statistically significant physical characteristics at the catchment- and national-scale.

National scale	Catchment scale
<i>Monitoring point type</i>	<i>Monitoring point type</i>
<i>Aquifer type</i>	<i>Aquifer type</i>
<i>Subsoil type</i>	<i>Subsoil type</i>
<i>Soil drainage class</i>	<i>Soil drainage class</i>
	Soil association
	Sample depth [†]
	Groundwater vulnerability
	Subsoil thickness [†]
	Subsoil permeability
	Soil texture [†]

[†] These physical characteristics were not available to test for the national scale study (Chapter 3).

8.2.2 Discussion of overall study findings

As stated in Chapter 1, one of the aims of this study was to investigate parent a.i. which are actively used within the EU and their groundwater occurrence, yet their environmental lifetime is unknown. Using new analytical methods developed by this project (McManus *et al.*, 2013) MCPA and mecoprop(s) were commonly observed in groundwater within tillage dominated catchments. MCPA and mecoprop were also found to be common pesticides in groundwater during the national scale monitoring study. Thus the high incidence of these two compounds in groundwater warrants the EU to re-address their current registration status.

Newly investigated TPs DBA, PAC, and 4C2MP were also found in groundwater which were widespread at the catchment scale. Neither these nor any other TPs were analysed during national monitoring. The occurrence of these compounds in groundwater has not previously been reported, therefore the study has contributed to science and also highlighted other areas in need of research: the persistence and toxicity of these compounds, especially if the herbicide degradates (TPs) can retain the herbicidal activity of their parent a.i., exhibit toxicity, and express chronic adverse effects (Kolpin *et al.*, 1998b). DBA is not a pesticide compound applied in Ireland (Moody *Pers. Comm.* 2010) and up until findings of this study it was unheard of in Irish groundwaters. DBA is a TP of BAM (Fava *et al.*, 2005; Jensen *et al.*, 2009). DBA can form through hydrolysis of the

nitrile group of the parent a.i. dichlobenil and the subsequent hydroxylation of the three-position of the phenyl ring (Roberts, 1999). It is also possible that DBA in groundwater may arise from microbial activity. Wright *et al.* (2005) states that DBA may form following the breakdown of the algae causing cyanobacterium *Fischerella ambigua*, although the concentrations that would normally be found in groundwater are unknown. Thus more research on the toxicity, persistence, and source of DBA in groundwater is required. The high concentrations of DBA detected in Irish groundwater along with its high frequency of detection mean it can not be ignored or assumed harmless in the environment.

2,4-dichlorophenol (DCP) was detected in 14.15% of all samples collected during the catchment scale study (**Appendix 14**). DCP can also be a TP of chlorfenvinphos. The insecticide chlorfenvinphos is not currently approved for use in Ireland. It was removed in 2003 except for use on carrots, parsnips, cabbages, and swedes, but this use then ceased in 2007 (Conroy *Pers. Comm.* 2012). The exact source of DCP is the environment needs to be addressed. If DCP is a TP of chlorfenvinphos, then the persistence of DCP is very high and the a.i. chlorfenvinphos should not be allowed to re-activate its registration status in the EU.

Considerably less information is available on the TPs PAC and 4C2MP although Craig and Daly (2010) and Zertal *et al.* (2001; 2005) highlighted that 4C2MP is hazardous in the environment based on bioaccumulation, aqueous toxicity, and persistence in the environment. Chiron *et al.* (2009) states that 4C2MP may possess genotoxicological properties. The exact source of 4C2MP and PAC needs to be found as they may be toxic. If they occur from the parent a.i. MCPA, 2,4-D, or mecoprop(s), the current active status of these a.i. in plant protection products needs to be addressed.

Spliid and Køppen (1998) in a Danish study found that phenoxyacid herbicides such as bentazone and MCPA occurred more frequently in shallow groundwater between 1.5 – 5 m b.g.l. in areas dominated by clay with cracks and macropores where movement to anaerobic zones is fast and degradation is minimal. In this Irish study one site (FvPDa) had clayey characteristics and shallow groundwater (excluding the artesian BH). Out of the seven sites monitored, FvPDa had the second highest percentage of pesticide occurrence in samples following I/KWDa (**Table 7.11**). FvPDa had the second highest occurrence of TPs across all the sites, with TPs detected in 30% of samples (**Table 7.10**). Spliid and Køppen (1998) suggested that degradation would be minimal in these clayey

areas. From the current catchment scale study it would appear that parent a.i. degradation does occur at this anaerobic site (**Table 5.12**). If Spliid and Køppen (1998) had included the same TPs, then knowledge of the longevity of TPs in anaerobic environments could be better understood. Tuxen *et al.* (2002) stated that knowledge of phenoxyacid degradation in aquifers is poor. This study improves the understanding of the occurrence of TPs in groundwater through highlighting areas with physical characteristics like FvPDa as potential ‘hot-spots’ of TP occurrence. These areas should not be assumed as less of a risk to groundwater. They may actually pose more of a risk to surface water.

The I/KWDa site had the most detections of pesticides in groundwater (**Table 7.11**) among the seven sites and had the highest occurrence of TPs in groundwater (**Table 7.10**). Spliid and Køppen (1998) state that sandy locations which are aerobic would cause degradation of phenoxyacid herbicides before they could reach groundwater. However, the aerobic sand and gravel aquifer at the I/KWDa site also had high occurrence of the parent a.i. phenoxyacid herbicide (**Appendix 15**). The higher occurrence of pesticides in sand and gravel groundwater may be attributed to the higher effective porosity in these porous systems which will have a slower flow velocity than a fractured rock (Alley *et al.*, 2002). As Burkart and Kolpin (1993) indicated, slow infiltration rates through soil resulted in a higher proportion of atrazine TPs in groundwater. Lapworth *et al.* (2006) found that pesticides in groundwater were more common at sites with sand and gravel deposits, with high transmissivities rendering the aquifer vulnerable.

Malaguerra *et al.* (2012) found that most wells with detections of phenoxyacid herbicides had slightly reduced water and that phenoxyacid herbicides were largely absent in oxic water, potentially because these compounds are more biodegradable under aerobic conditions or because their mobility has caused them to be flushed from groundwater. However, during this catchment study the most aerobic site (I/KWDa) (**Table 5.12**) had the most pesticide detections in groundwater. Several studies have found that mecoprop degradation is higher under aerobic conditions (Johnson *et al.*, 2003; Buss *et al.*, 2006). At I/KWDa the aerobic sand and gravel aquifer, coupled with a legacy of intensive pesticide application has caused the high incidence of parent a.i.s and TPs in groundwater here. It should not be assumed that because an aquifer is aerobic it will not have pesticide detections. In fact, the aerobic nature of the material may aid the production of TPs.

Total pesticides and parent a.i. were significantly negatively associated with ORP (**Table 7.7**). A decrease in ORP (more reducing conditions) would result in a higher association

with total pesticides and parent a.i. in water using occurrence data across all seven sites including the frequent occurrence of pesticides at the anaerobic site FvPDa. This is the opposite for nitrate in groundwater where anaerobic conditions induce denitrification lowering nitrate levels (Chapelle *et al.*, 1995). Therefore where groundwater is not at risk from nitrate pollution, the groundwater may be at risk to pesticide pollution. In the UK Worrall and Besien (2005) did not find any significant relationship between nitrate and pesticides. Locations deemed not to be a risk due to low groundwater nitrate occurrence, may present a potential problem due to pesticide occurrence. Several studies have also indicated that pesticide application can change the microbial balance in soil which can then inhibit the denitrification of nitrate and in certain scenarios increase nitrous oxide production which would adversely affect climate change (Pell *et al.*, 1998). Thus the incidence of one pollutant, for example nitrate, should not be used as a proxy for the occurrence of another pollutant for example MCPA.

Many studies state that physical characteristics play a role in affecting pesticide leaching to groundwater (Kolpin *et al.*, 1998a; Fisher and Healy, 2008; Steele *et al.*, 2008) but rarely do studies actually indicate the characteristics. Through exploring the physical characteristics more associated with pesticide occurrence in groundwater, areas in the future can be highlighted as potentially more likely to allow pesticides to leach to groundwater, thus enabling the development and spatial targeting of mitigation strategies to control pesticide loss to groundwater and intensive agricultural catchments. This study has highlighted that pesticides are present in many areas, all with various characteristics. Managers in the future wanting to protect groundwater should carefully consider the MP type being sampled, the aquifer type, subsoil type, and the soil drainage class.

8.3 Recommendations for future research

Since this is the first analysis of several compounds (e.g. PAC and DBA) in groundwater additional research should be carried out to determine the source of these compounds, their toxicity, and their persistence in the environment. The monitoring of surface water for pesticides would benefit from event based sampling supplemented with passive sampling since the typically poor sampling frequency of grab sampling can miss spikes in the stream. This type of monitoring could also be carried out for springs, ditches, and drains to identify transport pathways of these compounds from diffuse agricultural sources. A

weakness of this study was the inability to collect event based samples from KWDa or KWDg constantly, especially as analysis of national scale data inferred that springs as MPs were more associated with pesticide detections. Undertaking research on the highly soluble phenoxyacid herbicide compounds is important since they have the capacity to be transported from groundwater to other aquatic receptors such as rivers and groundwater dependent terrestrial ecosystems.

It is also worth noting that the findings on quality of water depend on the compounds tested for. Most monitoring programmes do not quantify TPs and, as has been proven in this study, these are the compounds detected most frequently in groundwater, the most frequently detected in concentrations exceeding the EU DWS(i), and also the least understood regarding their persistence and toxicity. They may be harmless or harmful but until research into them is conducted, their presence in the environment will remain an unquantifiable threat to biota. Comparisons can then be made fairly about the quality of EU groundwater. The EU Drinking Water Directive states that “Only those pesticides which are likely to be present in a given supply are required to be monitored”. This should be readdressed since usage does not always mean a compound will be present in groundwater (Kolpin et al., 2000). See section 7.6.3.

- The toxicity and persistence of PAC, 4C2MP, DBA, and DCP should be found.
- The source of TPs in groundwater should be found to verify if they are actually derived from a.i. in plant protection products (PPP). If the source is a PPP then the registration status of that compound should be addressed, especially if they TP is toxic and persistent.
- Monitoring programmes should all test for a core suite of a.i. across the EU to enable comparisons. Also the main TP of each PPP should be quantified.

The study has also developed, validated, and successfully used two analytical methods which could be used in the future to quantify 21 compounds in groundwater to provide an improved approach to examining groundwater quality in the future. The seven sites selected and used across Ireland are now fully instrumented and could be used in the future to gain further insight into groundwater contamination.

8.4 Conclusions

This study has contributed to science by highlighting the existence of newly detected compounds in the environment, identifying physical and physico-chemical characteristics of the zone of contribution (ZOC) that are statistically associated with pesticide occurrence in groundwater, and highlighted differences between catchment and national scale monitoring programmes.

Conclusions in relation to the hypotheses are stated below:

- The pesticide a.i.s MCPA and mecoprop(s) were frequently detected both at the national- and catchment- scales. However, the majority of detections were TPs, notably PAC, DBA, and 4C2MP. Therefore Hypothesis 1 is accepted.
- Although pesticides were found in the greatest quantities where permeable deposits existed (I/KWDa), pesticides were also detected in high quantities within lower permeability deposits (FvPDa). The occurrence of pesticides in groundwater was also associated with a number of other physical characteristics, details of which are set out below and elsewhere within the thesis. Therefore, Hypothesis 2 is accepted.

The study conclusions are summarised in the points below in relation to the objectives listed in Chapter 1.

1. The most frequently detected compounds in descending order of frequency of occurrence in Irish groundwater from catchment scale sites were: mecoprop(s), phenoxyacetic acid (PAC), 4-chloro-2-methylphenol (4C2MP), 2,6-dichlorobenzoic acid (DBA), MCPA, 2,4-dichlorophenol (DCP), triclopyr, and 3,5,6-trichloro-2-pyridinol.
2. Currently in Ireland mecoprop, 2,4-D, MCPA, and triclopyr are active ingredients (a.i.) permitted in plant protection products (PPP). Throughout the two year catchment scale monitoring campaign, the maximum observed concentrations of these four a.i.s were 1.46 µg/L, 0.24 µg/L, 1.05 µg/L, and 0.07 µg/L, respectively.
3. TPs were not only found to be present in detectable concentrations in groundwater, but at concentrations in breach of the EU Drinking Water Standard for individual compounds (EU DWS(i)). The most frequently detected TPs were PAC, 4C2MP, DBA, DCP, and T2P. DBA and PAC regularly exceeded the EU DWS(i). DBA had

never been monitored for in Irish groundwater, while monitoring data for PAC in groundwater has never been published internationally. The maximum observed concentration of DBA and PAC was 120 µg/L and 4.15 µg/L, respectively.

4. The physical characteristics of ZOCs most associated with pesticide occurrence in groundwater were the type of monitoring point (MP), the sample depth, the soil association and texture, the soil drainage class, the subsoil type, thickness and permeability, the aquifer type, and also the groundwater vulnerability index.
5. Comparing the only two available pesticide monitoring datasets on Irish groundwater for the physical characteristics most associated with pesticide occurrence revealed that MP type, aquifer type, and subsoil type were associated at both monitoring scales. National scale monitoring also detected MCPA and mecoprop as the most frequently observed compounds. However, national scale monitoring did not quantify for any TPs in groundwater or any other a.i.s which were frequently detected at the catchment scale (e.g. triclopyr and fluroxypyr). A comparison of the percentage frequency of pesticide detections between the national and catchment scale revealed more detections at the catchment scale (18% compared to 3% (Table 8.1)). In addition, 8% of samples in this study exceeded the EU DWS for total pesticides.
6. At the national scale land use did not show any association with pesticide occurrence in groundwater. At the catchment scale six of the seven sites had arable land use, making it difficult to assess land use as an individual contributing factor.
7. Two analytical methods were developed to quantify a.i.s and TPs in groundwater. The banned a.i.s lindane and heptachlor were determined by gas chromatography to detection limits of 0.015 µg/L. Liquid chromatography was used to quantify for ten compounds currently permitted as a.i. in PPP and eight TPs to detection limits of 0.008 µg/L.
8. Pesticide a.i.s and TPs did not show any temporal trends, but occurred throughout the two years of monitoring and were affected by dilution.

References

- Aeschbach-Hertig, W. and Solomon, D. K. (2012) Noble gas thermometry in groundwater hydrology. *The noble gases as geochemical tracers. Advances in Isotope Geochemistry*. P. Burnard. Springer Verlag.
- Agertved, J., Rügge, K. and Barker, J.F. (1992) Transformation of the Herbicides MCP and Atrazine under Natural Aquifer Conditions. *Ground Water* **30** (4): 500-506.
- Agresti, A. (2002) *Categorical Data Analysis 2nd Edition*. Hoboken, New Jersey, John Wiley and Sons, Inc.
- Ahmad, R. and Rahman, A. (2009) Sorption Characteristics of Atrazine and Imazethapyr in Soils of New Zealand: Importance of Independently Determined Sorption Data. *Journal of Agricultural and Food Chemistry* **57** 10866-10875.
- Aiken, G. R., and Cotsaris, E. (1995) The Influence of Soil Properties and Hydrology on the Nature of Organic Matter in Aquatic Systems and Drinking Water Supplies. *Journal of the American Water Works Association* **87** 36-45.
- Akhtar, M. S., Stüben, D., Norra, S. and Memon, M. (2011) Soil structure and flow rate-controlled molybdate, arsenate and chromium(III) transport through field columns. *Geoderma* **161** 126-137.
- Alavanja, M. C. R. (2009) Pesticide Use and Exposure Extensive Worldwide. *Reviews on Environmental Health* **24** (4): 303-309.
- Aldwell, C. R., Thorn, R. H. and Daly, D. (1988) *Point source pollution in karst areas in Ireland*. IAH 21st Congress, Guilin, China,
- Alister, C., Araya, M. and Kogan, M. (2011) Effects of physicochemical soil properties of five agricultural soils on herbicide adsorption and leaching. *Ciencia e investigación agraria* **38** (2): 243-251.
- Allen-King, R., McKay, L. D. and Trudell, M. R. (1997) Organic Carbon Trichloroethene Sorption in a Clay-Rich Glacial Deposit. *Ground Water* **35** (1): 124-130.
- Alley, W. M., Healy, R. W., LaBaugh, J. W. and Reilly, T. E. (2002) Flow and Storage in Groundwater Systems. *Science* **296** 1985-1990.
- Andrade, A. I. A. S. S. and Stigter, T. Y. (2009) Multi-method assessment of nitrate and pesticide contamination in shallow alluvial groundwater as a function of hydrogeological setting and land use. *Agricultural Water Management* **96** (12): 1751-1765.

- Appelo, C. A. J. and Postma, D. (2006) *Geochemistry, groundwater and pollution Second Edition*. Leiden, The Netherlands, A.A. Balkema Publishers.
- Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Sinal-Gándara, J., Mejuto, J-C. and García-Río, L. (2008) The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture Ecosystems and Environment* **123**: 247 – 260.
- Armbruster, D.A. and Pry, T. (2008) Limit of Blank, Limit of Detection and Limit of Quantification. *The Clinical Biochemist Reviews* **29** (Suppl 1): S49 – S52.
- Baran, N., Lepiller, M. and Mouvet, C. (2008) Agricultural diffuse pollution in a chalk aquifer (Trois Fontaines, France): Influence of pesticide properties and hydrodynamic constraints. *Journal of Hydrology* **358** 56-69.
- Barbash, J. E., Thelin, G. P., Kolpin, D. W. and Gilliom, R. J. (2001) Major herbicides in groundwater: results from the national water-quality assessment. *Journal Environmental Quality* **30** 841 - 845.
- Basheer, C., Lee, H. K. and Obbard, J. P. (2002) Determination of organochlorine pesticides in seawater using liquid-phase hollow fibre membrane microextraction and gas chromatography–mass spectrometry. *Journal of Chromatography. A* **968** (1-2): 191-199.
- Batista, S., Silva, E., Galhardo, S., Viana, P. and Cerejeira, M. J. (2002) Evaluation of Pesticide Contamination of Ground Water in Two Agricultural Areas of Portugal. *International Journal of Environmental Analytical Chemistry* **82** (8): 601 - 609.
- Bedoux, G., Roig, B., Thomas, O., Dupont, V. and Le Bot, B. (2012) Occurrence and toxicity of antimicrobial triclosan and by-products in the environment. *Environmental Science and Pollution Research* **19** 1044-1065.
- Belardi, R. P. and Pawliszyn, J. B. (1989) The application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. *Water Pollution Research Journal of Canada* **24** (1): 179-191.
- Belkhiri, L., Boudoukha, A., Mouni, L. and Baouz, T. (2010) Multivariate statistical characterization of groundwater quality in Ain Azel plain, Algeria. *African Journal of Environmental Science and Technology* **4** (8): 526-534.
- Bengraïne, K. and Marhaba, T. F. (2003) Using principal component analysis to monitor spatial and temporal changes in water quality. *Journal of Hazardous Materials* **100** (1-3): 179-195.

- Beyerle, U., Aeschbach-Hertig, W., Imboden, D. M., Baur, H., Graf, T. and Kipfer, R. (2000) A Mass Spectrometric System for the Analysis of Noble Gases and Tritium from Water Samples. *Environmental Science and Technology* **34** 2042-2050.
- Blanchoud, H., Farrugia, F. and Mouche, J. M. (2004) Pesticide Uses and Transfers in Urbanised Catchments. *Chemosphere* **55** 905-913.
- Böhlke, J.-K. (2002) Groundwater recharge and agricultural contamination. *Hydrogeology* **10** 153-179.
- Boivin, A., Cherrier, R., Perrin-Ganier, C. and Schiavon, M. (2004) Time effect on bentazone sorption and degradation in soil. *Pesticide Management Science* **60** (8): 809-814. .
- Bolker, B. M., Brooks, M. E., Clark, C. J., Geange, S. W., Poulsen, J. R., Stevens, M. H. H. and White, J.-S. S. (2009) Generalized linear mixed models: a practical guide for ecology and evolution. *Trends in Ecology and Evolution* **24** (3): 127-135.
- Bottcher, A. B., Monke, E. J. and Huggins, L. F. (1981) Nutrient and sediment loadings from a subsurface drainage system. *Transactions of the American Society of Agricultural Engineers* **24** 1221-1226.
- Bradman, A., Castorina, R., Boyd Barr, D., Chevrier, J., Harnly, M. E., Eisen, E. A., McKone, T. E., Harley, K., Holland, N. and Eskenazi, B. (2011) Determinants of organophosphorous Pesticide Urinary Metabolite Leves in Young Children Living in an Agricultural Community. *International Journal of Environmental Research and Public Health* **8** 1061-1083.
- British Standards Institution. (2003) Water quality - sampling - part 3: Guidance on the preservation and handling of water samples. Geneva, Switzerland, ISO.
- British Standards Institution. (2009). Guidance on sampling of groundwaters. Water Quality - sampling. Geneva, Switzerland, International Standards Organisation.
- British Standards Institution. (2009). Water quality - sampling part 11: Guidance on sampling of groundwaters. Geneva, Switzerland, ISO.
- Broers, H. P. and van der Grift, B. (2004) Regional monitoring of temporal changes in groundwater quality. *Journal of Hydrology* **296** (1-4): 192-220.
- Brown, C. D., Hodgkinson, R. A., Rose, D. A., Syers, J. K. and Wilcockson, S. J. (1995) Movement of pesticides to surface waters from a heavy clay soil. *Pesticide Science* **43** 131-140.
- Brown, C. D. and van Beinum, W. (2009) Pesticide transport via sub-surface drains in Europe. *Environmental Pollution* **157** (12): 3314-3324.
- Bucheli, T. D., Müller, S. R., Voegelin, A. and Schwarzenbach, R. P. (1998) Bituminous Roof Sealing Membranes as Major Sources of the Herbicide (R,S)-Mecoprop in Roof

- Runoff Waters: Potential Contamination of Groundwater and Surface Waters. *Environmental Science & Technology* **32** (22): 3465-3471.
- Bueno, M. J. M., Gomez, M. J., Herrera, S., Hernando, M. D., Agüera, A. and Fernández-Alba, A. R. (2012) Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: Two years pilot survey monitoring. *Environmental Pollution* **164** (0): 267-273.
- Bulfin, M., Farrelly, N., Fealy, R., Green, S., Loftus, M., Meehan, R. and Radford, T. (2002). The Irish Forest Soils Project (FIPS-IFS). Dublin, Ireland, Teagasc Research and Development Programme Portfolio.
- Burkart, M. and Kolpin, D. W. (1993) Hydrologic and Land-Use Factors Associated with Herbicides and Nitrate in Near-Surface Aquifers. *Journal of Environmental Quality* **22** 646-656.
- Burkart, M., Kolpin, D. W. and Cole, K. (2001) Soil characteristics and agrichemicals in groundwater of the Midwestern United States. *Water Science and Technology* **43** (5): 251-260.
- Buss, S. R., Thrasher, J., Morgan, P. and Smith, J. W. N. (2006) A review of mecoprop attenuation in the subsurface. *Quarterly Journal of Engineering Geology and Hydrogeology* **39** (3): 283-292.
- Buttler, T., Martinkovic, W. and Nesheim, O. N. (2003). Factors Influencing Pesticide Movement to Ground Water. Gainesville, University of Florida.
- Carson, R. (1962) *Silent Spring*. U.S.A., Houghton Mifflin.
- Castro, M. AND Goblet, P. (2005) Calculation of Ground Water Ages - A comparative Analysis. *Ground Water* **43** (3): 368-380.
- Cawley, A. (1990) *The Hydrogeological Analysis of a karst aquifer system*. M.Eng.Sci. University College Galway Galway.
- Celis, R., Real, M., Hermosín, M. C. and Cornejo, J. (2005) Sorption and leaching behaviour of polar aromatic acids in agricultural soils by batch and column leaching tests. *European Journal of Soil Science* **56** 287-297.
- Central Statistics Office. (2011) Area Yield and Production of Selected Crops. Retrieved 2nd July 2011, from <http://www.cso.ie/en/index.html>.
- Cerejeira, M. J., Vianna, P., Batista, S., Pereira, T., Silva, E., Valério, M. J., Silva, A., Ferrer, M. and Silva-Fernandes, A. M. (2003) Pesticides in Portuguese surface and ground waters. *Water Research* **37** 1055-1063.

- Chapelle, F. H., McMahon, P. B., Dubrovsky, N. M., Fujii, R. F., Oaksford, E. T. and Vroblevsky, D. A. (1995) Deducing the distribution of thermal electron-accepting processes in hydrologically diverse ground water systems. *Water Resource Research* **31** (2): 359-372.
- Chebotarev, I. I. (1955) Metamorphism of natural waters in the crust of weathering. *Geochimica et Cosmochimica Acta* **8** 22-28.
- Chilton, P. J., Lawrence, A. R. and Stuart, M. E. (1998) Pesticides in groundwater: some preliminary results from recent research in temperate and tropical environments *Groundwater Contaminants and their Migration*. J. Mather, Banks, D., Dumbleton, S & Fermor, M London, Geological Society Special Publication **128**:
- Chiron, S., Comoretto, L., Rinaldi, E., Maurino, V., Minero, C. and Vione, D. (2009) Pesticide by-products in the Rhône delta (Southern France). The case of 4-chloro-2-methylphenol and of its nitroderivative. *Chemosphere* **74** (4): 599-604.
- Clausen, L., and Fabricius, I. (2002) Atrazine, isoproturon, mecoprop, 2,4-D, and bentazone adsorption onto iron oxides. *Journal of Environmental Quality* **30** (3): 858-869.
- Clausen, L., Arildskov, N. P., Larsen, F., Aamand, J. and Albrechtsen, H.-J. (2007) Degradation of the herbicide dichlobenil and its metabolite BAM in soils and subsurface sediments. *Journal of Contaminant Hydrology* **89** (3-4): 157-173.
- Clausen, L., Larsen, F. and Albrechtsen, H.-J. (2004) Sorption of the Herbicide Dichlobenil and the metabolite 2,6-Dichlorobenzamide on Soils and Aquifer sediments. *Environmental Science and Technology* **38** 4510-4518.
- Conry, M. and Ryan, P. (1967). The Soils of County Carlow. National Soil Survey of Ireland. Dublin 4, An Foras Taluntais.
- Coppola, L., Pilar Castillo, M. D. and Vischetti, C. (2011) Degradation of isoproturon and bentazone in peat- and compost- based biomixtures. *Pest Management Science* **67** 107-133.
- Coxon, C. and Drew, D. (1986) Groundwater flow in the lowland limestone aquifer of easter Co. Galway and eastern Co. Mayo, western Ireland. *New Directions in Karst*. K. a. S. Paterson, M (Eds). Norwich, 259-280.
- Coxon, C. E. (1986) *A study of the hydrology and geomorphology of turloughs*. Ph.D. Trinity College Dublin.
- Coxon, C. E. (2011) Agriculture and karst. *Karst Management*. P. E. van Beyen. Dordrecht, Springer. 103-138.

- Council Directive. (1980) Council Directive of 15 July 1980 relating to the quality of water intended for human consumption (80/778/EEC). *Official Journal of the European Commission* **L778** 1-19.
- Council Directive. (1991) Council Directive of 15 July 1991 concerning the placing of plant protection products on the market (91/414/EEC). *Official Journal of the European Commission* **L414** 1-287.
- Council Directive. (1998) Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. *Official Journal of the European Commission* **L330** 32-54.
- Craig, M. (2010). Classification of hazardous and non-hazardous substances in groundwater. Ireland, Environmental Protection Agency Version 1.
- Craig, M. and Daly, D. (2010). Methodology for establishing groundwater threshold values and the assessment of chemical and quantitative status of groundwater, including an assessment of pollution trends and trend reversal. Wexford, Ireland., Environmental Protection Agency. .
- Craig, M., Hunter-Williams, N. and Moe, H. (2005) *Screening Methodology for the Water Framework Directive Groundwater Quality Monitoring Network*. Proceedings of the National Conference "It doesn't just go away, you know..." SUDS and Groundwater Monitoring, Tullamore, Ireland, International Association of Hydrogeologists (Irish Group).
- Croll, B. T. (1991) Pesticides in surface waters and groundwaters. *Water and Environment Journal* **5** 389-395.
- Cross, P. and Edwards-Jones, G. (2011) Variation in pesticide hazard from arable crop production in Great Britain from 1992 to 2008: An extended time-series analysis. *Crop Protection* **30** 1579-1585.
- Daly, D. (2009) Ground water—the 'hidden resource'. *Biology and Environment: Proceedings of the Royal Irish Academy B* **109B** 221 - 236
- Daly, D., Dassargues, A., Drew, D., Dunne, S., Goldscheider, N., Neale, S., Popescu, I. C. and Zwahlen, F. (2002) Main concepts of the "European Approach" to karst-groundwater-vulnerability assessment and mapping. *Hydrogeology* **10** 340-345.
- Daly, D. and Warren, W. P. (1994). Groundwater vulnerability guidelines and definitions. The GSI Groundwater Newsletter. D. Daly. Dublin 4, The Geological Survey of Ireland.
- Daly, D. and Warren, W. P. (1998) Mapping groundwater vulnerability: the Irish perspective. *Groundwater Pollution, aquifer recharge and vulnerability*. N. S. Robins. London, Geological Society Special Publications. **130**: 179-190.

- Daly, E. P. (1981). Nitrate levels in the aquifers of the Barrow River valley. Dublin, Ireland. , Geological Survey of Ireland.
- Daly, E. P. (1995) *The principal characteristics of the flow regime in Irish aquifers*. Proceedings of the 15th Annual Groundwater Seminar on The Role of Groundwater in Sustainable Development., Killeshin Hotel, Portlaoise., International Association of Hydrogeologists (Irish Group).
- Danzo, B. J. (1997) Environmental Xenobiotics May Disrupt Normal Endocrine Function by Interfering with the Binding of Physiological Ligands to Steroid Receptors and Binding Proteins. *Environmental Health Perspectives* **105** 294-301. .
- DELG/EPA/GSI. (1999) Groundwater Protection Schemes. Retrieved 01 June 2011, from <http://www.gsi.ie/Programmes/Groundwater/Projects/Protection+Schemes+Guidelines.htm#intro>.
- Department of Agriculture, Fisheries and Food. (2004). Pesticide Usage Survey Report no. 2 Arable Crops. Dublin 2.
- Dillon, T. (2010) *Quantifying Flow in the Nuenna Catchment*. MSc Trinity College, Dublin.
- Drever, J. I. (1997) *The geochemistry of natural waters: surface and groundwater environments 3rd Edition*. New Jersey, Prentice-Hall, Inc.
- Drew, D. and Daly, D. (1993). Groundwater and karstification in mid-Galway, South Mayo and North Clare. Joint Report by Department of Geography, TCD and Geological Survey of Ireland.: 86.
- Drew, D. P. (2008) Hydrogeology of lowland karst in Ireland. *Quarterly Journal of Engineering Geology and Hydrogeology* **41** 61-72.
- Eades, J. F. (1976) Organochlorine pesticide residues in the Irish environment. *Irish Journal of Agricultural Research* **15** (3): 341 - 348.
- Elliott, J. A., Cesna, A. J., Best, K. B., Nicholaichuk, W. and Tollefson, L. C. (2000) Leaching rates and preferential flow of selected herbicides through tilled and untilled soil. *Journal of Environmental Quality* **29** 1650-1656.
- European Commission. (2000) Directive 2000/60/EC Of The European Parliament And Of The Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Official Journal of the European Commission* **L327** 1-72.
- European Commission. (2002) Implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. *Official Journal of the European Commission* **L221** 8.

- European Communities. (1980) Council Directive 80/68/EEC of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances *Official Journal of the European Commission* **L 020** 43-48.
- European Environment Agency. (2011) Corine Land Cover 2006 raster data - version 15 (08/2011). Retrieved 05 October 2011, from <http://www.eea.europa.eu/legal/copyright>.
- EPA (2003). Towards setting guideline values for the protection of groundwater in Ireland: Interim report. Johnstown Castle, Wexford, Ireland.: 30.
- EPA (2006). Water Framework Directive Monitoring Programme Prepared to meet the requirements of the EU Water Framework Directive (2000/60/EC) and National Regulations implementing the Water Framework Directive (S.I. No. 722 of 2003) and National Regulations implementing the Nitrates Directive (S.I. No. 788 of 2005). E. P. Agency.
- Eshel, G., Levy, G. J., Mingelgric, U. and Singer, M. J. (2004) Critical Evaluation of the Use of Laser Ray Diffraction for Particle-Size Distribution Analysis. *Soil Science Society of America Journal* **68** 736-743.
- Estévez, E., Cabrera, M. d. C., Molina-Díaz, A., Robles-Molina, J. and Palacios-Díaz, M. d. P. (2012) Screening of emerging contaminants and priority substances (2008/105/EC) in reclaimed water for irrigation and groundwater in a volcanic aquifer (Gran Canaria, Canary Islands, Spain). *Science of The Total Environment* **433** (0): 538-546.
- European Parliament. (2000) Directive of the European Parliament and of the Council 2000/60/EC Establishing a Framework for Community Action in the Field of Water Policy.
- European Parliament. (2006) Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. *Official Journal of the European Commission* **L372** 19-31.
- European Parliament. (2008) Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/456/EEC, 84/491/EEC, 86/208/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. *Official Journal of the European Union*: L 348.
- European Parliament. (2009) Directive 2009/128/EC Of The European Parliament And Of The Council of 21 October 2009 establishing a framework for Community action to

- achieve the sustainable use of pesticides. *Official Journal of the European Commission* **L309** 71-86.
- Faraji, H. and Helalizadeh, M. (2010) Determination of organochlorine pesticides in river water using dispersive liquid-liquid microextraction and gas chromatography-electron capture detection. *International Journal of Environmental Analytical Chemistry* **90** (11): 869-879.
- Farenhorst, A., Saiyed, I.M., Goh, T.B. and McQueen, P. (2010) The important characteristics of soil organic matter affecting 2,4-dichlorophenoxyacetic acid sorption along a catenary sequence. *Journal of Environmental Science* **45** (3): 204 – 213.
- Fava, L., Orru, M. A., Businelli, D., Scardala, S. and Funari, E. (2006) Leaching potential of some phenylureas and their main metabolites through laboratory studies. *Environmental Science and Pollution Research* **13** (6): 386-391.
- Fava, L., Orru, M. A., Crobe, A., Caracciolo, A. B., Bottoni, P. and Funari, E. (2005) Pesticide metabolites as contaminants of groundwater resources: assessment of the leaching potential of endosulfan sulfate, 2,6-dichlorobenzoic acid, 3,4-dichloroaniline, 2,4-dichlorophenol and 4-chloro-2-methylphenol. *Microchemical Journal* **79** (1-2): 207-211.
- Fava, L., Orru, M. A., Scardala, S. and Funari, E. (2007) Leaching potential of carbarnates and their metabolites and comparison with triazines. *Microchemical Journal* **86** (2): 204-208.
- Fealy, R. M., Green, S., Loftus, M., Meehan, R., Radford, T., Cronin, C. and Bulfin, M. (2009). Teagasc EPA Soil and Subsoils Mapping Project - Final Report. Teagasc. Dublin. **Volume I**.
- Feehan, J., Davis, Y., Ni Eidhin, C., Hayes, N., Page, D., Wall, B. and O'Leary, G. (2011). The Provision and Quality of Drinking Water in Ireland: A report for the years 2008-2009. Wexford, Environmental Protection Agency.
- Fetter, C. W. (2001) *Applied Hydrogeology: Fourth Edition*. New Jersey, Prentice-Hall, Inc. .
- Finizio, A., Azimonti, G. and Villa, S. (2011) Occurrence of pesticides in surface water bodies: a critical analysis of the Italian national pesticide survey programs. *Journal of Environmental Monitoring* **13** (49): 49-57.
- Firth, D. (1993) Bias reduction of maximum likelihood estimates. *Biometrika* **80** 27-28.
- Fisher, L. H. and Healy, R. W. (2008) Water movement within the unsaturated zone in four agricultural areas of the United States. *Journal of Environmental Quality* **37** 1051-1063.

- Fitzsimons, V., Daly, D., Wright, G. and Hunter-Williams, Y. (2005) "Rock Type versus Fractures"-current understanding in Irish aquifers. Proceedings of National Conference Groundwater in Ireland: 25th Anniversary Conference., Tullamore, Ireland, International Association of Hydrogeologists (Irish Group).
- Fontmorin, J. M., Huguet, S., Fourcade, F., Geneste, F., Floner, D. and Amrane, A. (2012) Electrochemical oxidation of 2,4-Dichlorophenoxyacetic acid: Analysis of by-products and improvement of the biodegradability *Chemical Engineering Journal* **195** 208-217.
- FOOTPRINT. (2006) The FOOTPRINT Pesticide Properties DataBase. Database collated by the University of Hertfordshire as part of the EU-funded FOOTPRINT project (FP6-SSP-022704) from <http://www.eu-footprint.org/ppdb.html>.
- Foster, S. S. D. (2000) Assessing and Controlling Impacts of Agriculture on Groundwater- from Barley Barons to Beef Bans. *Quarterly Journal of Engineering Geology and Hydrogeology* **33** 263-280. .
- Foster, S. S. D. and Chilton, P.J. (1991) Mechanisms of Groundwater Pollution by Pesticides. *Water and Environment Journal* **5** 186-193.
- Franzetti, S. and Guadagnini, A. (1996) Probabilistic estimation of well catchments in heterogeneous aquifers. *Journal of Hydrology* **174** (1-2): 149-171.
- Fredslund, L., Vinther, F. P., Brinch, U. C., Elsgaard, L., Rosenberg, P. and Jacobsen, C. S. (2008) Spatial Variation in 2-Methyl-4-chlorophenoxyacetic Acid mineralization and Sorption in a Sandy Soil at Field Level. *Journal of Environmental Quality* **37** 1918-1928.
- Frische, K., Schwarzbauer, J. and Ricking, M. (2010) Structural diversity of organochlorine compounds in groundwater affected by an industrial point source. *Chemosphere* **81** (4): 500-508.
- Fytianos, K., Meesters, R. J. W., Schroder, H. F. R., Gouliarmou, B. and Gantidis, N. (2006) Distribution of organochlorine pesticides in surface water and sediments in Lake Volvi (northern Greece). *International Journal of Environmental Analytical Chemistry* **86** (1): 109-118.
- Gardiner, M. and Radford, J. (1980). Soil associations of Ireland and their land use potential. Soil Survey Bulletin No. 36. Dublin, Ireland., An Foras Talúntais.
- Gardiner, M. J. and Ryan, P. (1964) Soils of Co. Wexford. National Soil Survey of Ireland. Dublin 4, An Foras Talúntais.
- Garthwaite, D. (1998). Golf Course Pesticide Usage 1994 – 1997. , Central Science Laboratory Pesticide Usage Survey Group. .

- Gatidou, G. and Iatrou, E. (2011) Investigation of photodegradation and hydrolysis of selected substituted urea and organophosphate pesticides in water. *Environmental Science and Pollution Research* **18** 949-957.
- Gaw, S., Close, M. E. and Flintoft, M. J. (2008) Fifth national survey of pesticides in groundwater in New Zealand. *New Zealand Journal of Marine and Freshwater Research* **42** 397-407.
- Gonçalves, C. M., Esteves da Silva, J. C. G. and Alpendurada, M. F. (2007) Evaluation of the pesticide contamination of groundwater sampled over two years from a vulnerable zone in Portugal. *Journal of Agricultural and Food Chemistry* **55** (15): 6227-6235.
- Goody, D. C., Darling, W. G., Abesser, C. and Lapworth, D. J. (2006) Using chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆) to characterise groundwater movement and residence time in a lowland Chalk catchment. *Journal of Hydrology* **330** 44-52.
- Goody, D. C., Mathias, S. A., Harrison, I., Lapworth, D. J. and Kim, A. W. (2007) The significance of colloids in the transport of pesticides through Chalk. *Science of The Total Environment* **385** (1-3): 262-271.
- Goppert, N. and Goldscheider, N. (2007) Solute and Colloid Transport in Karst Conduits under Low- and High-Flow Conditions. *Ground Water* **46** (1): 61-68.
- Goss, M. J., Barry, D. A. J. and Rudolph, D. L. (1998) Contamination in Ontario farmstead domestic wells and its association with agriculture: 1. Results from drinking water wells. *Journal of Contaminant Hydrology* **32** (3-4): 267-293.
- Government of Ireland. (2010) European Communities Environmental Objectives (Groundwater) Regulations. S.I. No. 9 of 2010. S. Instruments. Dublin 2, The Stationary Office.
- Gregoire, C., Elsaesser, D., Huguenot, D., Lange, J., Lebeau, T., Merli, A., Mose, R., Passeport, E., Payraudeau, S., Schütz, T., Schulz, R., Tapia-Padilla, G., Tournebize, J., Trevisan, M. And Wanko, A. (2009) Mitigation of agricultural nonpoint-source pesticide pollution in artificial wetland ecosystems. *Environmental Chemistry Letters* **7**: 205-231.
- Griffiths, K. J., MacDonald, A. M., Robins, N. S., Merritt, J., Booth, S. J., Johnson, D. and McConvey, P. J. (2011) Improving the characterization of Quaternary deposits for groundwater vulnerability assessments using maps of recharge and attenuation potential. *Quarterly Journal of Engineering Geology and Hydrogeology* **43** (1): 49-61.

- GSI. (1999) Data handling procedures in the aquifer classification process. Retrieved 15th October 2010 from http://www.gsi.ie/NR/rdonlyres/01C4199F-A257-48A0-A963-5CB65A779F6E/0/aquifer_classification_Oct06.pdf.
- GSI (2008a) National bedrock aquifer map 1:100,000 Dublin, Ireland.
- GSI (2008b) National generalised bedrock map 1:100,000 Dublin, Ireland.
- GSI (2009) National vulnerability map 1:50,000 Dublin, Ireland. .
- GSI (2011) Subsoil Permeability 2011 for the Republic of Ireland. Dublin, Ireland.
- Guggenmos, M. R., Daughney, C. J., Jackson, B. M. and Morgenstern, U. (2011) Regional-scale identification of groundwater-surface water interaction using hydrochemistry and multivariate statistical methods, Wairarapa Valley, New Zealand. *Hydrology and Earth System Sciences* **15** 3383-3398.
- Guzzella, L., Pozzoni, F. and Giuliano, G. (2006) Herbicide contamination of surficial groundwater in Northern Italy. *Environmental Pollution* **142** (2): 344-353.
- Haarstad, K. and Ludvigen, G.H (2007) Ten years of pesticide monitoring in Norwegian groundwater. *Groundwater Monitoring and Remediation* **27** (3): 75 – 89
- Hajšlová, J. and Čajka, J. Ed. (2007) *Gas chromatography - mass spectrometry (GC-MS). Food Toxicants Analysis: Techniques, Strategies and Developments* Elsevier Science Ltd.
- Hancock, T. C., Sandstorm, M. W., Vogel, J. R., Webb, R. M. T., Randall Bayless, E. and Barbash, J. E. (2008) Pesticide Fate and Transport throughout Unsaturated Zones in Five Agricultural Settings, USA. *Journal of Environmental Quality* **37** 1086-1100.
- Hangena, E., Gerkeb, E. E., Schaaf, W. and Hu"ttle, R. F. (2005) Assessment of preferential flow processes in a forest-reclaimed lignitic mine soil by multicell sampling of drainage water and three tracers. *Journal of Hydrology* **303** 16-37.
- Harris, G. L., Nicholls, P. H., Bailey, S. W., Howse, K. R. and Mason, D. J. (1994) Factors influencing the loss of pesticides in drainage from a cracking clay soil. *Journal of Hydrology* **159** 235-253.
- Harrison, I., Williams, G. M. and Carlick, C. A. (2003) Enantioselective biodegradation of mecoprop in aerobic and anaerobic microcosms. *Chemosphere* **53** 539-549.
- Hassan, J., Shamsipur, M., Es'haghi, A. and Fazili, S. (2011) Determination of Chlorophenoxy Acid Herbicides in Water Samples by Suspended Liquid-Phase Microextraction-Liquid Chromatography. *Chromatographia* **73** 999-1003.
- Helsel, D. R. (1987) Advantages of nonparametric procedures for analysis of water quality data. *Hydrological Sciences* **32** 179-190.

- Helsel, D. R. (1990) Less than obvious: statistical treatment of data below the detection limit. *Environmental Science & Technology* **24** (12): 1767-1774.
- Helsel, D. R. (2006) Fabricating data: How substituting values for nondetects can ruin results, and what can be done about it. *Chemosphere* **65** 2434-2439.
- Heron, G. and Christensen, T. H. (1992) Degradation of the herbicide mecoprop in an aerobic aquifer determined by laboratory batch studies. *Chemosphere* **24** (5): 547-557.
- Hiller, E., Khun, M., Zemanová, L., Jurkovič, L. and Bartal, M. (2006) Laboratory study of retention and release of weak acid herbicide MCPA by soils and sediments and leaching potential of MCPA. *Plant, Soil and the Environment* **52** (12): 550-558.
- Holman, I. P., Dubus, I. G., Hollis, J. M. and Brown, C. D. (2004) Using a linked soil model emulator and unsaturated zone leaching model to account for preferential flow when assessing the spatially distributed risk of pesticide leaching to groundwater in England and Wales. *Science of The Total Environment* **318** 73-88.
- Holtze, M. S., Hansen, H. C. B., Juhler, R. K., Sorensen, J. and Aamand, J. (2007) Microbial degradation pathways of the herbicide dichlobenil in soils with different history of dichlobenil-exposure. *Environmental Pollution* **148** (1): 343-351.
- Holtze, M. S., Sorensen, S. R., Sorensen, J. and Aamand, J. (2008) Microbial degradation of the benzonitrile herbicides dichlobenil, bromoxynil and ioxynil in soil and subsurface environments - Insights into degradation pathways, persistent metabolites and involved degrader organisms. *Environmental Pollution* **154** (2): 155-168.
- Hooker, K. (2005) *A field study of nireate leaching from tillage land in South East Ireland*. MSc Trinity College Dublin.
- Hornsby, A. G., Wauchope, R. D. and Herner, A. (1995) *Pesticide Properties in the Environment*. Springer-Verlag
- Hu, X.-L., Hunag, Y.-J., Tao, Y., Yin, D.-Q. and Liu, J.-F. (2010) Hollow fiber membrane supported thin liquid film extraction for determination of trace phenoxy acid herbicides and phenols in environmental water samples. *Microchim Acta* **168** 23-29.
- Hunter-Williams, N., Misstear, B. D. R., Daly, D., Johnstown, P., Lee, M., Cooney, P. and Hickey, C. (2011). A national groundwater recharge map for Ireland. Irish National Hydrology Conference. Athlone, Ireland.
- IAH (2011). Managing Karst 2011 Annual Field Trip, International Association of Hydrogeologists (Irish branch).
- Iker, B. C., Kambesis, P., Oehrle, S. A., Groves, C. and Barton, H. A. (2010) Microbial Atrazine Breakdown in a Karst Groundwater System and Its Effect on Ecosystem Energetics. *Journal of Environmental Quality* **39** 509-518.

- Irace-Guigand, S. and Aaron, J. J. (2003) The role of organic colloids in herbicide transfer to rivers: a quantitative study of triazine and phenylurea interactions with colloids. *Analytical and Bioanalytical Chemistry* **376** 431-435.
- Jablonowski, N. D., Schäffer, A. and Burauel, P. (2011) Still present after all these years: persistence plus potential toxicity raise questions about the use of atrazine. *Environmental Science and Pollution Research* **18** (2): 328-331.
- Jacobsen, C. S., van der Keur, P., Iversen, B. V., Rosenberg, P., Barlebo, H. C., Torp, S., Vosgerau, H., Juhler, R. K., Ernsten, V., Rasmussen, J., Brinch, U. C. and Jacobsen, O. H. (2008) Variation of MCPA, metribuzine, methyltriazine-amine and glyphosate degradation, sorption, mineralization and leaching in different soil horizons. *Environmental Pollution* **156** (3): 794-802.
- Jahangir, M. M. R. (2012) *Denitrification in subsoils and groundwater in Ireland* Ph.D. The University of Dublin, Trinity College Dublin, Ireland.
- Janniche, G. S., Lindberg, E., Mouvet, C. and Albrechtsen, H. J. (2010a) Mineralization of isoproturon, mecoprop and acetochlor in a deep unsaturated limestone and sandy aquifer. *Chemosphere* **81** (7): 823-831.
- Janniche, G. S., Mouvet, C. and Albrechtsen, H.-J. (2010b) Acetochlor sorption and degradation in limestone subsurface and aquifers. *Pest Management Science* **66** (12): 1287-1297.
- Janniche, G. S., Mouvet, C. and Albrechtsen, H. J. (2011) Vertical small scale variations of sorption and mineralization of three herbicides in subsurface limestone and sandy aquifer. *Journal of Contaminant Hydrology* **123** (3-4): 167-177.
- Janniche, G. S., Spliid, H. and Albrechtsen, H.-J. (2012) Microbial Community-Level Physiological Profiles (CLPP) and herbicide mineralization potential in groundwater affected by agricultural land use. *Journal of Contaminant Hydrology* **140-141** (0): 45-55.
- Jarvis, N. J. (2007) A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. *European Journal of Soil Science* **58** 532 – 546
- Jensen, G. G., Björklund, E., Simonsen, A. and Halling-Sørensen, B. (2009) Determination of 2,6-dichlorobenzamide and its degradation products in water samples using solid-phase extraction followed by liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A* **1216** (27): 5199-5206.

- Johnson, A. C., White, C., Lal Bhardwaj, C. and Dixon, A. (2003) The ability of indigenous micro-organisms to degrade isoproturon, atrazine and mecoprop within aerobic UK aquifer systems. *Pest Management Science* **59** (12): 1291-1302.
- Jørgenson, J. L. (2001) Aldrin and Dieldrin: A Review of Research on Their Production, Environmental Deposition and Fate, Bioaccumulation, Toxicology, and Epidemiology in the United States. *Environmental Health Perspectives* **109** (suppl 1) 113-139.
- Jørgensen, L. F. and Stockmarr, J. (2009) Groundwater monitoring in Denmark: characteristics, perspectives and comparison with other countries. *Hydrogeology* **17** 827-842.
- Kashanian, S., Shariati, Z., Roshanfekr, H. and Ghobadi, S. (2012) DNA Binding Studies of 3, 5, 6-Trichloro-2-Pyridinol Pesticide Metabolite *DNA and Cell Biology* **31** (7): 1341-1348
- Kayhanian, M., Singh, A. and Meyer, S. (2002) Impact of non-detects in water quality data on estimation of constituent mass loading. *Water Science and Technology* **45** (9): 219-225.
- Kelly, C. (2010) *Delineating source protection zones and zones of contribution for monitoring points*. Proceedings of the National Conference Groundwater in the Hydrological Cycle: pressures and protection, Tullamore, Ireland, International Association of Hydrogeologists (Irish Group).
- Kerle, E. A., Jenkins, J. J. and Vogue, P. A. (2007). Understanding Pesticide persistence and mobility for groundwater and surface water protection. Oregon, U.S.A, Oregon State University EM 8561-E.
- Kladivko, E. J., Van Scouoc, G. E., Monke, E. J., Oates, K. M. and Pask, W. (1991) Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. *Journal of Environmental Quality* **20** 264-270.
- Klint, M., Arvin, E. and Jfnsen, B. K. (1993) Degradation of the pesticides mecoprop and atrazine in unpolluted sandy aquifers. *Journal of Environmental Quality* **22** 262-266.
- Kolpin, D. W., Barbash, J. E. and Gilliom, R. J. (1998a) Occurrence of Pesticides in Shallow Groundwater of the United States: Initial Results from the National Water-Quality Assessment Program. *Environmental Science & Technology* **32** (5): 558-566.
- Kolpin, D. W., Basbash, J. E. and Gilliom, R. J. (2000) Pesticides in Ground Water of the United States, 1992-1996. *Ground Water* **38** (6): 857-863.
- Kolpin, D. W., Kalkhoff, S. J., Goolsby, D. A., Sneek-Fahrer, D. A. and Thurman, E. M. (1997) Occurrence of Selected Herbicides and Herbicide Degradation Products in Iowa's Ground Water, 1995. *Ground Water* **35** (4): 679-688.

- Kolpin, D. W., Thurman, E. M. and Linhart, S. M. (1998b) The Environmental Occurrence of Herbicides: The importance of degradates in groundwater. *Arch. Environ. Contam. Toxicol.* **35** (3): 385 – 390
- Kramers, G. (2009) *Preferential Flow in Irish Grassland Soils*. Ph.D. University College Dublin.
- Kramers, G., Richards, K. G. and Holden, N. M. (2009) Assessing the potential for the occurrence and character of preferential flow in three Irish grassland soils using image analysis. *Geoderma* **153** 362-371.
- K.T. Cullen and Co. Ltd. (1994). Environmental Subprogramme Measure 3 "Trace Organic Contaminants in Irish Groundwaters". Dublin 4.
- Lancas, F. M., Olivares, I. R. B. and Alves, P. M. (2007) Development, validation and application of a method to analyze phenols in water samples by solid phase micro extraction-gas chromatography-flame ionization detector. *Journal of Environmental Science and Health Part B-Pesticides, Food contaminants and Agricultural Wastes* **42** (5): 491-498.
- Lapworth, D. J., Gooddy, D. C., Stuart, M. E., Chilton, P. J., Cachandt, G. C., M., M. K. and Bishop, S., S. (2006) Pesticides in groundwater: some observations on temporal and spatial trends. *Water and Environment Journal* **20** 55-64
- Larsen, L. and Aamand, J. (2001) Degradation of herbicides in two sandy aquifers under different redox conditions. *Chemosphere* **44** 231-236.
- Li, H.-P., Li, G.-C. and Jen, J.-F. (2003) Determination of organochlorine pesticides in water using microwave assisted headspace solid-phase microextraction and gas chromatography. *Journal of Chromatography A*. **1012** 129-137.
- Lim, J.-W., Bae, G.-O., Kaown, D. and Lee, K.-K. (2010) Prediction of Groundwater Contamination with Multivariate Regression and Probabilistic Capture Zones. *Journal of Environmental Quality* **39** 1594-1603.
- Lindsey, B. D., Falls, W. F., Ferrari, M. J., Zimmerman, T. M., Harned, D. A., Sadorf, E. M. and Chapman, M. J. (2006). Factors affecting occurrence and distribution of selected contaminants in groundwater from selected areas in the Piedmont aquifer system, Eastern United States, 1993 – 2003.
- Lindsey, B. D., Katz, B. G., Berndt, M. P., Ardis, A. F. and Skach, K. A. (2010) Relations between sinkhole density and anthropogenic contaminants in selected carbonate aquifers in the eastern United States. *Environmental Earth Sciences* **60** 1073-1090. .
- Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M. and Gawlik, B. M. (2010) Pan-European survey on

- the occurrence of selected polar organic persistent pollutants in ground water. *Water Research* **44** (14): 4115-4126.
- Louch, D., Motlagh, S. and Pawliszyn, J. (1992) Dynamics of organic compounds extraction from water using liquid-coated fused silica fibres. *Anal. Chem.* **64** 1187-1199.
- Lucey, J. (2009). Water Quality in Ireland 2007 – 2008: Key indicators of the Aquatic Environment. E. P. A.-. Ireland. Wexford, Ireland.
- MacDonald, A. M., Darling, W. G., Ball, D. F. and Oster, H. (2003) Identifying trends in groundwater quality using residence time indicators: an example from the Permian aquifer in Dumfries, Scotland. *Hydrogeology* **11** 504-517.
- Malaguerra, F., Albrechtsen, H.-J., Thorling, L. and Binning, P. J. (2012) Pesticides in water supply wells in Zealand, Denmark: A statistical analysis. *Science of The Total Environment* **414** (0): 433-444.
- Marchese, S., Perret, D., Gentili, A., D'Ascenzo, G. and Faberi, A. (2002) Determination of phenoxyacid herbicides and their phenolic metabolites in surface and drinking water. *Rapid Communications in Mass Spectrometry* **16** (2): 134-141.
- Marín, J. M., Gracia-Lor, E., Sancho, J. V., López, F. J. and Hernández, F. (2009) Application of ultra-high-pressure liquid chromatography–tandem mass spectrometry to the determination of multi-class pesticides in environmental and wastewater samples: Study of matrix effects. *Journal of Chromatography A* **1216** (9): 1410-1420.
- McAleer, E. (2012) *The Effect of Land Use on Stream Nitrogen Dynamics in a Large Agricultural Watershed Dominated by Base flow*. MSc Queen's University Belfast.
- McCarthy, J. F. and Zachara, J.M (1989) Subsurface transport of contaminants. *Environmental Science and Technology* **23** (5): 496 – 502
- McGarrigle, M., Lucey, J. and Ó Cinnéide, M. (2010) Water Quality in Ireland 2007 – 2009. Environmental Protection Agency, Wexford, Ireland.
- McGechan, M. B. and Lewis, D. R. (2002) Transport of Particulate and Colloid-sorbed Contaminants through Soil, Part 1: General Principles. *Biosystems Engineering* **83** (3): 255-273.
- McGrath, D. (1995) Organic micropollutant and trace element pollution of Irish soils. *Science of The Total Environment* **164** 125 - 133.
- McKinlay, R., Plant, J. A., Bell, J. N. B. and Voulboulis, B. N. (2008) Endocrine disrupting pesticides: Implications for risk assessment. *Environment International* **34**: 168-183
- McManus, S.-L., Coxon, C. E., Richards, K. G. and Danaher, M. (2013) Quantitative solid phase microextraction – gas chromatography mass spectrometry analysis of the

- pesticides lindane, heptachlor and two heptachlor transformation products in groundwater. *Journal of Chromatography A* **1284**: 1 – 7.
- Mellander, P.-E., Jordan, P., Wall, D. P., Melland, A. R., Meehan, R., Kelly, C. and Shortle, G. (2012) Delivery and impact bypass in a karst aquifer with high phosphorus source and pathway potential. *Water Research* **46** (7): 2225-2236.
- Melo, A., Pinto, E., Aguiar, A., Mnsilha, C., Pinho, O. and Ferreira, I. M. P. L. V. O. (2012) Impact of intensive horticulture practices on groundwater content of nitrates, sodium, potassium, and pesticides. *Environmental Monitoring and Assessment* **184** 4539-4551.
- Milde, K., Milde, G., Ahlsdorf, B., Litz, U., Müller-Wegener. and Stock, R. (1988) *Protection of Highly Permeable Aquifers Against Contamination by Xenobiotics*. Karst Hydrology and Karst Environment Protection, IAH 21st Congress,
- Missteart, B. D. R., Brown, L. and Daly, D. (2009) A methodology for making initial estimates of groundwater recharge from groundwater vulnerability mapping. *Hydrogeology* **17** 275-285. .
- Missteart, B. D. R. and Daly, D., Eds. (2008) *Groundwater protection in a celtic region: the Irish example*. Groundwater in the Celtic Regions: Studies in Hard Rock and Quaternary Hydrogeology. London, Geological Society.
- Missteart, B. D. R. and Brown, L. (2008) Water Framework Directive: Recharge and groundwater vulnerability. STRIVE Report Series No. 6. Wexford, Ireland, Environmental Protection Agency.
- Moe, H. M. (2008). Risk to Groundwater from Diffuse mobile organics. Dublin.
- Moore, M. T., Denton, D. L., Cooper, C. M., Wrynski, J., Miller, J. L., Werner, I., Horner, G., Crane, D., Holcomb, D. B. and Huddleston, G. M. (2011) Use of vegetated agricultural drainage ditches to decrease pesticide transport from tomato and alfalfa fields in California, USA. *Environmental Toxicology and Chemistry* **30** (5): 1044-1049.
- Morris, B. (2005) The 1999 Cryptosporidium risk assessment exercise in England and Wales- a groundwater overview. *Water and Environment Journal* **19** 238-247.
- Morvan, X., Mouvet, C., Baran, N. and Gutierrez, A. (2006) Pesticides in the groundwater of a spring draining a sandy aquifer: Temporal variability of concentrations and fluxes. *Journal of Contaminant Hydrology* **87** (3-4): 176-190.
- Mostafalou, S. and Abdollahi, M. (2013) Pesticides and human chronic diseases: Evidences, Mechanisms, and Perspectives. *Toxicology and Applied Pharmacology* **268** (2): 157 – 177.

- Mudarra, M. and Andreo, B. (2011) Relative importance of the saturated and the unsaturated zones in the hydrogeological functioning of karst aquifers: The case of Alta Cadena (Southern Spain). *Journal of Hydrology* **397** (3-4): 263-280.
- Nadin, P. (2007). The use of plant protection products in the European Union data 1992 - 2003. Luxembourg, EuroStat.
- Nasrabadi, T., Nabi-Bidhendi, G., Karbassi, A., Grathwohl, P. and Mehrdadi, N. (2011) Impact of major organophosphate pesticides used in agriculture to surface water and sediment quality (Southern Caspian Sea basin, Haraz River). *Environmental Earth Sciences* **63** (4): 873-883.
- National Roads Authority. (2010) Guidelines for the management of Noxious Weeds and Non-Native Invasive Plant Species on National Roads, revision 1.
- National Summary Report. (2005). The Characterisation and Analysis of Ireland's River Basin Districts in accordance with Section 7 (2&3) of the European Communities (Water Policy) Regulations 2003 (S.I 722 of 2003). 166p.
- O'Callaghan Moran and Associates. (2007). Establishing Natural Background Levels for Groundwater in Ireland.
- Olujimi, O. O., Fatoki, O. S., Odendaal, J. and Okonkwo, O. (2011) Solid-Phase Extraction Method for the Analysis of Eleven Phenolic Pollutants in Water Samples *Asian Journal of Chemistry* **23** (2): 657-662.
- Onneby, K., Jonsson, A. and Stenstrom, J. (2010) A new concept for reduction of diffuse contamination by simultaneous application of pesticide and pesticide-degrading microorganisms *Biodegradation* **21** (1): 21-29.
- Oregon State. (2012) Groundwater Chemistry Background Discussion. Retrieved 16/08/2012, from <http://www.deq.state.or.us/wq/groundwater/docs/lubgwma/hydrogeologyrpt/appx4a.pdf>.
- Padkel, H. (1994) Groundwater contamination and analysis at hazardous waste sites. S. a. J. Lesage, R.E. New York, Marcel-Dekker. 381.
- Page, D., Burke, D., Wall, B. and O'Leary, G. (2007). The Provision and Quality of Drinking Water in Ireland: A report for the years 2006 - 2007. Wexford, Ireland, Environmental Protection Agency.
- Papadopoulou-Mourkidou, E., Karpouzas, D. G., Patsias, J., Kotopoulou, A., Milothridou, A., Kintzikoglou, K. and Vlachou, P. (2004) The potential of pesticides to contaminate the groundwater resources of the Axios river basin in Macedonia, Northern Greece. Part I.

- Monitoring study in the north part of the basin. *Science of The Total Environment* **321** (1-3): 127-146.
- Pawliszyn, J. (1989) *Applications of solid phase microextraction*. Cambridge, UK, The Royal Society of Chemistry.
- Pawliszyn, J. (2004). *Applications of Solid Phase Microextraction*, Royal Society of Chemistry: 169 - 187.
- Pawliszyn, J. B. and Alexandrou, N. (1989) Indirect supercritical fluid extraction of organics from water matrix samples. *Water Poll. Res. J. Canada* **24** 207-214.
- Pecoraino, G., Scalici, L., Avellone, G., Ceraulo, L., Favara, R., Candela, E. G., Provenzano, M. C. and Scaletta, C. (2008) Distribution of volatile organic compounds in Sicilian groundwaters analysed by head space-solid phase micro extraction coupled with gas chromatography mass spectrometry (SPME/GC/MS). *Water Research* **42** (14): 3563-3577.
- Pell, M., Stenberg, B. and Torstensson, L. (1998) Potential Denitrification and Nitrification Tests for Evaluation of Pesticide Effects in Soil. *Ambio* **27** (1): 24-28.
- Pesticide Control Service. (2006). Pesticide usage survey: report number 1 grassland and fodder crops 2003. St. Stephens Green, Dublin 2, Ireland, Government Publications.
- Pesticide Control Service (2007a). Pesticide usage survey report number 2 Arable Crops. D. o. A. a. Food. Celbridge, Co. Kildare, Ireland, Department of Agriculture and Food.
- Pesticide Control Service (2007b). Pesticide usage survey: report number 2 arable crops 2004. St. Stephens Green, Dublin 2, Ireland, Government Publications.
- Petty, D. G., Getsinger, K. D. and Woodburn, K. B. (2003) A review of the Aquatic Environmental Fate of Triclopyr and its Major Metabolites. *Journal of Aquatic Plant Management* **41** 69-75.
- Pico, Y., Fernandez, M., Ruiz, M. J. and Font, G. (2007) Current trends in solid-phase-based extraction techniques for the determination of pesticides in food and environment *Journal of Biochemical and Biophysical Methods* **70** (2): 117-131.
- Piwowarczyk, A. A. and Holden, N. M. (2012) Adsorption and Desorption Isotherms of the Nonpolar Fungicide Chlorothalonil in a Range of Temperate Maritime Agricultural Soils. *Water, Air and Soil Pollution* **223** (7): 3975-3985.
- Porazzi, E., Pardo Martinez, M., Fanelli, R. and Benfenati, E. (2005) GC-MS analysis of dichlobenil and its metabolites in groundwater. *Talanta* **68** 146-154.
- Premrov, A. (2011) *Evaluation of measures to reduce nitrate loss to groundwater from tillage land*. Ph.D Trinity College Dublin.

- Premrov, A., Coxon, C. E., Hackett, R., Brennan, D., Sills, P. and Richards, K. G. (2009a) *Over-winter green cover in a spring barley system: role in exporting dissolved organic carbon to shallow groundwater and implications for denitrification*. Proceedings of the 16th Nitrogen Workshop – Connecting Different Scales of Nitrogen use in Agriculture, Turin, Italy,
- Premrov, A., Coxon, C. E., Hackett, R., Kirwan, L. and Richards, K. G. (2012) Effects of over-winter green cover on groundwater nitrate and dissolved organic carbon concentrations beneath tillage land. *Science of The Total Environment* **438** 144-153.
- Premrov, A., Coxon, C. E., Hackett, R. and Richards, K. (2009b) *Estimating travel-time of nitrate from tillage land to shallow groundwater and towards a river using bromide tracer*. HydroEco 2009, Proceedings 2nd International Multidisciplinary Conference on Hydrology and Ecology: Ecosystems Interfacing with Groundwater and Surface Water, Vienna, Austria,
- Premrov, A., Schulte, R. P. O., Coxon, C. E., Hackett, R. and Richards, K. G. (2010) Predicting soil moisture conditions for arable free draining soils in Ireland under spring cereal crop production. *Irish Journal of Agricultural and Food Research* **49** 99-113.
- Ramos, L. (2012) Critical overview of selected contemporary sample preparation techniques. *Journal of Chromatography A* **1221** 84-98.
- Ratola, N., Santos, L., Herbert, P. and Alves, A. (2006) Uncertainty associated to the analysis of organochlorine pesticides in water by solid-phase microextraction/gas chromatography–electron capture detection—Evaluation using two different approaches. *Analytica Chimica Acta* **573-574** (0): 202-208.
- Reding, M.-A., Belvaus, X., Garnett, R. and Gustin, C. (2011). Presence of glyphosate and its soil metabolite aminomethylphosphonic acid (AMPA) in surface water: what does it mean for the environment and for human health? XIV Symposium in Pesticide Chemistry. Piacenza, Italy.
- Reichenberger, S., Bach, M., Skitschak, A. and Frede, H.-G. (2007) Mitigation strategies to reduce pesticide inputs to ground- and surface- water and their effectiveness: a review. *Science of The Total Environment* **384** 1 - 35
- Reitzel, L. A., Tuxen, N., Ledin, A. and Bjerg, P. L. (2004) Can Degradation Products Be Used as Documentation for Natural Attenuation of Phenoxy Acids in Groundwater? *Environmental Science and Technology* **38** 457-467.
- Reuber, M. D. (1987) Carcinogenicity of heptachlor and heptachlor epoxide. *Journal of Environmental Pathology, Toxicology and Oncology*. **7** (3): 85-114. .

- Richards, K., Coxon, C. E. and Ryan, M. (2005) Unsaturated zone travel time to groundwater on a vulnerable site. *Irish Geography* **38** (1): 57-71. .
- Richardson, S. D. (2012) Environmental Mass Spectrometry: Emerging Contaminants and Current Issues. *Analytical Chemistry* **84** 747-778.
- Richardson, S. D. and Ternes, T. A. (2011) Water Analysis: Emerging Contaminants and Current Issues. *Analytical Chemistry* **83** (12): 4614-4648.
- Roberts, T. R. (1999) *Metabolic pathways of Agrochemicals: Part 2. Insecticides and Fungicides*. The Royal Society of Chemistry.
- Rodil, R., Quintana, J. B., López-Mahía, P., Muniategui-Lorenzo, S. and Prada-Rodríguez, D. (2009) Multi-residue analytical method for the determination of emerging pollutants in water by solid-phase extraction and liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A* **1216** (14): 2958-2969.
- Rodvang, S. J. and Simpkins, W. W. (2001) Agricultural contaminants in Quaternary aquitards: A review of occurrence and fate in North America. *Hydrogeology* **9** 44-59.
- Roulier, S. and Jarvis, N. (2003) Modeling macropore flow effects on pesticide leaching: Inverse parameter estimation using microlysimeters. *Journal of Environmental Quality* **32** 2341-2353.
- Rowell, D. L. (1993) *Soil Science: Methods and Applications*. Essex, England, Longman Scientific and Technical
- Ryan, J. N. and Elimelech, N. (1996) A review of colloid mobilization and transport to groundwater. *Colloids and Surfaces A: physicochemical and Engineering Aspects* **107** 1 - 56.
- SANCO/825/00 (2000) Guidance document on pesticide residue analytical methods rev.8.1.
- SAS Institute. (2004) The SAS system for Windows. Release 6.10., SAS Inst., Cary, NC.
- Sauret-Szczepanski, N., Mirabel, P. and Wortham, H. (2006) Development of a SPME-GC-MS/MS method for the determination of pesticides in rainwater: laboratory and field experiments. *Environmental Pollution* **139** 133 - 142
- Scheyer, A., Morville, S., Mirabel, P. and Millet, M. (2006) Analysis of trace levels of pesticides in rainwater using SPME and GC-tandem mass spectrometry. *Analytical and Bioanalytical Chemistry* **384** 475-487.
- Schulte, R. P. O., Diamond, J., Finkele, K., Holden, N. M. and Brereton, A. J. (2005) Predicting the soil moisture conditions of Irish grasslands. *Irish Journal of Agricultural and Food Research* **44** 95-110.
- Schwartz, F. W. and Zhang, H. (2003) *Fundamentals of ground water*. Wiley.

- Scribner, E. A., Thurman, E. M., Goolsby, D. A., Meyer, M. T., Battaglin, W. A. and Kolpin, D. W. (2005). Summary of Significant Results from Studies of Triazine Herbicides and Their Degradation Products in Surface Water, Ground Water, and Precipitation in the Midwestern United States During the 1990s. Reston, Virginia., United States Geological Survey.
- Silva, E. I., Batista, S., Viana, P., Antunes, P., SerÃ'dio, L., Cardoso, A. T. and Cerejeira, M. J. (2006) Pesticides and nitrates in groundwater from oriziculture areas of the Baixo Sado region (Portugal). *International Journal of Environmental Analytical Chemistry* **86** (13): 955 - 972.
- Simpson, N. J. K. (2000) *Solid-Phase Extraction: Principles, Techniques, and Applications: Principles, Strategies, and Applications*. New York, Marcel Dekker Inc.
- Sinclair, C. J., Boxall, A. B. A., Parsons, S. A. and Thomas, M. R. (2006) Prioritization of Pesticide Environmental Transformation Products in Drinking Water Supplies†. *Environmental Science & Technology* **40** (23): 7283-7289.
- Skark, C., Zullei-seibert, N., Schöttler, U. and Schlett, C. (1998) The Occurrence of Glyphosate in Surface Water. *International Journal of Environmental Analytical Chemistry* **70** (1-4): 93-104.
- Sklivagou, E., Papadopoulou, K. and Bakoulis, A. (2010) Determination of acid herbicides in water by LC/MS/MS. *Desalination and Water Treatment* **13** 320-327.
- Solymosné Majzik, E., Tóth, F., Bneke, L. and Kiss, Z. (2006) SPE-LC-MS-MS Determination of Phenoxy Acid Herbicides in Surface and Ground Water. *Chromatographia* **63** 105-109.
- Sørensen, S. R., Schultz, A., Jacobsen, O. S. and Aamand, J. (2006) Sorption, desorption and mineralisation of the herbicides glyphosate and MCPA in samples from two Danish soil and subsurface profiles. *Environmental Pollution* **141** 184-194.
- Souza, A. G., Amorin, L. C. A. and Cardeal, Z. L. (2010) Studies of the Analysis of Pesticide Degradation in Environmental Samples. *Current Analytical Chemistry* **6** 237-248.
- Sperazza, M., Moore, J. N. and M.S., H. (2004) High-resolution particle size analysis of naturally occurring very fine-grained sediment through laser diffractometry. *Journal of Sedimentary Research* **74** (5): 736-743.
- Spliid, N. H. and Køppen, B. (1998) Occurrence of pesticides in Danish shallow groundwater. *Chemosphere* **37** 1307-1316.
- Steele, G. V., Johnson, H. M., Sandstorm, M. W., Capel, P. D. and Barbash, J. E. (2008) Occurrence and fate of pesticides in four contrasting agricultural settings in the United States. *Journal of Environmental Quality* **37** 1116 – 1132

- Stephenson, G. R., Ferris, I. G., Holland, P. T. and Nordberg, M. (2006) Glossary of terms relating to pesticides (IUPAC Recommendations 2006). *Pure Applied Chemistry* **78** (11): 2075-2154.
- Stuart, M. E., Goody, D. C., Hughes, A. G. and Jackson, C. R. (2006) A Field and Modeling Study to Determine Pesticide Occurrence in a Public Water Supply in Northern England, UK. *Ground Water Monitoring & Remediation* **26** (4): 128-136.
- Stuyt, L. C. P. M., Dierickx, W. and Martinez Beltran, J. (2000) *FAO Irrigation and Drainage Paper (FAO), no. 60 / FAO*. Rome, Italy., FAO.
- Sundaram, B., Feitz, A., Caritat, P., de, P., A., Brodie, R., Coram, J. and Ransley, T. (2009). Groundwater Sampling and Analysis – A Field Guide, Geoscience Australia. **Record 2009/27: 95**.
- Surfer (2002). Surfer 8 User's Guide, Golden Software, Inc., Colorado, U.S.A.
- Swartz, M., Misstear, B. D. R., Daly, D. and Farrell, E. R. (2003) Assessing subsoil permeability for groundwater vulnerability. *Quarterly Journal of Engineering Geology and Hydrogeology* **36** 173-184.
- Tett, V. A., Willetts, A. J. and Lappin-Scott, H. M. (1994) Enantioselective degradation of the herbicide mecoprop by mixed and pure bacterial cultures. *FEMS Microbiology Ecology* **14** 191-200.
- The British Columbia Groundwater Association. (2007) Sodium in Groundwater. Retrieved 16/08/2012, from [http://www.env.gov.bc.ca/wsd/plan_protect_sustain/groundwater/library/ground_fact_sheets/pdfs/na\(020715\)_fin2.pdf](http://www.env.gov.bc.ca/wsd/plan_protect_sustain/groundwater/library/ground_fact_sheets/pdfs/na(020715)_fin2.pdf).
- The British Columbia Groundwater Association. (2007b) Hardness in Groundwater. Retrieved 16/08/2012, from [http://www.env.gov.bc.ca/wsd/plan_protect_sustain/groundwater/library/ground_fact_sheets/pdfs/hardness\(020715\)_fin2.pdf](http://www.env.gov.bc.ca/wsd/plan_protect_sustain/groundwater/library/ground_fact_sheets/pdfs/hardness(020715)_fin2.pdf).
- Thurman, E. M. and Meyer, M.T. (1996) Herbicide Metabolites in Surface Water and Groundwater: Introduction and overview. *Herbicide Metabolites in Surface Water and Groundwater*. M. e. a. Meyer. Washington, ACS Symposium Series, American Chemical Society.
- Travers, P. (2011) *Stream Flow Analysis of the Nuenna*. MSc Trinity College DublinDublin.
- Tuxen, N., de Liphay, J. R., Albrechtsen, H.-J., Aamand, J. and Bjerg, P. L. (2002) Effect of Exposure History on Microbial Herbicide Degradation in an Aerobic Aquifer Affected by a Point Source. *Environmental Science & Technology* **36** (10): 2205-2212.

- USEPA. (1996) Low Stress (low flow) purging and sampling procedure for the collection of ground water samples from monitoring wells Revision 2. from http://www.epa.gov/region6/qa/qadevtools/mod5_sops/groundwater/sampling/r1_lowf_low.pdf.
- Van Brahana, J. (2008) *Karst Aquifers: Encyclopedia of Water Science, Second Edition*. .
- Vervoort, R. W. and Cattle, S. R. (2003) Linking hydraulic conductivity and tortuosity parameters to pore space geometry and pore-size distribution. *Journal of Hydrology* **272** (1–4): 36-49.
- Vione, D., Khanra, S., Das, R., Minero, C., Maurino, V., Brigante, M. and Mailhot, G. (2010) Effect of dissolved organic compounds on the photodegradation of the herbicide MCPA in aqueous solution. *Water Research* **44** 6053-6062.
- Vogesser, M. And Seger, C. 2010. Pitfalls Associated with the Use of Liquid Chromatography-Tandem Mass Spectrometry in the Clinical Laboratory. *Clinical Chemistry* **56** (8): 1234 – 1244.
- Vroumsia, T., Steiman, R., Seigle-Murandi, F., Benoit-Guyod, J. L. and Groupe pour l'Étude du Devenir des Xénobiotiques dans, I. E. (2005) Fungal bioconversion of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenol (2,4-DCP). *Chemosphere* **60** (10): 1471-1480.
- Walsh, P. (2011) *Investigation of point recharge, flow and nutrient levels in a lowland karst system in the South-East of Ireland*. MSc Trinity College DublinDublin 2.
- Wang, P. and Keller, A. A. (2009) Sorption and desorption of atrazine and diuron onto water dispersible soil primary size fractions. *Water Research* **43** (5): 1448-1456.
- Wang, X., Piao, X., Chen, J., Hu, J., Xu, F. and Tao, S. (2006) Organochlorine pesticides in soil profiles from Tianjin, China. *Chemosphere* **64** (9): 1514-1520.
- Williams, P. W. (1966) Limestone Pavements with Special Reference to Western Ireland. *Transactions of the Institute of British Geographers* **40** 155-172.
- Worrall, F. and Besien, T. (2005) The vulnerability of groundwater to pesticide contamination estimated directly from observations of presence or absence in wells. *Journal of Hydrology* **303** 92-107.
- Worrall, F., Besien, T. and Kolpin, D. W. (2002) Groundwater vulnerability: interactions of chemical and site properties. *Science of The Total Environment* **299** (1-3): 131-143.
- Worrall, F. and Kolpin, D. W. (2004) Aquifer vulnerability to pesticide pollution –combining soil, land-use and aquifer properties with molecular descriptors. *Journal of Hydrology* **293** 191 - 204.

- Wright, A. D., Papendorf, O. and König, G. M. (2005) Ambigol C and 2,4-Dichlorobenzoic Acid, Natural Products Produced by the Terrestrial Cyanobacterium *Fischerella ambigua*. *Journal of Natural Products* **68** 459-461.
- Yang, X.-B., Ying, G.-G. and Kookana, R. (2010) Rapid multiresidue determination for currently used pesticides in agricultural drainage waters and soils using gas chromatography-mass spectrometry. *Journal of Environmental Science and Health, Part B* **45** 152-161
- Yaron, B. (1989) General principles of pesticide movement to groundwater. *Agriculture, Ecosystems and Environment* **26** 275 – 297
- Zaporozec, A. (1972) Graphical Interpretation of Water-Quality Data. *Ground Water* **10** (2): 32-43.
- Zertal, A., Jacquet, M., Lave'drine, B. and Sehili, T. (2005) Photodegradation of chlorinated pesticides dispersed on sand. *Chemosphere* **58** 1431-1437.
- Zertal, A., Sehili, T. and Boule, P. (2001) Photochemical behaviour of 4-chloro-2-methylphenoxyacetic acid: Influence of pH and irradiation wavelength. *Journal of Photochemistry and Photobiology A: Chemistry* **146** 37-48.
- Zhang, W.-J., Jiang, F.-B. and Ou, J.-F. (2011) *Global pesticide consumption and pollution: with China as a focus*. Proceedings of the International Academy of Ecology and Environmental Sciences, **1** (2): 125 – 144.
- Zipper, C., Suter, M. J.-F., Haderlein, S. B., Gruhl, M. and Kohler, H.-P. E. (1998) Changes in the enantiomeric ratio of (R)- to (S)-mecoprop indicate in situ biodegradation of this chiral herbicide in a polluted aquifer. *Environmental Science and Technology* **32** 2070-2076.

Appendix 1

Active ingredients used on particular land uses within the Republic of Ireland and the percentage of PPP with each particular a.i.

Active ingredient (a.i)	Count number of products a.i. used in	total number of products available for use	% of products with particular a.i. present
GRASSLAND			
MCPA	27	90	30
dicamba	20	90	22
fluroxypyr	20	90	22
mecoprop-p	17	90	19
2,4-D	15	90	17
triclopyr	14	90	16
clopyralid	8	90	9
propiconazole	5	90	6
chlorpyrifos	4	90	4
amidosulfuron	2	90	2
thifensulfuron (-methyl)	2	90	2
mecoprop	1	90	1
metasulfuron (-methyl)	1	90	1
deltamethrin	1	90	1
sulphur	1	90	1
pyrethrins	1	90	1
FORAGE MAIZE			
fluroxypyr	14	47	30
mesotrione	6	47	13
pendimethalin	5	47	11
terbuthylazine	5	47	11
chlorpyrifos	4	47	9
chlorpyrifos	4	47	9
bromoxynil	2	47	4
clopyralid	2	47	4
methiocarb	2	47	4
2,4-D	1	47	2
nicosulfuron	1	47	2
Thiram	1	47	2
pirimicarb	1	47	2
isoxaflutole	1	47	2
flufenacet	1	47	2
s-metolachlor	1	47	2
pyrethrins	1	47	2
rimsulfuron	1	47	2
chlomepyralid	1	47	2
dimethenamid-p	1	47	2

UNDERSOWN BARLEY			
MCPA	18	28	64
2,4-D	6	28	21
mecoprop-p	5	28	18
2,4-DB	5	28	18
dicamba	4	28	14
tribenuron-methyl	1	28	4
PREHARVEST BARLEY			
glyphosate	36	43	84
diquat	7	43	16
SPRING BARLEY			
epoxiconazole	30	264	11.4
MCPA	25	264	9.5
fluroxypyr	19	264	7.2
mecoprop-p	18	264	6.8
metsulfuron-methyl	17	264	6.4
propiconazole	17	264	6.4
fenpropimorph	13	264	4.9
chlorothalonil	11	264	4.2
prothioconazole	10	264	3.8
dicamba	9	264	3.4
azoxystrobin	9	264	3.4
prochloraz	9	264	3.4
2,4-D	8	264	3.0
boscalid	8	264	3.0
tebuconazole	7	264	2.7
pyraclostrobin	7	264	2.7
chlormequat	6	264	2.3
2,4-DB	6	264	2.3
bromoxynil	5	264	1.9
tribenuron-methyl	5	264	1.9
pendimethalin	5	264	1.9
cypermethrin	5	264	1.9
thifensulfuron-methyl	5	264	1.9
metconazole	5	264	1.9
chlorpyrifos	4	264	1.5
trifloxystrobin	4	264	1.5
fluxapyroxad	3	264	1.1
spiroxime	3	264	1.1
flusilazole	3	264	1.1
cyproconazole	3	264	1.1
carbendazim	3	264	1.1
fluoxastrobin	3	264	1.1
proquinazid	3	264	1.1
sulphur	3	264	1.1
mancozeb	3	264	1.1
mepiquat chloride	3	264	1.1
picoxystobin	2	264	0.8
cyprodinil	2	264	0.8
kresoxim-methyl	2	264	0.8
folpet	2	264	0.8
pinoxadem	2	264	0.8
fludioxonil	2	264	0.8
esfenvalerate	2	264	0.8
ioxynil	2	264	0.8

diflufenican	2	264	0.8
metrafenone	2	264	0.8
clopyralid	2	264	0.8
methiocarb	2	264	0.8
bixafen	2	264	0.8
fenpropidin	2	264	0.8
carfentrazone-ethyl	1	264	0.4
carboxin	1	264	0.4
thiram	1	264	0.4
pirimcarb	1	264	0.4
florasulam	1	264	0.4
isoprazam	1	264	0.4
prohexadione calcium	1	264	0.4
Famoxadone	1	264	0.4
quinoxifen	1	264	0.4
imazalil	1	264	0.4
tralkoxydim	1	264	0.4
iodosulfuron-methyl-sodium	1	264	0.4
dichlorprop-p	1	264	0.4
flutriafol	1	264	0.4
deltamethrin	1	264	0.4
amidosulfuron	1	264	0.4
lambda-cyhalothrin	1	264	0.4
triticonazole	1	264	0.4
silthiofam	1	264	0.4
trinexapac ethyl	1	264	0.4
fenaxprop-p	1	264	0.4
pyrethrins	1	264	0.4
pyrimethanil	1	264	0.4
ethepon	1	264	0.4

Appendix 2

Pesticide application records for KWDa

Year: 2011/2012	
PPP	a.i.
Proline	Prothioconazole
Bravo 500	Chlorothalonil
Opus	Epoxiconazole
Prosaro	Tebuconazole and prothioconazole
Round Up	Glyphosate
IPU	Isoproturon
Doxstar	Fluroxypyr and triclopyr

Pesticide application records for I/KWDa

Crop: Wild oats			
Year: 2003/2004			
Date	PPP	a.i.	Rate
21/11/2003	Sumi-Alpha	Esfenvalerate	1.65 L/ha
23/4/2004	Bravo 500	Chlorothalonil	1.5 L/ha
26/5/2004	Sherman	Pendimethalin	8 L/ha
26/5/2004	Corbel	Fenpropimorph	5 L/ha
26/5/2004	Amistar	Azoxystrobin	5 L/ha
Crop: Winter barley			
Year: 2004/2005			
Date	PPP	a.i.	Rate
10/11/2004	Sumi-Alpha	Esfenvalerate	1.65 L/ha
10/11/2004	Trump	Isoproturon; pendimethalin	4 L/ha
4/4/2005	Grasp	Tralkoxydim	1.4 L/ha
11/4/2005	Stereo	Propiconazole; cyprodinil	1.8 L/ha
29/4/2005	Cerone	Ethepon	1 L/ha
29/4/2005	Bravo 500	Chlorothalonil	1 L/ha
11/5/2005	Proline	Prothioconazole	0.6 L/ha
11/5/2005	Bravo 500	Chlorothalonil	1 L/ha

Crop: Spring wheat**Year:** 2005/2006

Date	PPP	a.i.	Rate
28/4/2006	Foundation	Dicamba; mecoprop-p	1 L/ha
28/4/2006	BiPlay	Metsulfuron(-methyl); tribenuron(-methyl)	29 g/ha
20/5/2006	Puma Extra	Fenoxaprop-P	0.6 L/ha
20/5/2006	Moddus	Trinexapac ethyl	0.1 L/ha
20/5/2006	Bravo 500	Chlorothalonil	0.7 L/ha
22/6/2006	Prosaro	Tebuconazole; prothioconazole	0.6 L/ha
22/6/2006	Amistar	Azoxystrobin	0.5 L/ha
22/6/2006	Corbel	Fenpropimorph	0.3 L/ha

Crop: Spring barley**Year:** 2006/2007

Date	PPP	a.i.	Rate
1/5/2007	Sumi-Alpha	Esfenvalerate	1.65 L/ha
25/4/2007	Ally Max SX	Metsulfuron(-methyl); tribenuron(-methyl)	30 g/ha
25/4/2007	Duplosan	Mecoprop-p	1.5 L/ha
22/5/2007	Axial	Pinoxaden	5% v/v
22/5/2004	Adigor	Methylated Rapeseed Oil	1.25 L/ha
22/5/2007	Rocca	Propiconazole; Cyprodinil	1.25 L/ha
12/6/2007	Fandango	Fluoxastrobin; Prothioconazole	1 L/ha
12/6/2007	Bravo 500	Chlorothalonil	1 L/ha

Crop: Spring barley**Year:** 2007/2008

Date	PPP	a.i.	Rate
4/4/2008	Sumi-Alpha	Esfenvalerate	1.65 L/ha
8/5/2008	Ally Max SX	Metsulfuron(-methyl); tribenuron(-methyl)	30 g/L
8/5/2008	Duplosan	Mecoprop-p	1 L/ha
28/5/2008	Axial	Pinoxaden	0.25 L/ha
28/5/2008	Adigor	Methylated Rapeseed Oil	1.25 L/ha
28/5/2008	Proline	Prothioconazole	0.4 L/ha
28/5/2008	Pluton	Fenpropimorph; Flusilazole	0.3 L/ha
17/6/2008	Fandango	Fluoxastrobin; Prothioconazole	1 L/ha
17/6/2008	Bravo 500	Chlorothalonil	1 L/ha

Crop: Spring barley**Year:** 2008/2009

Date	PPP	a.i.	Rate
30/4/2009	Harmony M SX	Metsulfuron (-methyl); thifensulfuron (-methyl)	60 g/ha
30/4/2009	Duplosan	Mecoprop-p	1 L/ha
30/4/2009	Adigor	Methylated Rapeseed Oil	1 L/ha

30/4/2009	Axial	Pinoxaden	0.25 L/ha
26/5/2009	Proline	Prothioconazole	0.4 L/ha
26/5/2009	Corbel	Fenpropimorph	0.25 L/ha
16/6/2009	Moddus	Trinexapac ethyl	0.5 L/ha
16/6/2009	Bravo 500	Chlorothalonil	1 L/ha

Crop: Spring barley

Year: 2009/2010

Date	PPP	a.i.	Rate
10/5/2010	Ally Max SX	Metsulfuron(-methyl); tribenuron(-methyl)	30 g/ha
10/5/2010	Foundation	Dicamba; mecoprop-p	0.75 L/ha
21/5/2010	Grasp	Tralkoxydim	0.6 L/ha
20/5/2010	Corbel	Fenpropimorph	
15/6/2010	Fandango	Fluoxastrobin; Prothioconazole	
15/6/2010	Bravo 500	Chlorothalonil	1 L/ha

Crop: Spring barley

Year: 2010/2011

Date	PPP	a.i.	Rate
28/4/2011	Sumi-Alpha	Esfenvalerate	165 ml/ha
28/4/2011	Ally-Max SX	Metsulfuron(-methyl); tribenuron(-methyl)	32 g/ha
28/4/2011	Galaxy	Clopyralid; fluroxypyr; florasulam	1 L/ha
17/5/2011	Axial	Pinoxaden	0.25 L/ha
17/5/2011	Adigor	Methylated Rapeseed Oil	1 L/ha
17/5/2011	Punch C	Carbendazim; flusilazole	0.5 L/ha
17/5/2011	Corbel	Fenpropimorph	0.4 L/ha
10/6/2011	Proline	Prothioconazole	0.5 L/ha
10/6/2011	Bravo 500	Chlorothalonil	1 L/ha
10/6/2011	Amistar	Azoxystrobin	0.6 L/ha

Crop: Spring barley

Year: 2011/2012

Date	PPP	a.i.	Rate
7/11/2011	Sumi-Alpha	Esfenvalerate	165 ml/ha
8/3/2012	Foundation	Dicamba; mecoprop-p	1.25 L/ha
29/3/2012	Tocata	Fenpropimorph; esfenvalerate; metrafenone	1.25 L/ha
27/4/2012	Jenton	Fenpropimorph; pyraclostrobin	1 L/ha
27/4/2012	Folicur 250 EW	Tebuconazole	0.5 L/ha
1/6/2012	Zoxis	Azoxystrobin	0.5 L/ha
1/6/2012	Beam	Tebuconazole; spiroxamine	1 L/ha

Pesticide application records for FvWDa.

(No records available for 2009).

Crop: Spring wheat		*PPP now removed from market	
Year: 2003			
Date	PPP	a.i.	Rate
16/3/2003	Caliber SX	Thifensulfuron (-methyl); tribenuron (-methyl)	1 pk/7 acres
16/3/2003	CMPP	CMPP*	0.1 pt/acre
16/3/2003	CeCeCe 750	Chlormequat	0.1 pt/acre
16/3/2003	“Aphicide”	Cypermethrin	0.4 oz/acre
16/3/2003	Ultima	Maleic hydrazide; Pelargonic acid	1.6 oz/acre
16/3/2003	Forester	Cypermethrin	0.4 oz/acre
16/3/2003	Puma extra	Fenoxaprop-P	1 oz/acre
16/3/2003	Amistar	Azoxystrobin	0.4 oz/acre
16/3/2003	Sumi-Alpha	Esfenvalerate	0.4 oz/acre
16/4/2003	Cer-Aide	Chlormequat	0.15 pt/acre
16/4/2003	Caliber	Thifensulfuron (-methyl); tribenuron (-methyl)	1.4 g/acre
16/4/2003	Stellox	Bromoxynil; Ioxynil	0.1 pt/acre
16/4/2003	Moddus	Trinexapac ethyl	0.4 oz/acre
16/4/2003	Allegro Plus	Fenpropimorph; Epoxiconazole; Kresoxim Methyl	1.3 oz/acre
Crop: Sugar beet			
Year: 2004			
Date	PPP	a.i.	Rate
30/3/2004	Hussar	Iodosulfuron-methyl-sodium	10 pk/10 acres
30/3/2004	CMPP	CMPP*	1 ¼ pt/acre
30/3/2004	Opus	Epoxiconazole	3 oz/acre
30/3/2004	CeCeCe 750	Chlormequat	½ pt/acre
20/4/2004	CeCeCe 750	Chlormequat	¾ pt/acre
20/4/2004	Marina	Pendimethalin	7 oz/acre
20/4/2004	Ultima	Maleic hydrazide; Pelargonic acid	1 pt/acre
20/5/2004	Opus	Epoxiconazole	14 oz/acre
20/5/2004	Bravo 500	Chlorothalonil	10 oz/acre
20/5/2004	Corbel	Fenpropimorph	5 oz/acre
20/5/2004	Puma Extra	Fenoxaprop-P	1 pk/10 acres
20/6/2004	Amistar	Azoxystrobin	7 oz/acre
20/6/2004	Folicur 250 EW	Tebuconazole	7 oz/acre
20/6/2004	Sumi-Alpha	Esfenvalerate	3 oz/acre

Crop: Sugar beet**Year:** 2005

Date	PPP	a.i.	Rate
15/5/2005	CMPP	CMPP*	1 pk/acre
15/5/2005	Harmony SX	Thifensulfuron (-methyl)	1 pk/10 acres
15/5/2005	CeCeCe 750	Chlormequat	0.1 pt/acre
15/5/2005	Ultima	Maleic hydrazide; Pelargonic acid	0.14 pt/acre
25/5/2005	CeCeCe 750	Chlormequat	0.1 pt/acre
25/5/2005	Opus	Epoxiconazole	7 oz/acre
25/5/2005	Bravo 500	Chlorothalonil	10 oz/acre
25/6/2005	Opus	Epoxiconazole	12 oz/acre
25/6/2005	Bravo 500	Chlorothalonil	10 oz/acre
25/6/2005	Corbel	Fenpropimorph	7 oz/acre
10/7/2005	Corbel	Fenpropimorph	5 oz/acre
10/7/2005	Amistar	Azoxystrobin	5 oz/acre
10/7/2005	Proline	Prothioconazole	7 oz/acre
10/7/2005	Sumi-Alpha	Esfenvalerate	3 oz/acre

Crop: Spring barley**Year:** 2006

Date	PPP	a.i.	Rate
10/3/2006	<i>Unknown</i>	Simazine	1 pt/acre
10/4/2006	Hussar	Iodosulfuron-methyl-sodium	200 g/acre
10/4/2006	CMPP	CMPP*	1 pt/acre
10/4/2006	CeCeCe 750	Chlormequat	½ pt/acre
10/4/2006	Toppel 10	Cypermethrin	3 oz/acre
24/4/2006	CeCeCe 750	Chlormequat	¾ pt/acre
24/4/2006	Combi-Top	*	2 kg/acre
24/4/2006	Bravo 500	Chlorothalonil	10 oz/acre
10/5/2006	Proline	Prothioconazole	7 oz/acre
10/5/2006	Corbel	Fenpropimorph	5 oz/acre
10/5/2006	Opus	Epoxiconazole	5 oz/acre
20/5/2006	Bravo 500	Chlorothalonil	14 oz/acre
20/5/2006	MB 500	Carbendazim	7 oz/acre
20/5/2006	Amistar	Azoxystrobin	5 oz/acre
6/6/2006	Punch C	Carbendazim; flusilazole	8 oz/acre
10/6/2006	Bravo 500	Chlorothalonil	14 oz/acre
10/6/2006	MB 500	Carbendazim	7 oz/acre
10/6/2006	Amistar	Azoxystrobin	5 oz/acre
21/6/2006	Amistar	Azoxystrobin	7 oz/acre
21/6/2006	Folcrur 250 EW	Tebuconazole	7 oz/acre
21/6/2006	Sumi-Alpha	Esfenvalerate	3 oz/acre

21/6/2006	Epsom salts	Magnesium sulphate; heptahydrate	2 kg/10 acres
-----------	-------------	----------------------------------	---------------

Crop: Spring barley**Year:** 2007

Date	PPP	a.i.	Rate
20/5/2007	Harmony XL	Thifensulfuron (-methyl)	7 acres
20/5/2007	CMPP	CMPP*	0.1 pt/acre
20/5/2007	Punch C	Carbendazim; flusilazole	3.6 oz/acre
20/5/2007	Punch C	Carbendazim; flusilazole	7 oz/acre
20/5/2007	Bravo 500	Chlorothalonil	14 oz/acre
20/5/2007	Axial	Pinoxaden	3 oz/acre
9/6/2007	Proline	Prothioconazole	6 oz/acre
9/6/2007	Amistar	Azoxystrobin	6 oz/acre
9/6/2007	Bravo 500	Chlorothalonil	14 oz/acre
9/6/2007	Time's up weedkiller	Maleic hydrazide; pelargonic acid	¾ pt/acre

Crop: Spring barley**Year:** 2008

Date	PPP	a.i.	Rate
14/5/2008	Ally Max SX	Metsulfuron (-methyl); tribenuron (-methyl)	1 pk/10 acres
14/5/2008	CMPP	CMPP*	0.1 pt/acre
14/5/2008	Toppel 10	Cypermethrin	30 g/acre
14/5/2008	Punch C	Carbendazim; flusilazole	1 pk/120 acres
21/5/2008	Stereo 312.5 EC	Propiconazole; cyprodinil	17 ½ oz/acres
21/5/2008	Amistar	Azoxystrobin	5 oz/acres
21/5/2008	Axial	Pinoxaden	3 oz/acres
21/5/2008	Adigor	Methylated Rapeseed Oil	4 oz/acres
12/6/2008	Amistar	Azoxystrobin	5 oz/acres
12/6/2008	Proline	Prothioconazole	7 oz/acres
12/6/2008	Corbel	Fenpropimorph	5 oz/acres

Crop: Spring barley**Year:** 2010

Date	PPP	a.i.	Rate
15/04/2010	Karate zeon	lambda-Cyhalothrin	35 ml/ha
15/04/2010	Finy	Metsulfuron (-methyl)	0.1 pk/acre
15/04/2010	Fluxyr 200 EC	Fluroxypyr	¼ L/acre
15/04/2010	MCPA	MCPA	½ pt/acre
15/04/2010	CeCeCe 460	Chlormequat	2 L/ha
21/05/2010	Axial	Pinoxaden	0.2 L/ha
21/05/2010	Adigor	Methylated Rapeseed Oil	0.06 pk/acre
21/05/2010	Zephyr	Trifloxystrobin; prothioconazole	0.3 L/ha
21/05/2010	Helix	Spiroxamine; prothioconazole	¼ L/acre

2/06/2010	Bravo 500	Chlorothalonil	1 L/ha
2/06/2010	Modem	Pyraclostrobin	0.2 L/ha
2/06/2010	Helix	Spiroxamine; prothioconazole	¼ L/acre
2/06/2010	Bravo 500	Chlorothalonil	1 L/ha
Crop: Spring barley			
Year: 2011			
Date	PPP	a.i.	Rate
23/04/2011	Karate Zeon	lambda-Cyhalothrin	35 ml/ha
23/04/2011	Finy	Metsulfuron (-methyl)	0.1 pk/acre
23/04/2011	Fluxyr	Fluroxypyr	¼ L/acre
19/05/2011	Axial	Pinoxaden	0.2 L/acre
19/05/2011	Adigor	Methylated Rapeseed Oil	0.06 pk/acre
19/05/2011	Zephyr	Trifloxystrobin; prothioconazole	0.3 L/ha
19/05/2011	Helix	Spiroxamine; prothioconazole	¼ L/acre
16/06/2011	Bravo 500	Chlorothalonil	1 L/ha
16/06/2011	Modem	Pyraclostrobin	0.2 L/acre
16/06/2011	Helix	Spiroxamine; prothioconazole	¼ L/acre
16/06/2011	Bravo 500	Chlorothalonil	1 L/ha
16/06/2011	Karate Zeon	lambda-Cyhalothrin	35 ml/ha

Pesticide application records for FvPDa.

(No records available from 2010 or 2011. Contractor would have applied same products as in 2009).

Crop: Spring barley			
Year: 2009			
Date	PPP	a.i.	Rate
21/5/2009	Fandango	Fluoxastrobin; prothioconazole	0.11 L/acre
21/5/2009	Toppel 10	Cypermethrin	0.11 L/acre
21/5/2009	Ally Max SX	Metsulfuron (-methyl); Tribenuron (-methyl)	9.3 g/acre
21/5/2009	Moddus	Trinexapac ethyl	0.33 L/acre
21/5/2009	Duplosan-KV	Mecoprop-P	0.55 L/acre
2/6/2009	Axial	Pinoxaden	0.11 L/acre
2/6/2009	Adigor	Methylated Rapeseed Oil	0.55 L/acre
24/5/2009	Bravo 500	Chlorothalonil	0.55 L/acre
24/5/2009	Mastercrop barley	Fenpropimorph; epoxiconazole;	0.16 L/acre

	pack	pyraclostrobin; boscalid	
Crop: Spring barley			
Year: 2012			
Date	PPP	a.i.	Rate
16/5/2012	Biplay SX	Metsulfuron (-methyl); tribenuron (-methyl)	35 g/ha
16/5/2012	Galaxy	Clopyralid; fluroxypyr; florasulam	¾ L/ha
16/5/2012	Mortone	MCPA	¼ L/ha
1/6/2012	Proline	Prothioconazole	0.4 L/ha
1/6/2012	Credo	Chlorothalonil; picoxystrobin	1 L/ha
1/6/2012	Croplink Enhancer	Methylated Rapeseed Oil	1 L/ha
1/6/2012	Croplink Avena	Pinoxaden	¼ L/ha
4/7/2012	Proline		0.4 L/ha
4/7/2012	Credo		1 L/ha

Pesticide applications for FmWDa₁.

Crop: Spring Barley			
Year: 2008			
Date	PPP	a.i.	Rate
15/5/2008	Ally Max SX	Metsulfuron (-methyl); Tribenuron (-methyl)	1.9 oz/acre
15/5/2008	Oxytril CM	Bromoxynil; ioxynil	0.03 pts/acre
15/5/2008	Toppel 10	Cypermethrin	0.1 L/acre
15/5/2008	Proline	Prothioconazole	0.16 L/acre
15/5/2008	Corbel	Fenpropimorph	0.16 L/acre
15/5/2008	Flexity (for mildew)	Metrafenone	4.8 L/acre
11/6/2008	Opus	Epoxiconazole	½ L/acre
11/6/2008	Amistar	Azoxystrobin	½ L/acre
11/6/2008	Bravo 500	Chlorothalonil	½ L/acre
11/6/2008	Mettle	Fluoxastrobin; prothioconazole	14 oz/acre
Crop: Spring Barley			
Year: 2009			
Date	PPP	a.i.	Rate
22/5/2009	Heritage Maxx	Azoxystrobin	0.8 oz/acre
22/5/2009	Stellox	Bromoxynil; ioxynil	0.05 pt/acre
22/5/2009	Topple 10	Cypermethrin	0.8 oz/acre
22/5/2009	Amistar	Azoxystrobin	½ L/acre
22/5/2009	Punch C	Carbendazim; flusilazole	0.1 L/acre

23/5/2009	Harmony XL	Thifensulfuron (-methyl)	1 oz/acre
23/5/2009	Twin prop	Mecoprop-p	0.06 pt/acre
23/5/2009	Topple 10	Cypermethrin	1 oz/acre
23/5/2009	Proline	Prothioconazole	0.4 oz/acre
23/5/2009	Flexity	Metrafenone	¼ oz/acre
20/6/2009	Amistar Opti	Chlorothalonil; azoxystrobin	0.66 oz/ acre
20/6/2009	Punch C	Carbendazim; flusilazole	0.1 L/acre
21/6/2009	Credo	Chlorothalonil; picoxystrobin	⅓ pt/acre
21/6/2009	Rubric	Epoxiconazole	½ pt/acre

Crop: Spring Barley

Year: 2010

Date	PPP	a.i.	Rate
20/5/2010	Harmony XL	Thifensulfuron (-methyl)	1 oz/acre
20/5/2010	Galaxy	Clopyralid; fluroxypyr; Florasulam	1 oz/acre
24/5/2010	Heritage Maxx	Azoxystrobin	1 oz/acre
24/5/2010	Galaxy	Clopyralid; fluroxypyr; Florasulam	1 oz/acre
2/6/2010	Helix	Spiroxamine; prothioconazole	½ L/acre
2/6/2010	Proline	Prothioconazole	1 L/acre
2/6/2010	Tern 750 EC	Fenpropidin	1 L/acre
21/6/2010	Amistar	Azoxystrobin	½ pt/acre
21/6/2010	Bravo 500	Chlorothalonil	¾ pt/acre
21/6/2010	Proline	Prothioconazole	¼ pt/acre
21/6/2010	Amistar	Azoxystrobin	½ pt/acre
21/6/2010	Bravo 500	Chlorothalonil	¾ pt/acre
21/6/2010	Proline	Prothioconazole	¼ pt/acre

Crop: Spring Barley

Year: 2011

Date	PPP	a.i.	Rate
17/5/2011	Harmony Max SX	Metsulfuron (-methyl); Thifensulfuron methyl	0.1 oz/acre
17/5/2011	Ally Max SX	Metsulfuron (-methyl); Thifensulfuron methyl	3.3 g/acre
17/5/2011	Swipe-P	Bromoxynil; ioxynil;	0.1 L/acre

		mecoprop-p	
17/5/2011	Topple 10	Cypermethrin	0.1 L/acre
17/5/2011	Proline	Prothioconazole	0.1 L/acre
17/5/2011	Winger	Fenpropidin	0.1 L/acre
17/5/2011	Combitox Plus	Mecoprop-p	0.2 L/acre
14/6/2011	Amistar Opti	Chlorothalonil;	0.6 L/acre
		Azoxystrobin	
14/6/2011	Proline	Prothioconazole	0.16 L/acre
15/6/2011	Siltra Xpro	Prothioconazole;	0.25 L/acre
		bixafen	
15/6/2011	Bravo 500	Chlorothalonil	0.4 L/acre

Pesticide applications for FmWDa₂.

Crop: Spring Barley (Sebastian malt)

Year: 2008

Date	PPP	a.i.	Rate
6/5/2008	Cleanrun Pro	MCPA; mecoprop-p	1 pk/8acres
6/5/2008	Optica	Mecoprop-p	¾ pt/acre
6/5/2008	Proline	Prothioconazole	4 ½ fl.oz/acre
6/5/2008	Tandus	Fluroxypyr	1 ¾ floz/acre
6/5/2008	Sitrine	Cypermethrin	3 ½ floz/acre
8/6/2008	Opus	Epoxiconazole	10 floz/acre
8/6/2008	Amistar	Azoxystrobin	15 floz/acre

Crop: Spring Barley (Sebastian malt)

Year: 2009

Date	PPP	a.i.	Rate
22/5/2009	Optica	Mecoprop-p	1 pt/acre
22/5/2009	Proline	Prothioconazole	¼ pt/acre
22/5/2009	Topple 10	Cypermethrin	1 L/acre
12/6/2009	Amistar	Azoxystrobin	¼ pt/acre
12/6/2009	Cer-Aide	Chlormequat	½ pt/acre
12/6/2009	Empire 20	Chlorpyrifos	1 pack/7 acres
12/6/2009	Bravo 500	Chlorothalonil	1 pt/acre

Crop: Spring Barley (Sebastian malt)**Year:** 2010

Date	PPP	a.i.	Rate
15/5/2010	Harmony Max SX	Metsulfuron (-methyl); Thifensulfuron methyl	400 g/14 acres
15/5/2010	Galaxy	Clopyralid; fluroxypyr; Florasulam	0.7 L/Ha
15/5/2010	Proline	Prothioconazole	0.35 L/Ha
11/6/2010	Topple 10	Cypermethrin	1 L/acre
11/6/2010	Allegro Plus	Fenpropimorph; Epoxiconazole; Kresoxim Methyl	1 L/Ha
11/6/2010	Bravo 500	Chlorothalonil	1 L/Ha

Crop: Spring Barley (Cocktail malt)**Year:** 2011

Date	PPP	a.i.	Rate
19/5/2011	Harmony Max SX	Metsulfuron (-methyl); Thifensulfuron methyl	10 pks/acre
19/5/2011	Duplosan KV	Mecoprop-p	¾ pt/acre
19/5/2011	Proline	Prothioconazole	4 ½ floz/acre
19/5/2011	Jenton	Fenpropimorph; Pyraclostrobin	10 floz/acre
16/6/2011	Bravo 500	Chlorothalonil	14 floz/acre
16/6/2011	Siltra Xpro	Prothioconazole; bixafen	10 floz/acre

Appendix 3

Borehole logs

Artesian borehole well at FvPDa:

BOREHOLE CONSTRUCTION		SAMPLE		SOIL VAPOUR (ppm)	GROUNDWATER	DEPTH (m)	GEOLOGY	BOREHOLE NUMBER: <u>MOOLE BH</u> <u>MACAMORE</u>		Page 1 of 1	
NUMBER	TYPE	NUMBER	TYPE					DRILLING DATES: <u>5-7/10/09</u>	DRILLING METHOD: <u>ROTARY AIR</u>	DRILLER: <u>J.S. DRILLING</u>	BOREHOLE DIAMETER: <u>84</u>
								DESCRIPTION	COMMENTS		
								0-1.2m	macamore topsoil dry		
								1.2-2.5m	gravel imbedded within clay becoming increasingly wetter	@2.5m static H ₂ O	
								2.5-4.0m	gray colour very wet, clayey		
								4.0-6.7m	dense, dark, dry clay	@6.7m sandy lens	
								6.7-9.5m	thicker, denser, clay. water content increasing.	@9.4m minor H ₂ O strike	
								9.5-10.5m	gravel & shales		
								10.5-11.9m	weathered bedrock black & white shale	MASSIVE H ₂ O STRIKE (ARTESIAN)	
								Stopped drilling as risk of flooding field!			
LOCATION / NOTES: 								LEGEND ☒ Disturbed Sample ☐ Undisturbed Sample * Headspace Analysis + Down Borehole Analysis ~ Groundwater Table ▽ Perched Water Table		BOREHOLE LOG JOB TITLE: <u>MULTILEVEL PIEZOMETERS</u> LOCATION: <u>BALLYCAREW</u> CLIENT: REF No: JOB No:	

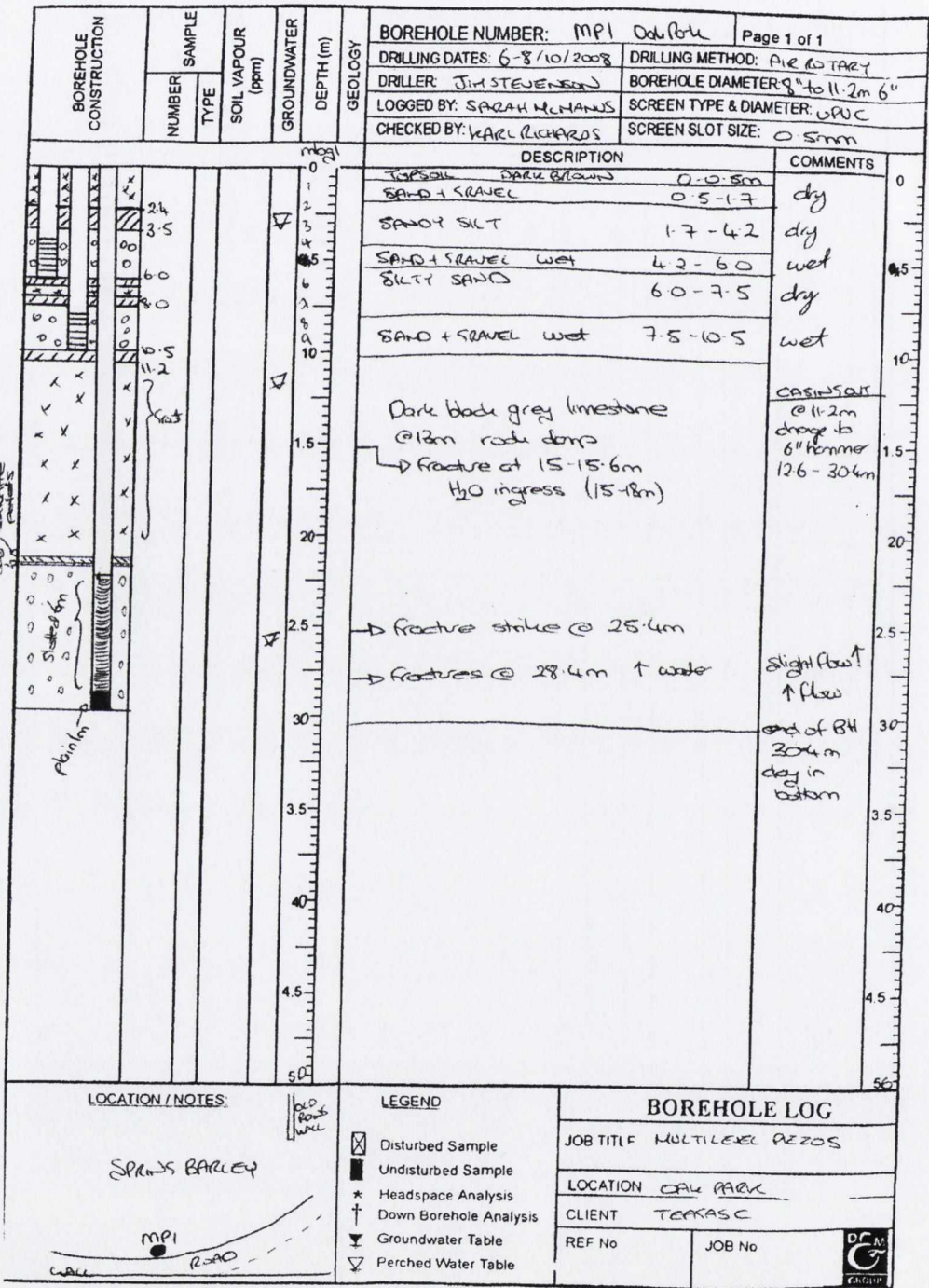
Lower BH at FvWDa:

BOREHOLE CONSTRUCTION		SAMPLE		SOIL VAPOUR (ppm)	GROUNDWATER	DEPTH (m)	GEOLOGY	BOREHOLE NUMBER: COURSE BOTTOM		Page 1 of 1	
NUMBER	TYPE	LOGGED BY: SALEM NCHAMUS	CHECKED BY:					DRILLING DATES: 15/10/09	DRILLING METHOD: ROTARY AIR	BOREHOLE DIAMETER: 8"	SCREEN TYPE & DIAMETER: 60mm HOPE
								DESCRIPTION	COMMENTS		
								0-0.5m = Chiroche topsoil			
								0.5-4.0 = Gravels & pebbles (@0.75m = chips of rhyolite 2-3.1m = quartz fragments 3.1-4.0m = lighter colour, larger fragments).			
								4.0-5.7m = Very dry & dusty - air hammer crushing rock. pieces of dark grey & burnt orange.			
								5.7-10.5m = highly weathered rhyolite (soft to drill).			
								10.5-15.5m = more gravels, becoming darker with depth.			
								15.5-17.6m = Increasing wetness of dgs. veg. cohesive. water @ 16.2m.			
								@17.6m end of borehole			
LOCATION / NOTES:								LEGEND ☒ Disturbed Sample ■ Undisturbed Sample * Headspace Analysis † Down Borehole Analysis ▽ Groundwater Table ▽ Perched Water Table		BOREHOLE LOG JOB TITLE: RAIL CANE W. MULTIPIEZOMETERS LOCATION: RAIL CANE W. WEIR CLIENT: REF No: JOB No: DR: G	

Upper BH at FvWDa:

BOREHOLE CONSTRUCTION		SAMPLE		SOIL VAPOUR (ppm)	GROUNDWATER	DEPTH (m)	GEOLOGY	BOREHOLE NUMBER: <u>CLOPPROCHE TOP</u>		Page 1 of 1	
NUMBER	TYPE	NUMBER	TYPE					DRILLING DATES: <u>16/19/01/2009</u>	DRILLING METHOD: <u>ROTARY AIR</u>		
								DRILLER: <u>J.S. DRILLING</u>	BOREHOLE DIAMETER: <u>8"</u>		
								LOGGED BY: <u>SARAH McHANE</u>	SCREEN TYPE & DIAMETER: <u>60mm HOPE</u>		
								CHECKED BY:	SCREEN SLOT SIZE: <u>0.5mm</u>		
								DESCRIPTION	COMMENTS		
0m						0	TOP SOIL	0-1.5m = stony claystone ssil. deep orange brown. may contain rock fragments		0	
1.5m						1.5		1.5-2.0m = lighter color + rock present		0.5	
3m						3		2.0-3.0m = dry, grey, weathered rhyolite.	changed hammer & end of gauge @ 3m.	1	
4m						4		3.0-4.0m = dark lens		1.5	
5m						5		4-4.5m = pebbles, lighter grey		2	
6m						6		4.5-6.0m = lightest grey yet, dry & stony.		2.5	
7.5m						7.5		6.0-8.5m = darker & pebbly.		3	
8.5m						8.5		8.5-13.0m =	@ 8.1m had bad	3.5	
						10		water content increasing.	@ 9.6m had bad	4	
						12		Significant water find.		4.5	
13m						13			@ 13m = end of borehole	5	
LOCATION / NOTES:								LEGEND		BOREHOLE LOG	
								☒ Disturbed Sample ☐ Undisturbed Sample ☐ Headspace Analysis ☐ Down Borehole Analysis ☐ Groundwater Table ☐ Perched Water Table		JOB TITLE <u>BALUCAN NEW MULTILEVEL RECONSTRUCTION</u> LOCATION <u>WELFORD</u> CLIENT REF No JOB No	

MP1 (Upper BH) at I/KWda:



MP2 (Lower BH) at I/KWDa:

STARTED DRILLING @ 12pm 9/10/08.
MP2 FINISHED @ 5:30pm 14/10/08

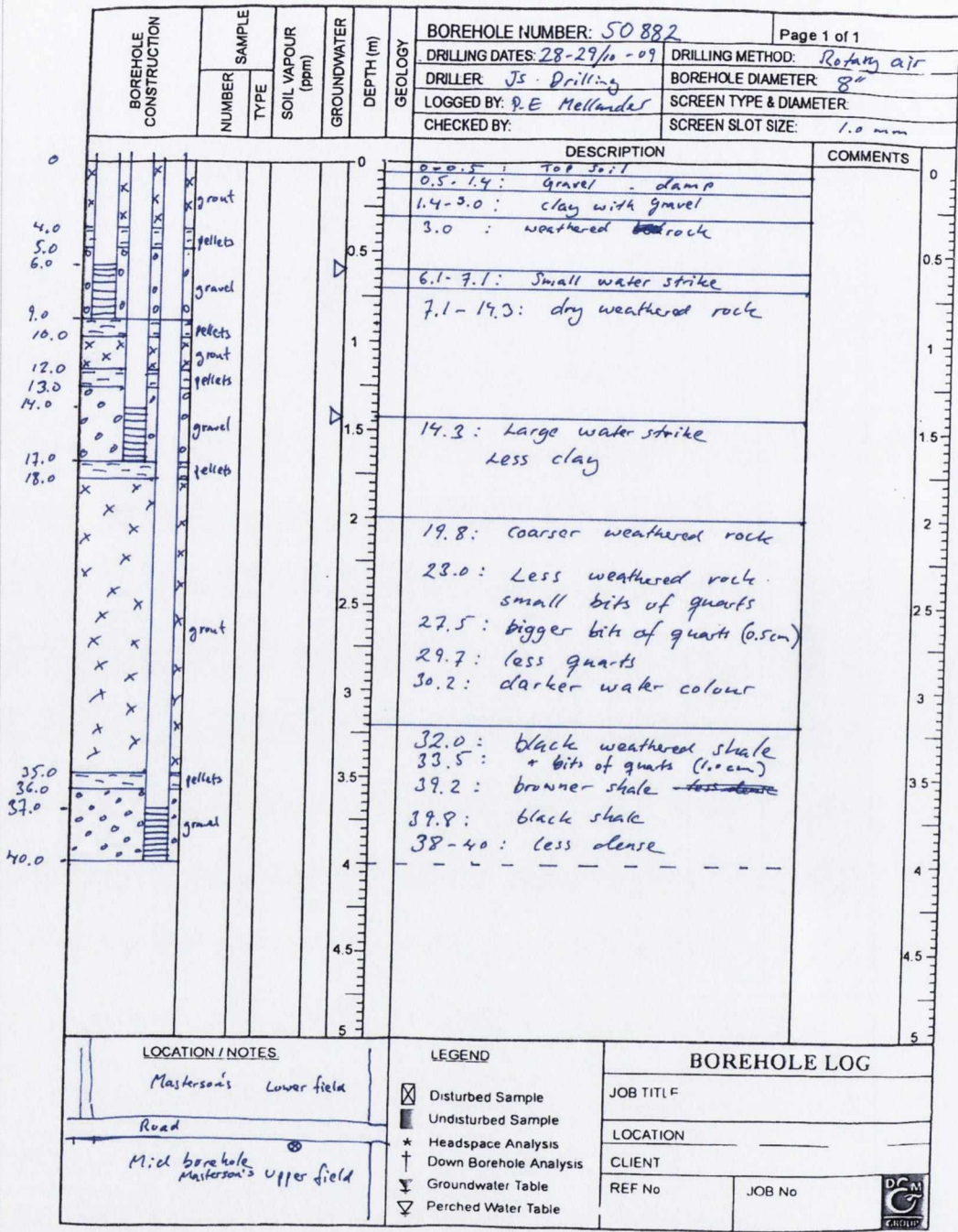
MP2a at I/KWDa:

Logging done by: Alina Premrov
Borehole number: **P17**
Location: Sawmills Field, Oak Park, Carlow
Date drilled: 04.10.2006; Installed: 04.10.2006

DRILLING DEPTH [m]	STRATA [maOD]	GRAPHIC	DESCRIPTION	INSTALLATIONS**
			Topsoil:	Casing above ground: 1.17 m
0	Ground level 58.7 [maOD] Topsoil approx. 0.4 m 58.3 [maOD]		-slightly gravelly SAND-	Ground level: 58.7 [maOD]
1.20 m			-SAND-	Bentonite from 1.70 m below ground level to 2.20m.
	SAND		-SAND- -SAND (fine sand)- -slightly gravelly SAND-	Gravel from 2.20 m below ground level to bottom
2.40 m				
			-gravelly SAND- -SAND - -SAND with few stones-	Starting perforated: 2.84 m below ground level or 55.9 [maOD]
3.60 m				
	SAND		-SAND with few stones- -SAND with few stones (probably slightly silty/clayey) -	Bottom: 4.84 m below ground level or 53.9 [maOD]
4.80 m	53.9 [maOD]			
	SILT/CLAY		-very sandy SILT/CLAY with few stones-	
5.80 m	Drilling depth: 52.9 [maOD]			

** 4 non-perforated and 2 perforated piezometer pipes.

Middle BH at FmW_{D1}:

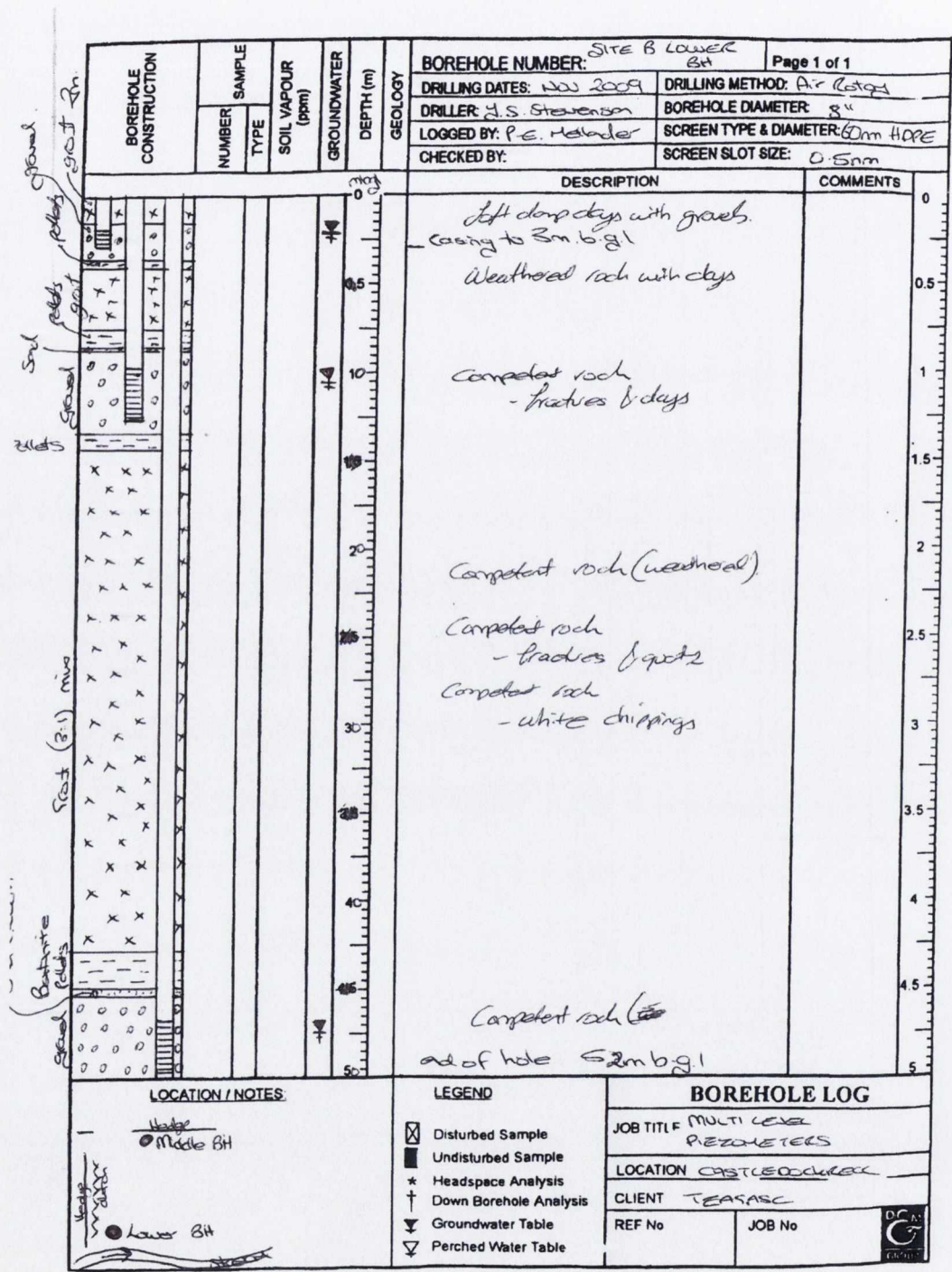


Upper BH at FmWDA₁:

BOREHOLE CONSTRUCTION		SAMPLE		SOIL VAPOUR (ppm)	GROUNDWATER	DEPTH (m)	GEOLOGY	BOREHOLE NUMBER: 50883		Page 1 of 1
NUMBER	TYPE							DRILLING DATES: 30/10 & 2/11-09	DRILLING METHOD: Rotary air	
								DRILLER: J.S. Drilling	BOREHOLE DIAMETER: 8"	
								LOGGED BY: P.E. Mellander	SCREEN TYPE & DIAMETER:	
								CHECKED BY:	SCREEN SLOT SIZE: 1.0 mm	
							0	0.0-0.4: TOP SOIL	COMMENTS	0
							0.5	0.4-1.2: Brown clay with gravel		0.5
							1.0	1.2: Weathered rock white colour		1.0
							1.5			1.5
							2.0	16.1 Small water strike		2.0
							2.5	18.0 More water		2.5
							3.0			3.0
							3.5	23.0 Sandy weathered materials		3.5
							4.0			4.0
							4.5	37.0 Coarser weathered rock with bits of quartz		4.5
							5.0			5.0

LOCATION / NOTES		LEGEND		BOREHOLE LOG	
Top of Masterson's upper field		☒ Disturbed Sample ☐ Undisturbed Sample * Headspace Analysis † Down Borehole Analysis ∇ Groundwater Table ∇ Perched Water Table		JOB TITLE LOCATION CLIENT REF No JOB No	
Upper borehole 					

Lower BH at FmWDa₂:



Middle BH at FmWDa₂:

BOREHOLE CONSTRUCTION		SAMPLE NUMBER	TYPE	SOIL VAPOUR (cm)	GROUNDWATER (cm)	DEPTH (m)	GEOLOGY	BOREHOLE NUMBER: <u>Six E. Mucos est</u>			Page 1 of 1	
DRILLING DATES: <u>Nov 2009</u>	DRILLING METHOD: <u>pie direct</u>							BOREHOLE DIAMETER: <u>8"</u>	LOGGED BY: <u>P.E. Winkler</u>	SCREEN TYPE & DIAMETER: <u>6mm type</u>	SCREEN SLOT SIZE: <u>0.5mm</u>	
								DESCRIPTION	COMMENTS			
								Top soils clay & gravel Weathered rock Compacted rock - fractured with calcite logs Compacted rock - fractured with calc & clay. - Ending to 9m. Compacted rock - dry fractured with clays Compacted rock - fractured clay Compacted rock - fractured dry. Limestone droppings with clays. Limestone droppings - more fractured Limestone droppings - fractured km bgl = end of hole.				
LOCATION / NOTES								LEGEND		BOREHOLE LOG		
<u>hedge</u> ● <u>mainline est</u> <u>Dist</u> ● <u>km bgl</u>								☒ Disturbed Sample ☐ Undisturbed Sample * Headspace Analysis † Down Borehole Analysis ▽ Groundwater Table ▽ Perched Water Table		JOB TITLE: <u>MULTI LEVEL PERIMETERS</u> LOCATION: <u>CARLE PLACE</u> CLIENT: <u>TEAFASC</u> REF No: JOB No:		

Upper BH at FmWDA₂:

BOREHOLE CONSTRUCTION		SAMPLE NUMBER	TYPE	SOIL VAPOUR (ppm)	GROUNDWATER	DEPTH (m)	GEOLOGY	BOREHOLE NUMBER: <u>SITE 3 UPPER BH</u>		Page 1 of 1	
								DRILLING DATES: <u>Nov 2008</u>		DRILLING METHOD: <u>Aug 2008</u>	
								DRILLER: <u>J. S. Delaney</u>		BOREHOLE DIAMETER: <u>2"</u>	
								LOGGED BY: <u>P. E. M. M. M.</u>		SCREEN TYPE & DIAMETER: <u>2.5m 40PS</u>	
								CHECKED BY:	SCREEN SLOT SIZE: <u>2.5mm</u>		
								DESCRIPTION	COMMENTS		
								clay & gravel - drip weathered rock with clay		0	
								→ clay to 6.5m log! weathered rock - white with clay		0.5	
								compacted rock - with clay		1	
										1.5	
								compacted rock - fractured		2	
										2.5	
								end of hole = 3.2m log!		3	
										3.5	
										4	
										4.5	
										5	
LOCATION / NOTES: <u>upper BH</u>								LEGEND		BOREHOLE LOG	
								☒ Disturbed Sample		JOB TITLE: <u>MULTI LEVEL</u>	
								☐ Undisturbed Sample		LOCATION: <u>Piedmont</u>	
								* Headspace Analysis		CLIENT: <u>TRASAC</u>	
								↑ Down Borehole Analysis		REF No: JOB No:	
								☐ Groundwater Table			
								☐ Perched Water Table			

Appendix 4

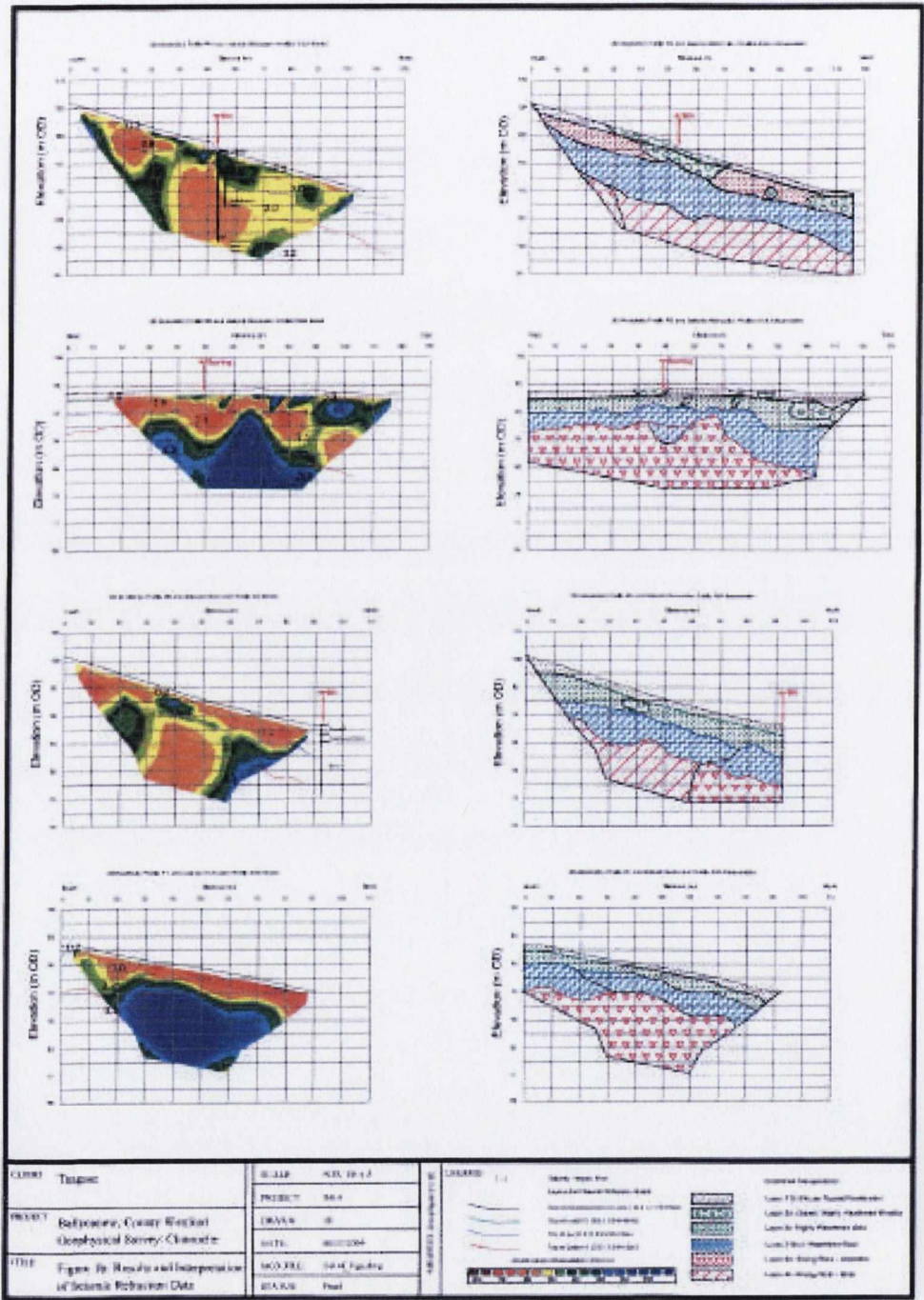
Phi sizes and corresponding soil classification.

Phi Ø	µm	Category
-1	2000	V. Coarse Sand
-0.5	1414.21	V. Coarse Sand
0	1000	Coarse Sand
0.5	707.1	Coarse Sand
1	500	Medium Sand
1.5	353.55	Medium Sand
2	250	Fine Sand
2.5	176.78	Fine Sand
3	125	V. Fine Sand
3.5	88.39	V. Fine Sand
4	62.5	Coarse Silt
4.5	44.19	Coarse Silt
5	31.25	Medium Silt
5.5	22.1	Medium Silt
6	15.63	Fine Silt
6.5	11.05	Fine Silt
7	7.81	V. Fine silt
7.5	5.52	V. Fine silt
8	3.9	Clay
8.5	2.76	Clay
9	1.95	Clay
9.5	1.38	Clay

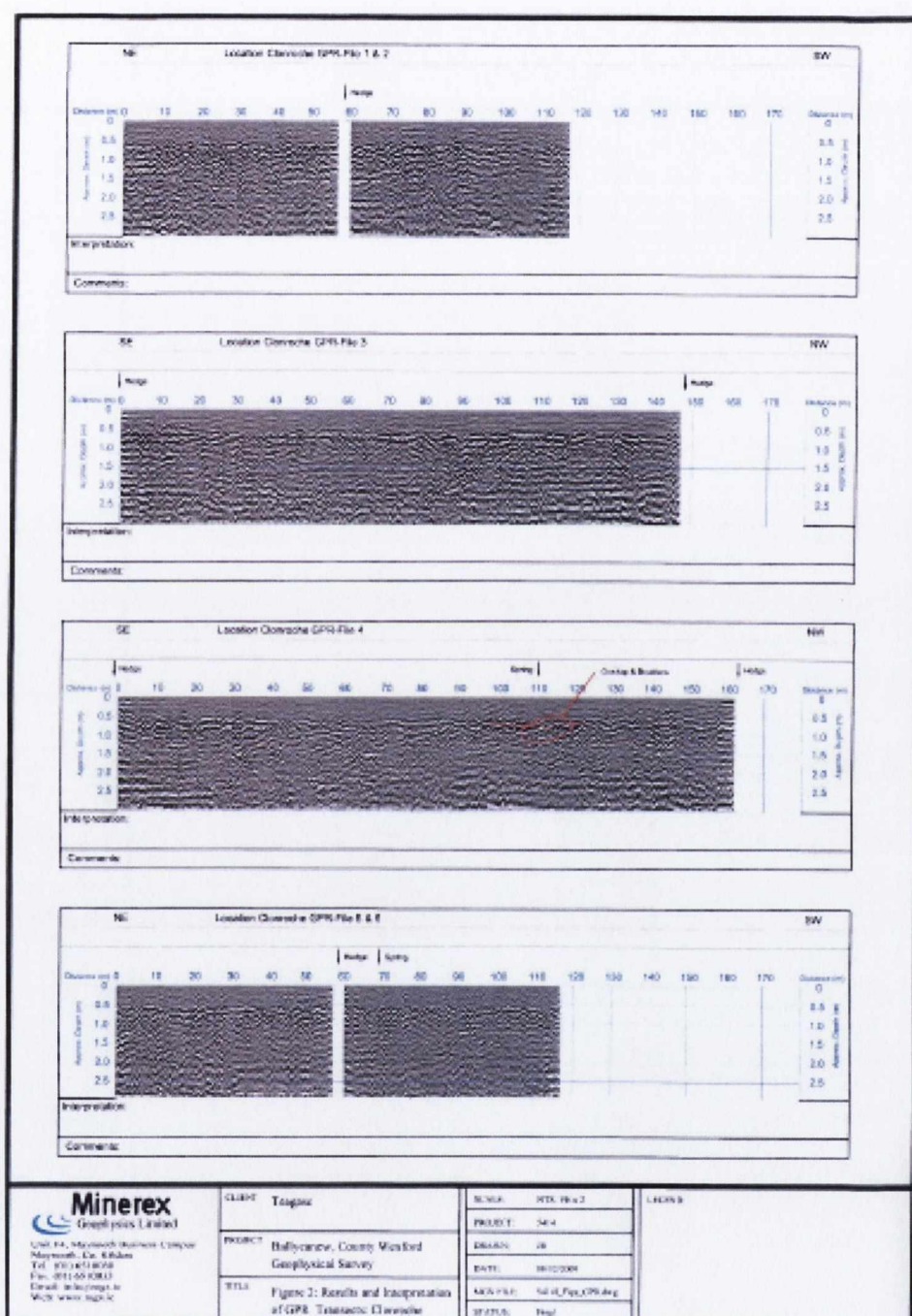
Appendix 5

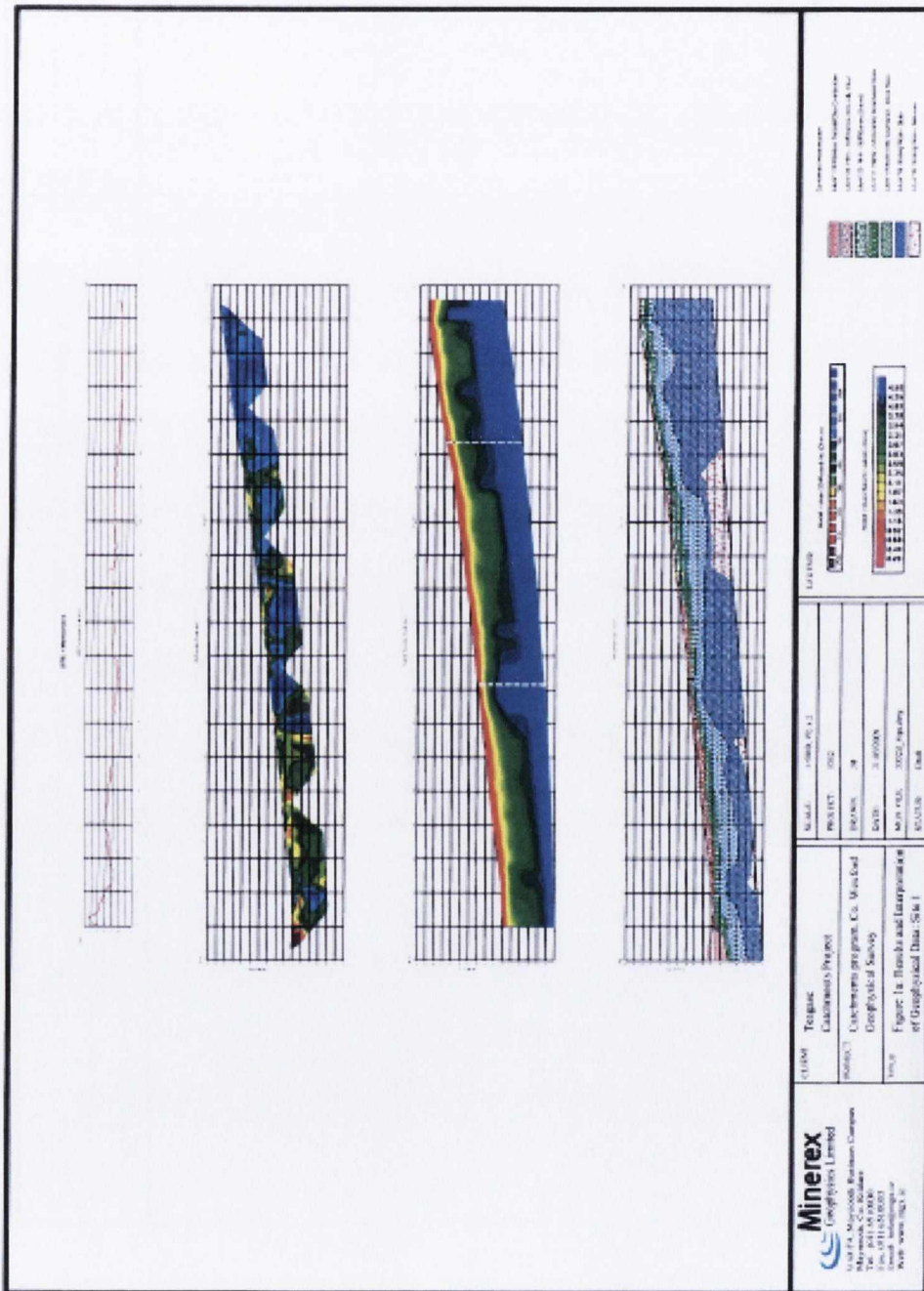
Geophysical surveys

Results & interpretation for FvWDa.

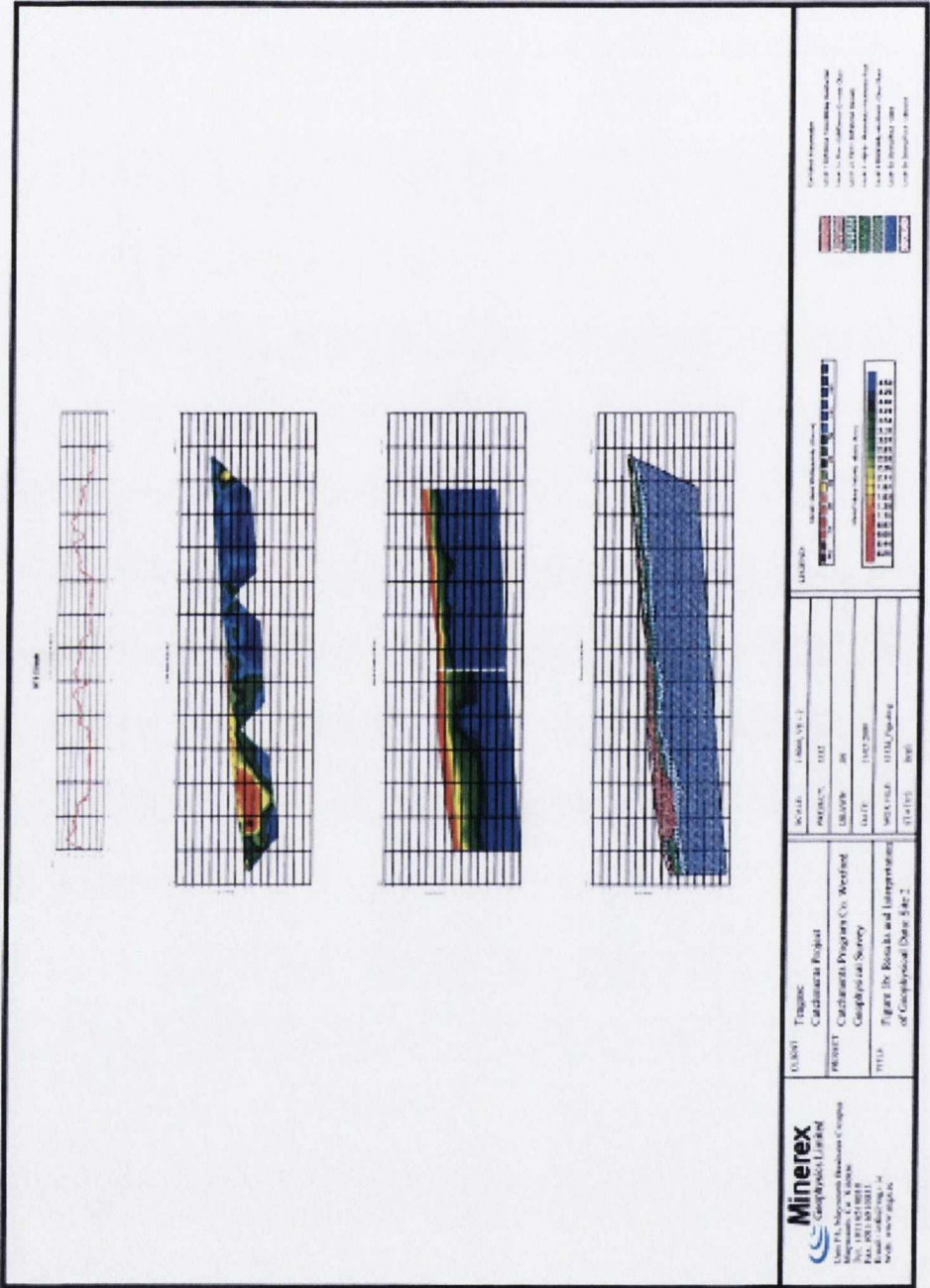


Results & interpretation of ground penetrating radar (GPR) at FvWDa.

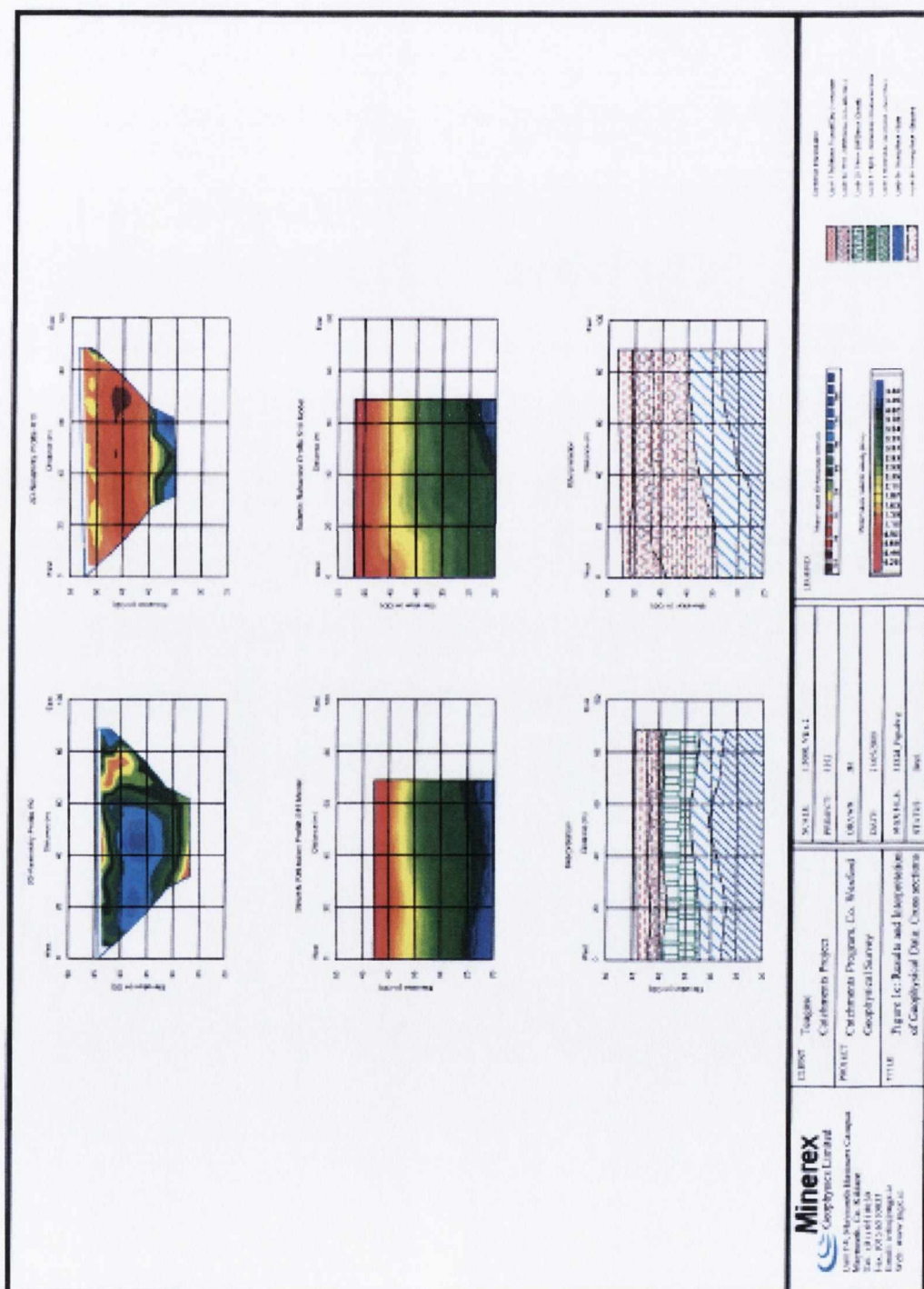


2D-resistivity for FmWDA₁.

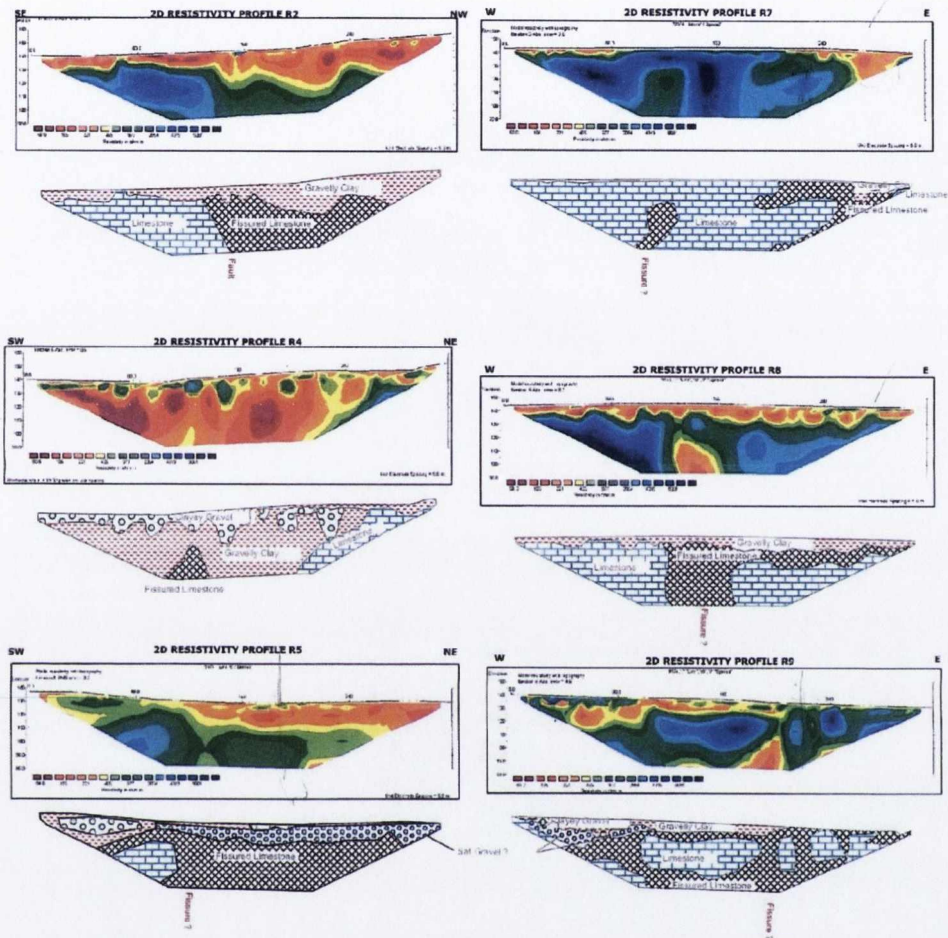
2D-resistivity for FmWda₂.



2D-resistivity, seismic refraction and interpretation for FmWDa. R9 & S19 represent site 1 while R10 & S18 represent site 2.

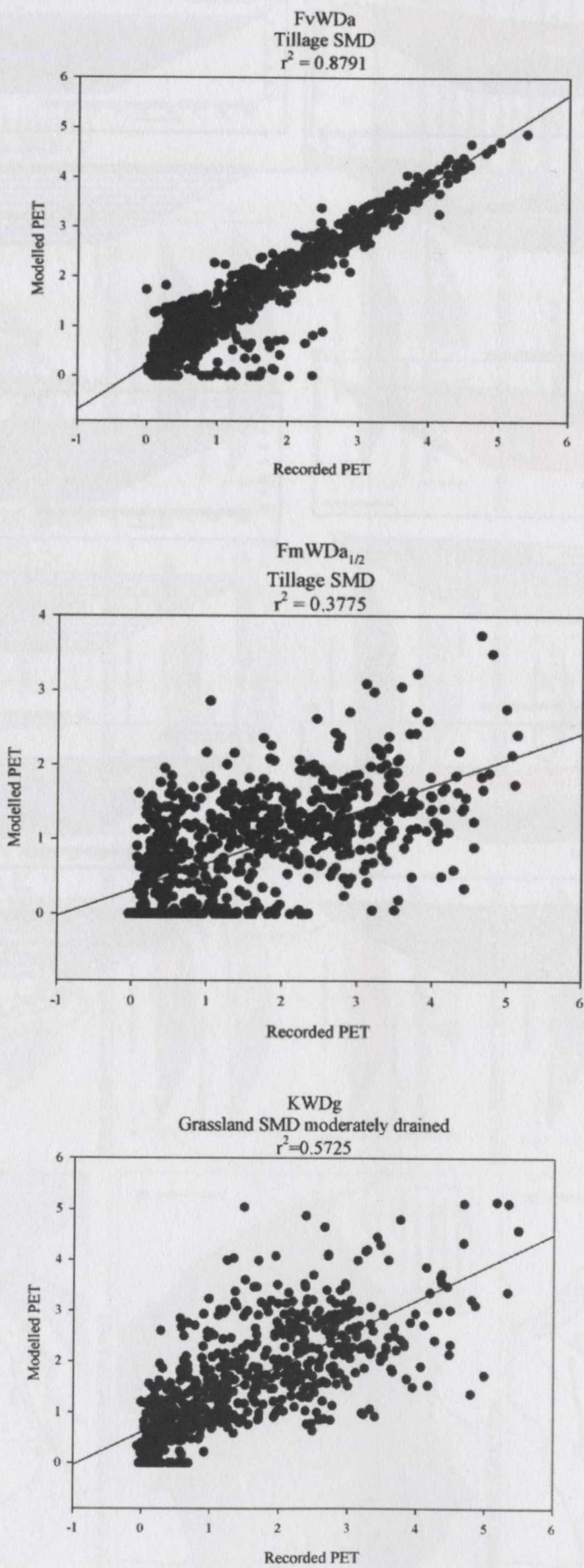


Transect geophysics for KWDa.



Appendix 6

Coefficients of variation (r^2) between modelled potential evapotranspiration (PET) and recorded PET



Site	MP	pH		ORP (mV)		RDO (mg/L)		Conductivity (µS/cm)		Turbidity (NTU)		Temperature (°C)	
		Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD
KWDg	Sp.	7.3	0.2	126.6	109.4			559.3	41.6	0.0	0.0	10.8	3.4
KWDa	Boiling Sp.	7.4	0.3	189.2	64.9	7.2	2.6	491.4	99.9	15.7	29.4	10.5	0.6
KWDa	Sp. under bridge	7.6	0.3	196.5	38.0	8.5	0.7	402.7	20.1	51.2	83.0	10.3	0.1
I/KWDa	MP2 shallow	7.6	0.2	152.9	61.2	7.4	1.7	479.9	59.5	393.4	273.3	11.2	2.5
I/KWDa	MP2 interface	7.9	0.5	108.7	83.8	6.7	1.9	354.5	129.3	249.3	288.5	12.0	2.5
I/KWDa	MP2 deep	7.5	0.3	121.7	91.9	6.7	2.4	466.1	79.9	154.5	225.9	12.0	2.8
I/KWDa	MP1 shallow	7.4	0.2	154.1	30.8	9.0	5.0	470.2	92.1	213.4	245.8	11.2	2.1
I/KWDa	MP1 interface	7.5	0.4	152.9	72.2	10.1	9.7	414.3	136.7	349.8	407.3	11.3	2.8
I/KWDa	MP1 deep	7.6	0.3	148.9	76.5	54.6	210.0	453.6	114.3	95.7	216.2	12.1	2.6
FvWDa	Lower BH	6.4	0.4	170.6	85.9	8.5	1.3	170.0	50.5	252.2	286.3	11.0	2.6
FvWDa	Upper BH	6.6	0.6	161.8	80.3	8.0	2.2	215.3	85.1	384.6	334.7	11.3	2.6
FvWDa	Lower Sp.	6.5	0.3	187.0	55.0	9.2	1.1	159.8	24.2	168.0	274.2	10.2	1.2
FvWDa	Upper Sp.	6.4	0.5	171.9	74.8	8.4	1.0	125.0	51.2	134.6	365.5	12.9	8.2
FvWDa	House Sp.	6.3	0.4	173.0	106.1	7.8	1.3	107.1	7.0	39.9	63.6	11.4	1.6
FvPDa	Artesian BH	7.3	0.4	-48.4	57.7	1.9	1.6	171.9	42.9	44.3	154.2	11.2	0.7
FvPDa	1b	7.4	0.2	-63.1	91.3	4.0	2.7	285.3	55.1	131.4	186.8	11.9	2.2
FvPDa	2b	6.8	0.3	9.6	53.9	3.5	2.5	162.8	15.7	170.2	207.5	11.5	1.6
FvPDa	4b	7.6	0.2	22.4	37.7	4.9	1.6	251.2	80.2	415.8	582.5	12.2	3.8
FvPDa	5b	7.8	0.1	-87.4	89.2	26.8	97.7	303.0	39.3	199.8	135.9	12.3	2.1
FvPDa	7b	7.3	0.3	-39.4	61.2	4.2	2.9	411.0	96.3	212.1	144.2	12.3	2.6
FvPDa	8b	7.5	0.2	-36.9	73.6	23.9	92.1	489.4	57.0	355.1	179.1	11.8	2.4
FvPDa	9a	7.8		2.5	18.5	4.8	0.4	308.4	15.4	615.9	135.4	14.2	2.2
FvPDa	9b	7.7	0.3	-71.8	93.4	3.9	2.7	362.1	184.9	372.3	606.1	11.8	2.6
FvPDa	Drain	6.5	0.4	74.0	51.5	7.7	0.9	133.2	19.0	95.9	347.3	11.2	1.3
FvPDa	Stream	7.7	0.3	-7.6	30.4	9.8	1.1	217.6	24.5	12.1	16.8	10.7	3.1
FmWDa1	Upper BH shallow	6.7	0.5	159.3	49.7	9.0	3.0	176.7	65.4	455.0	322.9	8.6	1.6
FmWDa1	Upper BH interface	6.8	0.9	159.6	58.4	10.0	1.1	175.9	76.1	515.1	995.0	8.8	1.2
FmWDa1	Upper BH deep	6.5	0.6	150.1	71.0	9.2	2.8	169.2	46.5	88.1	128.0	10.0	1.7
FmWDa1	Middle BH shallow	6.6	0.5	173.0	95.8	9.7	1.6	184.8	63.8	406.7	650.8	10.4	1.9
FmWDa1	Middle BH interface	6.4	0.3	176.2	86.9	9.6	1.0	170.3	33.2	399.6	578.2	10.9	1.9
FmWDa1	Middle BH deep	6.5	0.6	156.4	82.6	8.7	2.3	174.7	60.8	151.0	222.6	12.0	3.4
FmWDa1	Lower BH shallow	6.3	0.4	162.4	77.5	9.3	1.5	167.4	44.8	350.7	456.6	11.3	1.9
FmWDa1	Lower BH interface	6.2	0.5	153.5	79.3	9.1	1.6	172.0	34.2	52.9	56.9	11.2	2.2
FmWDa1	Lower BH deep	6.5	0.6	134.2	78.3	9.0	1.9	208.8	44.7	52.4	76.5	11.0	1.7
FmWDa1	Stream	6.8	0.4	91.8	50.7	9.7	0.8	188.7	28.3	23.1	47.2	10.8	2.2
FmWDa2	Upper BH shallow	6.9	0.6	57.0	75.0	6.6	1.6	211.0	7.1	36.5	19.7	9.3	1.3
FmWDa2	Upper BH interface	6.8	0.2	152.4	101.5	8.2	1.3	226.5	40.2	159.2	274.3	10.4	3.4
FmWDa2	Upper BH deep	6.6	0.4	137.2	99.1	8.3	1.7	225.9	37.5	60.9	99.5	11.5	2.7
FmWDa2	Middle BH shallow	7.1	0.4	112.6	99.4	6.6	2.8	274.9	69.4	566.7	687.1	10.0	2.9
FmWDa2	Middle BH interface	6.9	0.4	132.5	94.2	7.6	2.2	210.6	53.6	91.5	169.5	11.7	2.6
FmWDa2	Middle BH deep	6.9	0.4	127.2	105.5	8.1	2.5	227.4	45.8	55.2	146.6	11.5	2.4
FmWDa2	Lower BH shallow	6.8	0.4	167.2	108.8	5.3	2.3	197.8	44.8	247.4	435.9	10.8	2.9
FmWDa2	Lower BH interface	6.7	0.4	164.3	80.4	6.0	3.2	210.7	55.0	231.8	410.7	11.2	2.2
FmWDa2	Lower BH deep	6.7	0.5	132.4	109.0	6.2	2.7	202.8	41.5	26.3	46.1	11.4	2.2
FmWDa2	Stream	7.3	0.3	57.9	54.1	8.3	2.8	201.5	38.9	10.9	18.4	10.2	1.9

Appendix 7

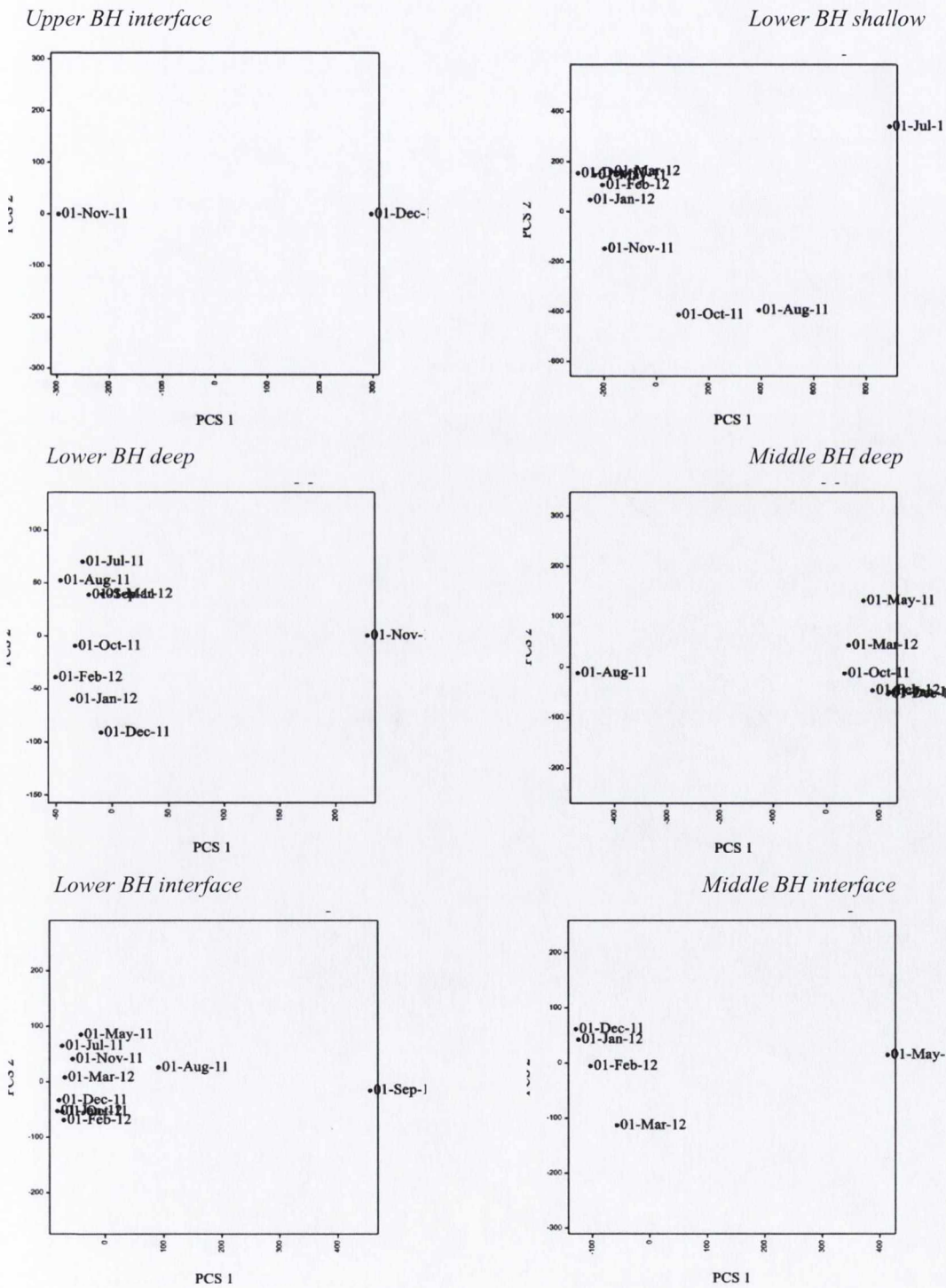
Summary of hydrochemical variables for each monitoring point (MP).

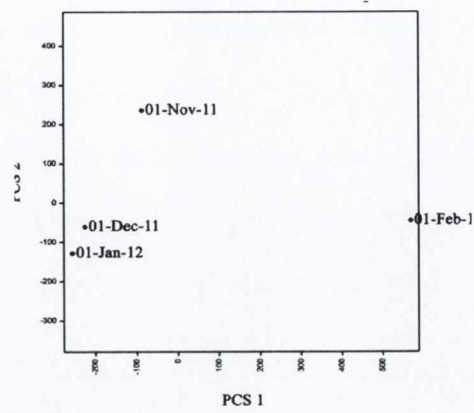
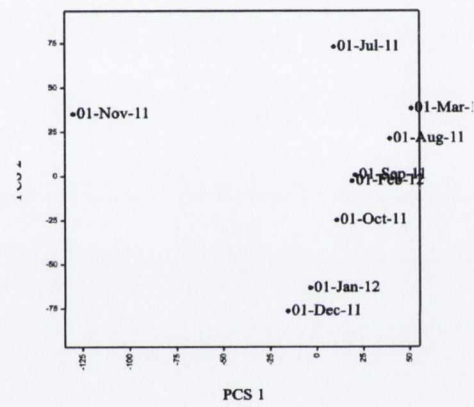
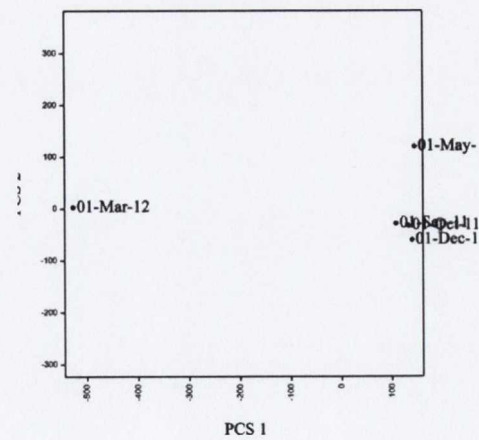
Site	MP	Ca (mg/L)		Cu (µg/L)		Fe (µg/L)		K (mg/L)		Mg (mg/L)		Mn (µg/L)		Na (mg/L)		Zn (µg/L)		Bicarbonate alkalinity as CaCO ₃ (mg/L)	
		Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD
KWDg	Sp.	72.6	53.5	0.4	1.1	10.5	19.3	2.2	1.4	3.3	2.7	1.0	3.4	6.8	3.3	0.2	0.5	348.9	46.4
KWDa	Boiling Sp.	66.1	55.5	1.0	1.8	8.3	23.4	1.9	1.4	8.0	7.4	0.5	1.3	5.6	2.8	0.3	0.9	317.3	84.8
KWDa	Sp. under bridge	58.3	49.7	0.1	0.4	15.0	32.7	1.4	0.9	4.1	4.4	0.4	1.2	5.0	4.0	0.0	0.0	293.4	32.7
KWDa	MP2 shallow	72.4	42.3	0.7	1.1	9.3	12.1	4.5	4.1	7.7	4.7	0.5	1.1	5.5	2.7	0.0	0.2	247.9	55.3
KWDa	MP2 interface	48.9	37.6	0.7	1.1	54.7	151.1	1.5	1.2	3.8	4.3	92.1	375.4	11.3	7.9	0.1	0.3	179.9	103.4
KWDa	MP2 deep	51.1	38.6	0.4	0.9	27.3	66.7	2.5	2.9	4.2	5.6	20.4	87.1	11.3	9.3	0.0	0.0	183.2	125.9
KWDa	MP1 shallow	75.1	46.9	0.5	1.0	241.2	527.9	1.2	0.9	8.2	7.2	41.8	97.0	6.2	3.6	0.7	1.8	309.6	47.8
KWDa	MP1 interface	64.4	40.9	0.5	0.8	95.1	268.5	1.0	0.7	5.1	4.3	10.7	40.6	5.7	4.0	0.3	1.4	250.1	84.3
KWDa	MP1 deep	64.1	44.4	0.5	0.8	29.7	70.4	1.4	1.1	6.1	4.7	3.0	10.5	5.8	2.6	0.0	0.2	249.8	63.7
FvWda	Lower BH	12.9	14.1	0.4	0.8	233.5	485.5	1.3	0.9	3.9	3.3	32.1	54.2	8.5	4.4	1.1	1.9	33.6	14.6
FvWda	Upper BH	15.4	15.1	1.7	5.6	339.5	624.6	1.2	0.8	4.6	4.2	54.7	167.4	8.7	4.6	2.2	4.4	45.7	25.8
FvWda	Lower Sp.	10.8	9.6	0.3	1.0	12.4	19.2	1.6	0.9	3.6	3.6	26.1	65.6	8.5	5.2	0.4	0.8	29.5	3.8
FvWda	Upper Sp.	4.1	4.3	0.0	0.0	19.6	49.3	1.5	1.0	2.9	3.2	0.9	2.1	7.0	4.2	0.3	0.7	13.3	4.9
FvWda	House Sp.	4.6	3.9	0.3	0.7	24.2	54.5	1.2	0.8	2.5	2.4	1.2	4.3	8.3	4.6	0.4	0.8	21.2	5.2
FvPda	Artesian BH	21.2	21.7	0.0	0.0	256.8	331.4	1.0	0.8	4.3	3.2	206.1	272.6	11.5	5.5	0.0	0.0	102.5	8.4
FvPda	1b	21.4	17.9	0.4	0.9	193.3	423.5	1.7	1.7	9.3	8.3	868.6	716.5	11.7	7.2	2.1	8.5	190.6	46.5
FvPda	2b	15.6	16.2	0.4	0.8	650.7	2403.9	1.6	1.8	4.1	4.4	210.9	237.4	9.9	6.1	2.1	6.2	82.4	54.0
FvPda	4b	5.6	6.9	0.0	0.0	398.8	844.2	0.2	0.2	1.2	1.5	135.1	185.2	5.8	5.7	0.0	0.0		
FvPda	5b	39.4	27.1	0.6	1.4	370.9	875.1	2.8	2.2	8.9	6.5	331.9	316.6	13.5	7.1	2.2	3.8	237.6	32.3
FvPda	7b	53.4	37.8	0.4	0.8	89.7	176.4	2.1	1.8	8.6	7.2	494.3	414.3	8.9	5.8	0.9	2.0	315.0	29.1
FvPda	8b	47.8	31.9	0.7	1.2	211.5	287.5	3.2	2.2	12.7	9.7	212.9	287.8	19.7	10.8	0.7	1.3	355.2	60.9
FvPda	9a	3.7	5.3	0.0	0.0	796.6	1086.9	0.5	0.1	1.2	1.7	130.7	184.8	29.9	34.2	0.0	0.0		
FvPda	9b	31.8	24.7	0.7	1.1	262.7	544.3	3.0	2.0	8.5	7.1	230.4	258.7	26.7	22.4	0.8	1.4	252.7	109.2
FvPda	Drain	10.0	9.9	0.4	0.9	14.6	35.7	1.6	1.0	4.1	3.4	2.8	10.5	7.7	4.4	0.5	0.8	43.8	26.7
FvPda	Stream	35.0	4.2	0.8	1.3	142.8	147.1	2.6	0.5	8.2	2.8	17.5	25.9	10.6	3.2	0.6	1.1	124.9	16.3
FmWda1	Upper BH shallow	8.4	8.5	0.9	1.7	335.8	636.5	1.3	0.8	3.1	3.0	16.0	26.4	6.7	4.2	0.1	0.1	46.6	28.9
FmWda1	Upper BH interface	13.1	15.6	0.8	1.3	400.8	1256.9	1.6	0.8	4.2	3.1	17.3	45.3	9.0	4.4	1.6	3.0	60.0	58.4
FmWda1	Upper BH deep	10.9	9.9	0.5	1.0	88.2	203.0	1.3	0.8	4.5	3.4	52.7	192.4	9.1	5.5	0.9	3.5	43.1	28.5
FmWda1	Middle BH shallow	7.8	7.6	0.5	1.0	126.2	254.9	1.3	1.0	3.4	3.3	2.9	6.0	7.1	4.8	0.5	1.4	32.2	8.7
FmWda1	Middle BH interface	7.7	8.0	0.7	1.4	54.8	85.9	1.1	0.9	3.2	3.3	1.4	3.0	6.9	4.8	1.4	4.0	43.1	19.3
FmWda1	Middle BH deep	9.6	9.3	0.3	1.0	116.3	206.2	1.2	0.8	5.0	5.0	10.7	20.5	8.7	4.9	0.9	2.2	48.5	48.0
FmWda1	Lower BH shallow	8.6	6.9	0.6	1.1	226.9	416.7	1.1	0.8	4.7	3.7	14.1	38.6	8.7	4.8	0.5	1.1	37.0	13.2
FmWda1	Lower BH interface	7.4	6.0	0.3	0.9	78.0	182.3	1.1	0.8	4.4	3.5	5.0	13.8	8.2	4.3	0.7	1.6	29.1	5.4
FmWda1	Lower BH deep	9.2	7.1	0.3	0.8	45.6	120.3	1.0	0.7	4.7	3.8	2.2	5.2	8.6	4.7	0.3	0.6	45.0	7.2
FmWda1	Stream	23.9	35.9	0.1	0.2	21.1	22.7	1.7	0.7	6.6	2.2	0.9	2.0	11.0	2.9	0.3	0.9	32.9	7.9
FmWda2	Upper BH shallow	15.5	12.6	0.0	0.0	34.0	31.5	1.9	1.1	4.9	4.2	2.7	4.5	8.4	4.9	4.4	4.2	41.8	0.1
FmWda2	Upper BH interface	12.4	9.4	0.6	1.3	50.9	98.1	1.2	0.8	4.9	4.1	7.9	24.5	8.1	5.0	1.0	2.5	57.8	34.6
FmWda2	Upper BH deep	14.0	10.4	0.7	1.2	48.6	97.9	1.3	0.9	5.6	4.2	8.3	20.1	11.2	8.8	1.0	2.3	51.8	17.5
FmWda2	Middle BH shallow	21.8	17.4	0.4	0.8	168.2	529.5	2.1	1.7	4.7	4.3	4.7	13.0	8.8	5.5	0.7	2.0	95.4	19.5
FmWda2	Middle BH interface	13.2	11.7	0.6	1.0	49.4	83.9	1.1	0.9	5.0	4.4	21.0	68.5	9.1	6.8	0.3	0.7	52.2	22.3
FmWda2	Middle BH deep	14.5	10.9	0.7	1.1	46.8	94.4	1.7	1.8	5.1	3.9	19.7	66.8	13.2	14.4	0.2	0.7	57.6	16.2
FmWda2	Lower BH shallow	10.1	8.5	0.9	1.7	4.9	7.5	1.1	0.6	3.6	3.3	0.2	0.3	8.3	5.0	0.2	0.4	55.2	17.5
FmWda2	Lower BH interface	13.1	9.2	0.5	0.9	90.4	246.7	1.2	0.8	4.8	4.0	12.6	34.8	9.4	5.7	0.7	1.3	49.7	9.5
FmWda2	Lower BH deep	14.2	7.9	0.3	0.9	15.6	18.7	1.3	0.7	6.0	3.6	32.3	108.3	13.0	7.8	3.9	10.7	53.8	12.4
FmWda2	Stream	21.2	19.2	0.2	0.5	8.7	10.5	1.9	0.9	6.7	2.2	0.9	1.5	9.7	2.3	0.2	0.4	43.0	12.8

Site	MP	NPOC (mg/L)		Total Nitrogen (mg/L)		Chloride (mg/L)		Ammonium-N (mg/L)		Total oxidised nitrogen (mg/L)		Nitrite (mg/L)		Nitrate (mg/L)		total reactive P (mg/L)		Total carbon (mg/L)	
		Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD
KWDg	Sp.	2.6	0.9	2.1	1.7	16.5	2.3	0.0	0.0	1.6	0.8	0.0	0.0	1.5	0.8	0.0	0.0	59.2	31.1
KWDa	Boiling Sp.	1.4	2.2	5.0	1.7	13.4	2.0	0.0	0.0	5.0	1.5	0.0	0.0	4.8	1.9	0.0	0.0	62.2	23.7
KWDa	Sp. under bridge	13.3	34.0	5.8	2.4	12.1	2.6	0.1	0.1	5.0	3.0	0.0	0.0	2.8	3.4	0.0	0.0	53.5	35.5
I/KWDa	MP2 shallow	1.1	0.9	14.6	4.0	15.0	4.4	0.0	0.0	13.1	5.7	0.0	0.0	12.3	6.4	0.0	0.0	38.3	19.3
I/KWDa	MP2 interface	0.7	0.5	13.2	3.8	17.5	4.1	0.0	0.0	11.9	3.1	0.0	0.1	11.9	3.1	0.0	0.0	27.6	23.1
I/KWDa	MP2 deep	2.6	9.4	12.7	1.7	19.2	4.9	0.0	0.0	10.8	3.9	0.1	0.2	10.7	3.8	0.0	0.0	29.7	26.7
I/KWDa	MP1 shallow	0.5	0.2	10.5	4.4	11.2	4.4	0.1	0.3	9.6	2.1	0.2	0.6	9.4	1.8	0.0	0.1	57.0	14.7
I/KWDa	MP1 interface	0.7	0.5	10.7	2.2	11.0	3.7	0.0	0.0	9.9	2.6	0.0	0.0	9.9	2.6	0.0	0.0	38.4	22.6
I/KWDa	MP1 deep	0.7	0.7	11.3	1.6	16.1	9.5	0.0	0.0	10.2	2.7	0.0	0.1	10.1	2.7	0.0	0.0	41.4	19.9
FvWDa	Lower BH	1.8	7.1	6.9	2.1	20.8	1.1	0.0	0.0	7.3	0.9	0.0	0.0	7.3	0.9	0.0	0.0	9.2	5.4
FvWDa	Upper BH	2.1	7.5	8.5	2.0	19.8	3.8	0.0	0.0	7.2	2.6	0.0	0.0	7.2	2.6	0.0	0.0	12.0	8.9
FvWDa	Lower Sp.	9.1	32.7	8.3	1.6	18.1	4.3	0.0	0.0	7.6	1.5	0.0	0.0	7.6	1.5	0.0	0.0	20.7	40.2
FvWDa	Upper Sp.	0.3	0.2	7.7	1.1	22.3	1.3	0.0	0.0	6.6	2.6	0.0	0.0	6.6	2.6	0.0	0.0	3.1	2.0
FvWDa	House Sp.	0.4	0.4	3.9	1.7	18.6	2.2	0.0	0.0	3.1	0.9	0.0	0.0	3.0	1.1	0.0	0.0	6.1	3.1
FvPDa	Artesian BH	0.3	0.4	1.3	3.2	16.0	1.1	0.0	0.0	0.1	0.4	0.0	0.0	0.1	0.4	0.0	0.0	20.7	9.4
FvPDa	1b	4.7	12.4	0.5	0.5	21.5	7.1	0.1	0.1	0.2	0.3	0.0	0.0	0.2	0.3	0.0	0.0	41.7	22.0
FvPDa	2b	1.4	4.1	0.3	0.4	20.0	3.8	0.0	0.0	0.3	0.6	0.0	0.0	0.3	0.6	0.0	0.0	17.0	12.1
FvPDa	4b	1.9	1.1	0.9	0.8	16.5	7.7	0.0	0.1	0.6	0.6	0.0	0.0	0.6	0.6	0.0			
FvPDa	5b	3.0	3.8	0.6	0.7	17.8	4.6	0.2	0.1	0.2	0.4	0.0	0.0	0.2	0.4	0.0	0.0	49.1	26.5
FvPDa	7b	1.8	1.0	0.4	0.3	19.4	11.9	0.1	0.1	0.1	0.2	0.0	0.0	0.1	0.2	0.0	0.0	56.6	27.6
FvPDa	8b	2.7	1.8	0.6	0.3	19.6	3.2	0.3	0.2	0.2	0.4	0.0	0.0	0.2	0.4	0.0	0.0	61.1	30.7
FvPDa	9a	4.7	2.9	0.9	0.1	12.7	6.1	0.2	0.2	0.3	0.2	0.0	0.0	0.3	0.2				
FvPDa	9b	3.6	7.3	1.4	1.9	21.1	6.1	0.7	1.0	0.7	2.4	0.0	0.0	0.7	2.3	0.0	0.1	50.2	31.2
FvPDa	Drain	0.7	1.0	4.1	2.2	21.3	3.4	0.0	0.0	3.6	1.2	0.0	0.0	3.3	1.6	0.0	0.0	10.1	7.8
FvPDa	Stream	4.0	2.3	2.8	1.6	21.9	2.4	0.0	0.0	1.8	1.7	0.0	0.0	1.7	1.7	0.0	0.0	22.4	14.8
FmWDa1	Upper BH shallow	0.3	0.2	5.8	2.2	12.4	4.6	0.1	0.1	5.2	2.5	0.0	0.0	5.2	2.5	0.0	0.0	10.7	9.4
FmWDa1	Upper BH interface	0.5	0.4	5.1	2.3	11.5	4.3	0.0	0.1	4.5	2.4	0.0	0.0	4.5	2.4	0.0	0.1	7.8	8.6
FmWDa1	Upper BH deep	1.4	3.5	5.5	1.5	14.6	5.6	0.0	0.0	4.8	2.0	0.0	0.0	4.8	2.0	0.0	0.0	12.4	8.8
FmWDa1	Middle BH shallow	0.3	0.3	6.2	0.9	13.4	4.3	0.0	0.0	5.5	1.9	0.0	0.0	5.1	2.4	0.0	0.0	8.3	4.4
FmWDa1	Middle BH interface	3.6	11.7	6.1	1.1	13.8	3.7	0.0	0.0	5.3	2.1	0.0	0.0	5.3	2.1	0.0	0.0	13.7	16.0
FmWDa1	Middle BH deep	5.7	21.9	6.2	1.0	15.2	2.3	0.0	0.0	5.4	1.8	0.0	0.0	5.4	1.8	0.0	0.0	17.6	25.1
FmWDa1	Lower BH shallow	1.5	4.8	6.4	1.3	16.7	3.6	0.0	0.1	5.7	2.3	0.0	0.0	5.7	2.3	0.0	0.0	8.8	5.1
FmWDa1	Lower BH interface	1.7	4.2	6.3	1.2	16.3	2.6	0.0	0.0	5.6	2.2	0.0	0.0	5.6	2.2	0.0	0.0	9.0	5.2
FmWDa1	Lower BH deep	0.4	0.7	6.1	0.7	16.8	5.4	0.0	0.0	4.7	2.4	0.0	0.0	4.7	2.4	0.0	0.0	11.0	6.7
FmWDa1	Stream	1.2	0.9	6.6	2.0	19.0	2.2	0.2	0.5	6.2	2.2	0.0	0.0	6.2	2.2	0.0	0.0	11.1	11.3
FmWDa2	Upper BH shallow	0.6	0.5	7.9	0.6	20.5	1.2	0.0	0.0	8.1	1.0	0.0	0.0	8.1	1.0	0.0	0.0	12.9	2.4
FmWDa2	Upper BH interface	0.6	0.4	9.2	2.1	20.8	2.1	0.0	0.0	8.4	2.9	0.0	0.0	7.4	3.9	0.0	0.0	13.9	10.1
FmWDa2	Upper BH deep	0.5	0.3	8.6	2.1	19.6	4.1	0.0	0.0	7.5	2.8	0.0	0.0	7.5	2.8	0.0	0.0	14.2	7.9
FmWDa2	Middle BH shallow	0.7	0.5	5.7	2.5	17.1	4.7	0.0	0.0	5.5	2.0	0.0	0.0	5.5	2.0	0.0	0.0	20.8	9.6
FmWDa2	Middle BH interface	1.3	3.3	7.1	1.7	17.6	3.0	0.0	0.0	6.1	2.2	0.0	0.0	5.8	2.5	1.0	4.1	17.1	10.4
FmWDa2	Middle BH deep	0.8	1.2	6.8	2.5	20.4	10.1	0.1	0.1	5.9	3.0	0.0	0.0	5.9	3.0	0.0	0.1	15.6	11.3
FmWDa2	Lower BH shallow	0.5	0.5	6.1	1.5	16.9	3.0	0.0	0.0	5.9	1.9	0.0	0.0	5.9	1.9	0.0	0.0	11.4	5.9
FmWDa2	Lower BH interface	0.6	0.5	6.8	2.4	18.7	2.7	0.0	0.0	6.5	2.9	0.0	0.0	6.1	3.2	0.0	0.0	12.6	6.6
FmWDa2	Lower BH deep	1.1	2.2	7.0	2.1	20.5	6.5	0.0	0.0	6.4	2.6	0.0	0.0	6.4	2.6	0.8	2.8	13.4	7.3
FmWDa2	Stream	1.4	0.5	6.9	0.9	20.7	10.0	0.0	0.0	6.1	2.3	0.0	0.0	6.1	2.3	0.0	0.1	10.8	6.9

Appendix 8

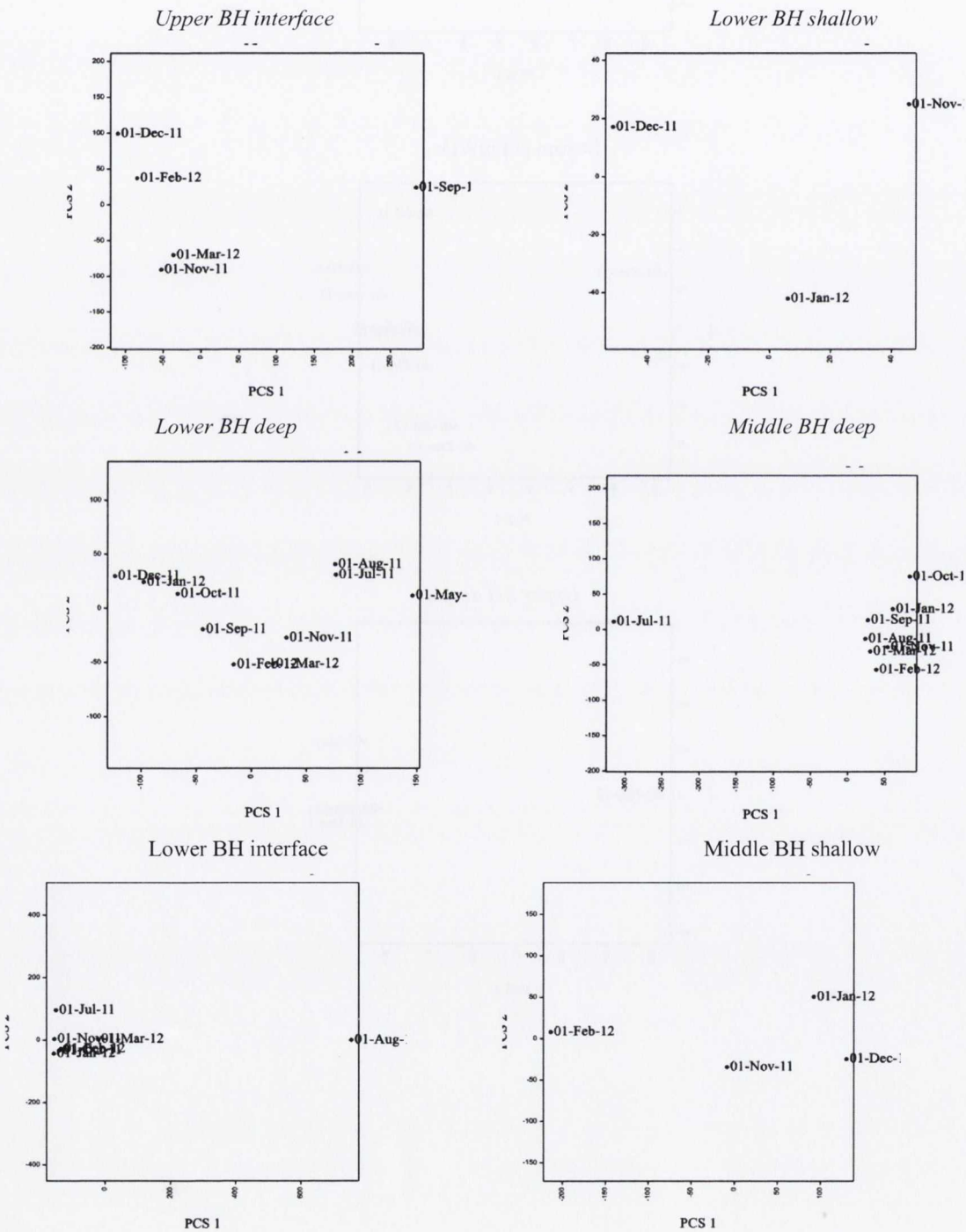
Scree plots from Principal Component Analysis (PCA) of hydrochemical composition for each monitoring point (MP) at fractured-metasediments well-drained arable (FmWDa₁) site 1.

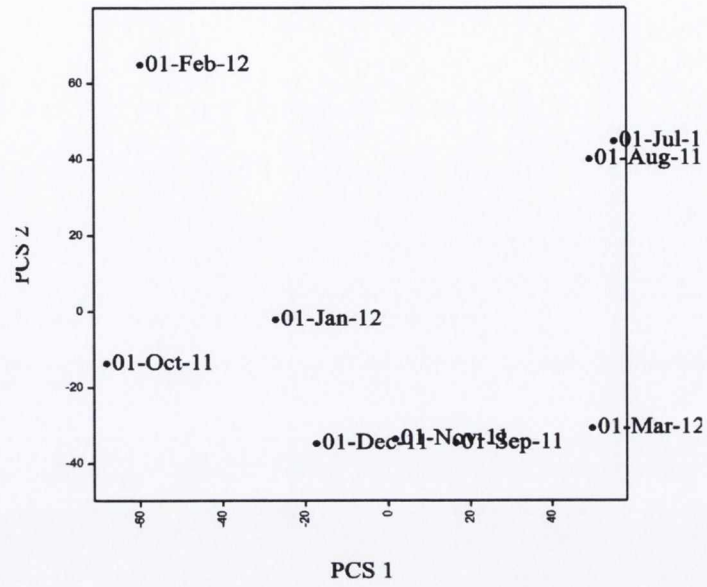
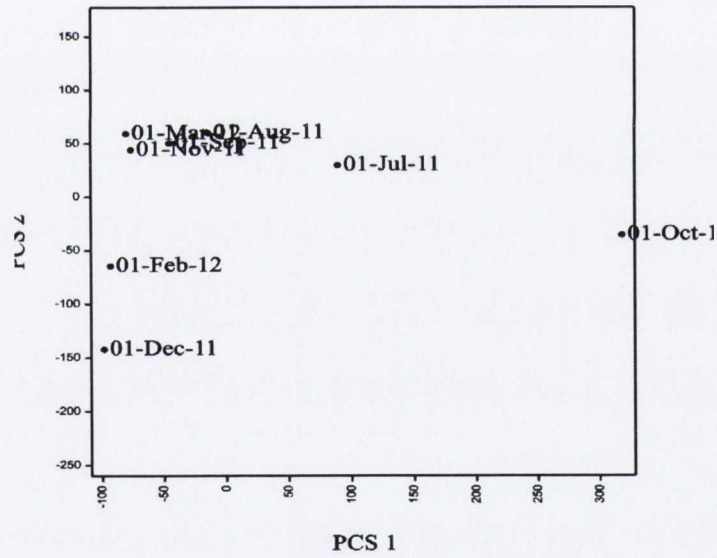


Middle BH shallow*Stream at FmWDa₁**Upper BH deep*

Appendix 9

Scree plots from Principal Component Analysis (PCA) of hydrochemical composition for each monitoring point (MP) at fractured-metasediments well-drained arable (FmWda₂) site 2.



Stream at FmWDa₂*Upper BH deep*

Appendix 10

Compounds quantified for during monthly catchment scale monitoring, their CAS registry number, and their chemical grouping

Compound	Acronym	CAS number	Chemical grouping
4-chloro-2-methylphenol	4C2MP	1570-64-5	Phenoxyacid
2,4,5-trichlorophenol	TCP	95-95-4	Phenoxyacid
3,5,6-trichloro-2-pyridinol	T2P	6515-38-4	Phenoxyacid
2,4-dichlorophenol	DCP	120-83-2	Phenoxyacid
3,5-dibromo-hydroxybenzoic acid	BrAc	3337-62-0	Phenoxyacid
2,3,6-TBA	TBA	50-31-7	Phenoxyacid
2,4-D	-	94-75-7	Phenoxyacid
bentazone	-	25057-89-0	Phenoxyacid
bromoxynil	-	1689-84-5	Phenoxyacid
2,6-dichlorobenzoic acid	DBA	50-84-0	Benzonitrile
dicamba	-	1918-00-0	Phenoxyacid
fluroxypyr	-	69377-81-7	Phenoxyacid
triclopyr	-	55335-06-3	Phenoxyacid
MCPA	-	94-74-6	Phenoxyacid
mecoprop	mecoprop(s)	71526-69-7	Phenoxyacid
mecoprop-p	mecoprop(s)	16484-77-8	Phenoxyacid
phenoxyacetic acid	PAC	122-59-8	Phenoxyacid
3,5-dichloroenzamide	BAM	2008-58-4	Benzonitrile
chloramben	-	133-90-4	Phenoxyacid
2,4-DB	-	94-82-6	Phenoxyacid
acifluorfan	-	50594-66-6	Phenoxyacid
dichlorprop (2,4-DP)	-	120-36-5	Phenoxyacid
2,4,5-trichlorophenoxyacetic acid	2,4,5-T	93-76-5	Phenoxyacid
dinoseb (DNBP)	-	88-85-7	Phenoxyacid
2,4,5-TP (fenoprop)	-	93-72-1	Phenoxyacid
dalapon	-	75-99-0	Phenoxyacid
imazapyr	-	81334-34-1	Phenoxyacid
ioxynil	-	1689-83-4	Phenoxyacid

MCPB	-	94-81-5	Phenoxyacid
picloram	-	1918-02-1	Phenoxyacid
lindane	-	58-89-9	Organochlorine
heptachlor	-	76-44-8	Organochlorine
exo-heptachlor epoxide	-	1024-57-3	Organochlorine
endo-heptachlor epoxide	-	28044-83-9	Organochlorine
dieldrin	-	60-57-1	Organochlorine
azinphos-methyl	-	86-50-0	Organophosphorous
bromophos-ethyl	-	4824-78-6	Organophosphorous
bromophos-methyl	-	2104-96-3	Organophosphorous
chlorfenvinphos	-	470-90-6	Organophosphorous
chlorpyriphos-ethyl	-	2921-88-2	Organophosphorous
chlorpyriphos-methyl	-	5598-13-0	Organophosphorous
semeton-S-methyl	-	62-73-7	Organophosphorous
diazinon	-	333-41-5	Organophosphorous
dichlorvos	-	115-32-2	Organophosphorous
dicofol	-	60-51-5	Organophosphorous
dimethoate	-	298-04-4	Organophosphorous
disulfoton	-	919-86-8	Organophosphorous
etrimphos	-	38260-54-7	Organophosphorous
fenotrothion	-	55-38-9	Organophosphorous
fenthion	-	122-14-5	Organophosphorous
fonofos	-	944-22-9	Organophosphorous
malathion	-	121-75-5	Organophosphorous
methacifros	-	7786-34-7	Organophosphorous
methamidophos	-	338-45-4	Organophosphorous
mevinphos, (E)	-	62610-77-9	Organophosphorous
mevinphos, (Z)	-	10265-92-6	Organophosphorous
parathion-ethyl	-	56-38-2	Organophosphorous
parathion-methyl	-	298-00-0	Organophosphorous
phosphamidon	-	13171-21-6	Organophosphorous
pirimiphos-ethyl	-	23505-41-1	Organophosphorous
pirimiphos-methyl	-	29232-93-7	Organophosphorous
propetamphos	-	31218-83-4	Organophosphorous

Appendix 11

List of compounds analysed during external laboratory analyses in March and April 2010.

Compound	Cas. No.
2,3,6-TBA	50.31-7
2,4,5-TP (fenoprop, silvex)	93-72-1
2,4,5-T (2,4,5-trichlorophenoxyacetic acid)	93-76-5
2,4-DB	94-82-6
dichloroprop (2,4-DP)	120-36-5
2,4-D (2,4-dichlorophenoxyacetic acid)	94-75-7
Acifluorfen	50594-66-6
Bentazone	25057-89-0
Bromoxynil	1689-84-5
Chloramben	133-90-4
2,6-dichlorobenzoic acid (DBA)	50-30-6
Dalapon	75-99-0
Dicamba	1918-00-9
dinoseb (DNBP)	88-85-7
Fluroxypyr	69377-81-7
Ioxynil	1689-83-4
MCPA (4-chloro-o-tolyloxyacetic acid)	94-74-6
MCPB	94-81-5
mecoprop (MCP)	93-65-2
pentachlorophenol (PCP)	87-86-5
Picloram	1918-02-1

**List of compounds analysed during external laboratory analyses in March
2012 for organophosphorous herbicides.**

Compound	Cas. No.
azinphos-methyl	86-50-0
bromophos-ethyl	4824-78-6
bromophos-methyl	2104-96-3
chlorfenvinphos	470-90-6
chlorpyriphos-ethyl	2921-88-2
chlorpyriphos-methyl	5598-13-0
dichlorvos	62-73-7
diazinon	333-41-5
dicofol	115-32-2
dimethoate	60-51-5
disulfoton	298-04-4
dimeton-S-methyl	919-86-8
etrimphos	38260-54-7
fenthion	55-38-9
fentriothion	122-14-5
fonofos	944-22-9
malathion	121-75-5
mevinphos, (E)	7786-34-7
mevinphos, (Z)	338-45-4
methacrifos	62610-77-9
methamidophos	10265-92-6
parathion-ethyl	56-38-2
parathion-methyl	298-00-0
phosphamidon	13171-21-6
primiphos-ethyl	23505-41-1
primiphos-methyl	29232-93-7
propetamphos	31218-83-4

Appendix 12

Within laboratory repeatability (WLr) validation results for the organochlorine herbicide method. EU DWS(i) = 0.1 µg L⁻¹ for lindane and 0.03 µg L⁻¹ for heptachlor, *exo*- and *endo*- heptachlor epoxide.

Analyte		lindane	heptachlor	<i>exo</i> - heptachlor epoxide	<i>endo</i> - heptachlor epoxide
Validation levels (n=6) (µg/L)	0.5 × MAC	0.05	0.015	0.015	0.015
	1.0 × MAC	0.1	0.03	0.03	0.03
	1.5 × MAC	0.15	0.05	0.05	0.05
Recovery (%)	0.5 × MAC	101.1	100	101.5	101.5
	1.0 × MAC	96.1	101.1	101.1	99.3
	1.5 × MAC	100.8	100.9	99.8	100.6
Coefficient of Variation (%)	0.5 × MAC	2.6	6.5	10.5	6.6
	1.0 × MAC	1.9	5.7	6.2	4.1
	1.5 × MAC	1.4	2.7	2.3	3.3

The MAC (maximum admissible concentration) is equivalent to the PL (permitted limit).

Appendix 13

Within laboratory repeatability (WLr) validation results for the phenoxyacid and benzonitrile herbicide method.

Analyte	Validation level			Absolute recovery (%)			Coefficient of variation (%)		
	1	2	3	1	2	3	1	2	3
BAM	0.02	0.04	0.06	95	105	88	18	12	22
PAC	0.02	0.04	0.06	110	105	109	18	2	13
dicamba	0.02	0.04	0.06	106	116	108	13	11	10
TBA	0.02	0.04	0.06	97	111	94	18	9	16
bentazone	0.02	0.04	0.06	112	101	97	23	8	10
fluroxypyr	0.02	0.04	0.06	92	118	99	30	5	15
BrAc	0.02	0.04	0.06	101	99	79	16	13	15
DCP	0.02	0.04	0.06	109	103	99	16	8	5
T2P	0.02	0.04	0.06	113	109	94	8	9	10
MCPA	0.02	0.04	0.06	109	90	71	32	20	18
2,4-D	0.02	0.04	0.06	112	107	98	14	8	5
triclopyr	0.02	0.04	0.06	113	108	102	15	8	8
bromoxynil	0.02	0.04	0.06	112	106	94	16	15	17
4C2MP	0.02	0.04	0.06	100	109	103	46	5	25
DBA	0.02	0.04	0.06	103	96	88	45	42	41
TCP	0.02	0.04	0.06	105	108	97	12	7	9
mecoprop(s)	0.02	0.04	0.06	115	96	102	19	16	11

Appendix 14

Raw data for the percentage frequency of occurrence for all seven sites where monthly samples were collected

Compound abbreviation	No of samples analysed for each particular compound	Detections ≥ 0.1µg/L	Detections < 0.1µg/L	no of non- detections	% frequency detections ≥ 0.1µg/L	% frequency detections < 0.1µg/L	% frequency of non- detections	Total detections (%)
mecoprop(s)	740	12	259	469	1.62	35.00	63.38	36.62
PAC	681	74	154	453	10.87	22.61	66.52	33.48
4C2MP	509	8	125	376	1.57	24.56	73.87	26.13
2,4-D	740	2	190	548	0.27	25.68	74.05	25.95
DBA	568	69	28	471	12.15	4.93	82.92	17.08
MCPA	740	2	122	616	0.27	16.49	83.24	16.76
DCP	509	0	72	437	0.00	14.15	85.85	14.15
triclopyr	740	7	93	640	0.95	12.57	86.49	13.51
T2P	509	8	58	443	1.57	11.39	87.03	12.97
fluroxypyr	740	0	60	680	0.00	8.11	91.89	8.11
dieldrin	77	3	2	72	3.90	2.60	93.51	6.49

Compound abbreviation	No of samples analysed for each particular compound	Detections ≥ 0.1µg/L	Detections < 0.1µg/L	no of non- detects	% frequency detections ≥ 0.1µg/L	% frequency detections < 0.1µg/L	% frequency of non- detects	Total detections (%)
TCP	509	2	29	478	0.39	5.70	93.91	6.09
dicamba	740	1	39	700	0.14	5.27	94.59	5.41
BAM	509	9	17	483	1.77	3.34	94.89	5.11
exo-heptachlor epoxide	77	0	3	74	0.00	3.90	96.10	3.90
TBA	740	3	24	713	0.41	3.24	96.35	3.65
bromoxynil	740	0	13	727	0.00	1.76	98.24	1.76
bentazone	740	0	11	729	0.00	1.49	98.51	1.49
BrAc	509	0	2	507	0.00	0.39	99.61	0.39

Appendix 15
Raw data for the percentage frequency of occurrence for KWDg

Compound abbreviation	No of samples analysed for each particular compound	Detections $\geq 0.1\mu\text{g/L}$	Detections $< 0.1\mu\text{g/L}$	no of non-detects	% frequency detections $\geq 0.1\mu\text{g/L}$	% frequency detections $< 0.1\mu\text{g/L}$	% frequency of non-detects	Total detections (%)
<i>exo</i> -heptachlor epoxide	3	0	1	2	0.00	33.33	66.67	33.33
dieldrin	3	0	1	2	0.00	33.33	66.67	33.33
2,4-D	20	0	4	16	0.00	20.00	80.00	20.00
BrAc	13	0	1	12	0.00	7.69	92.31	7.69
DBA	15	1	0	14	6.67	0.00	93.33	6.67
PAC	18	0	1	17	0.00	5.56	94.44	5.56
mecoprop(s)	20	0	1	19	0.00	5.00	95.00	5.00
MCPA	20	0	1	19	0.00	5.00	95.00	5.00

Raw data for the percentage frequency of occurrence for KWDa

Compound abbreviation	No of samples analysed for each particular compound	Detections $\geq 0.1\mu\text{g/L}$	Detections $< 0.1\mu\text{g/L}$	no of non-detects	% frequency detections $\geq 0.1\mu\text{g/L}$	% frequency detections $< 0.1\mu\text{g/L}$	% frequency of non-detects	Total detections (%)
PAC	27	2	6	19	7.41	22.22	70.37	29.63
mecoprop(s)	29	0	3	26	0.00	10.34	89.66	10.34
2,4-D	29	0	3	26	0.00	10.34	89.66	10.34
4C2MP	21	0	2	19	0.00	9.52	90.48	9.52
DBA	23	1	1	21	4.35	4.35	91.30	8.70
TCP	21	0	1	20	0.00	4.76	95.24	4.76
BAM	21	1	0	20	4.76	0.00	95.24	4.76
triclopyr	29	0	1	28	0.00	3.45	96.55	3.45
dicamba	29	0	1	28	0.00	3.45	96.55	3.45
bromoxynil	29	0	1	28	0.00	3.45	96.55	3.45
dieldrin	4	0	0	4	0.00	0.00	100.00	0.00

Raw data for the percentage frequency of occurrence for I/KWDa

Compound abbreviation	No of samples analysed for each particular compound	Detections $\geq 0.1\mu\text{g/L}$	Detections $< 0.1\mu\text{g/L}$	no of non-detects	% frequency detections $\geq 0.1\mu\text{g/L}$	% frequency detections $< 0.1\mu\text{g/L}$	% frequency of non-detects	Total detections (%)
mecoprop(s)	124	2	58	64	1.61	46.77	51.61	48.39
2,4-D	124	0	56	68	0.00	45.16	54.84	45.16
4C2MP	85	2	34	49	2.35	40.00	57.65	42.35
PAC	112	17	22	73	15.18	19.64	65.18	34.82
DCP	85	0	26	59	0.00	30.59	69.41	30.59
MCPA	124	0	30	94	0.00	24.19	75.81	24.19
T2P	85	1	19	65	1.18	22.35	76.47	23.53
triclopyr	124	2	26	96	1.61	20.97	77.42	22.58
DBA	96	12	5	79	12.50	5.21	82.29	17.71
TCP	85	0	10	75	0.00	11.76	88.24	11.76
fluroxypyr	124	0	14	110	0.00	11.29	88.71	11.29
dicamba	124	1	9	114	0.81	7.26	91.94	8.06
TBA	96	0	7	89	0.00	7.29	92.71	7.29
exo-heptachlor epoxide	17	0	1	16	0.00	5.88	94.12	5.88
BAM	85	1	2	82	1.18	2.35	96.47	3.53
bromoxynil	124	0	1	123	0.00	0.81	99.19	0.81

Raw data for the percentage frequency of occurrence for FvWDa

Compound abbreviation	No of samples analysed for each particular compound	Detections $\geq 0.1\mu\text{g/L}$	Detections $< 0.1\mu\text{g/L}$	no of non-detects	% frequency detections $\geq 0.1\mu\text{g/L}$	% frequency detections $< 0.1\mu\text{g/L}$	% frequency of non-detects	Total detections (%)
PAC	99	5	20	74	5.05	20.20	74.75	25.25
mecoprop(s)	123	1	18	104	0.81	14.63	84.55	15.45
4C2MP	70	1	7	62	1.43	10.00	88.57	11.43
DBA	79	4	5	70	5.06	6.33	88.61	11.39
triclopyr	123	0	9	114	0.00	7.32	92.68	7.32
exo-heptachlor epoxide	15	0	1	14	0.00	6.67	93.33	6.67
MCPA	123	0	8	115	0.00	6.50	93.50	6.50
2,4-D	123	0	8	115	0.00	6.50	93.50	6.50
T2P	70	0	4	66	0.00	5.71	94.29	5.71
BAM	70	3	1	66	4.29	1.43	94.29	5.71
fluroxypyr	123	0	4	119	0.00	3.25	96.75	3.25
DCP	70	0	2	68	0.00	2.86	97.14	2.86
TBA	79	0	2	77	0.00	2.53	97.47	2.53
dicamba	123	0	3	120	0.00	2.44	97.56	2.44
TCP	70	0	1	69	0.00	1.43	98.57	1.43
BrAc	70	0	1	69	0.00	1.43	98.57	1.43

Raw data for the percentage frequency of occurrence for all groundwater monitoring points at FvPDa

Compound abbreviation	No of samples analysed for each particular compound	Detections $\geq 0.1\mu\text{g/L}$	Detections $< 0.1\mu\text{g/L}$	no of non-detections	% frequency detections $\geq 0.1\mu\text{g/L}$	% frequency detections $< 0.1\mu\text{g/L}$	% frequency of non-detects	Total detections (%)
Mecoprop(s)	185	5	90	90	2.70	48.65	48.65	51.35
PAC	155	34	29	92	21.94	18.71	59.35	40.65
2,4-D	185	1	72	112	0.54	38.92	60.54	39.46
4C2MP	112	2	40	70	1.79	35.71	62.50	37.50
MCPA	185	2	56	127	1.08	30.27	68.65	31.35
DCP	112	0	34	78	0.00	30.36	69.64	30.36
T2P	112	7	24	81	6.25	21.43	72.32	27.68
triclopyr	185	4	40	141	2.16	21.62	76.22	23.78
fluroxypyr	185	0	35	150	0.00	18.92	81.08	18.92
DBA	131	17	2	112	12.98	1.53	85.50	14.50
TCP	112	2	14	96	1.79	12.50	85.71	14.29
BAM	112	4	6	102	3.57	5.36	91.07	8.93
TBA	120	4	6	110	3.33	5.00	91.67	8.33
dicamba	185	0	13	110	0.00	7.03	59.46	7.03
bromoxynil	185	0	8	177	0.00	4.32	95.68	4.32
bentazone	185	0	4	181	0.00	2.16	97.84	2.16

Raw data for the percentage frequency of occurrence for all groundwater monitoring points at FmWDa₁

Compound abbreviation	No of samples analysed for each particular compound	Detections < 0.1µg/L	Detections ≥ 0.1µg/L	no of non- detects	% frequency detections ≥ 0.1µg/L	% frequency detections < 0.1µg/L	% frequency of non-detects	Total detections (%)
PAC	153	9	33	111	5.88	21.57	72.55	27.45
4C2MP	113	1	20	92	0.88	17.70	81.42	18.58
mecoprop(s)	166	0	30	136	0.00	18.07	81.93	18.07
DBA	142	16	6	120	11.27	4.23	84.51	15.49
2,4-D	166	0	22	144	0.00	13.25	86.75	13.25
MCPA	166	0	14	152	0.00	8.43	91.57	8.43
triclopyr	166	0	10	156	0.00	6.02	93.98	6.02
TBA	113	0	6	107	0.00	5.31	94.69	5.31
dicamba	166	0	8	158	0.00	4.82	95.18	4.82
T2P	113	0	5	108	0.00	4.42	95.58	4.42
exo-hep.epo.	28	0	1	27	0.00	3.57	96.43	3.57
BAM	113	0	3	110	0.00	2.65	97.35	2.65
TCP	113	0	2	111	0.00	1.77	98.23	1.77
DCP	113	0	2	111	0.00	1.77	98.23	1.77
bentazone	166	0	2	164	0.00	1.20	98.80	1.20
bromoxynil	166	0	2	164	0.00	1.20	98.80	1.20
BrAc	113	0	1	112	0.00	0.88	99.12	0.88
fluroxypyr	166	0	1	165	0.00	0.60	99.40	0.60

Raw data for the percentage frequency of occurrence for all groundwater monitoring points for FmWDa₂

Compound abbreviation	No of samples analysed for each particular compound	Detections $\geq$ 0.1µg/L		Detections < 0.1µg/L		% frequency detections $\geq$ 0.1µg/L		% frequency detections < 0.1µg/L		% frequency of non-detects		Total detections (%)
		0.1µg/L	0.1µg/L	0.1µg/L	0.1µg/L	0.1µg/L	0.1µg/L	0.1µg/L	0.1µg/L	non-detects	non-detects	
PAC	135	5	36	94	3.70	26.67	69.63	30.37				
mecoprop(s)	151	2	33	116	1.32	21.85	76.82	23.18				
2,4-D	151	0	33	118	0.00	21.85	78.15	21.85				
DBA	135	16	7	112	11.85	5.19	82.96	17.04				
T2P	126	0	17	109	0.00	13.49	86.51	13.49				
4C2MP	126	0	17	109	0.00	13.49	86.51	13.49				
MCPA	151	0	17	134	0.00	11.26	88.74	11.26				
triclopyr	151	1	13	137	0.66	8.61	90.73	9.27				
exo-heptachlor epoxide	33	0	3	30	0.00	9.09	90.91	9.09				
BAM	126	0	7	119	0.00	5.56	94.44	5.56				
TBA	151	0	5	146	0.00	3.31	96.69	3.31				
dicamba	151	0	5	146	0.00	3.31	96.69	3.31				
fluroxypyr	151	0	5	146	0.00	3.31	96.69	3.31				
DCP	126	0	4	122	0.00	3.17	96.83	3.17				
TCP	126	0	2	124	0.00	1.59	98.41	1.59				
bentazone	151	0	1	150	0.00	0.66	99.34	0.66				

Appendix 16

List of publications from this work

2013

Sarah-Louise McManus., Catherine E Coxon., Karl G Richards and Martin Danaher (2013) *Quantitative DI-SPME & GC/MS-SIS analysis of the pesticides lindane, heptachlor and two heptachlor transformation products in groundwater*. Journal of Chromatography A **1284**: 1 - 7.

2012

Sarah-Louise McManus, Karl G. Richards, Jim Grant, Anthony Mannix, and Catherine E. Coxon (2012) *Pesticide occurrence in Ground Water and the factors contributing to these detections in Ireland*. Environmental Monitoring and Assessment, *submitted, under review*.

Sarah-Louise McManus, Catherine E. Coxon and Karl G. Richards (2012) *Diffuse herbicide leaching to groundwater across six locations within Ireland*. Water Research, *under internal review*.

Sarah-Louise McManus, Mary Moloney, Catherine E. Coxon, Karl G. Richards and Martin Danaher (2012) *Rapid determination & application of 10 pesticides and 8 transformation products in groundwater using SPE and UHPLC-MS/MS*. Water Research, *under internal review*.

2011

S.L. McManus., K.G. Richards and C.E. Coxon (2011) *Pesticide leaching to groundwater from diffuse agricultural sources in an agricultural catchment*. Walsh Fellowship Seminar 2011 book of abstracts. Teagasc, Oak Park, Co. Carlow, p.46.

Sarah-Louise McManus, Per-Erik Mellander, Catherine E. Coxon, and Karl G. Richards (2011) *Pesticide Leaching to Groundwater in an Agricultural Catchment*. In proceedings of Catchment Science 2011, Teagasc/Defra, Wexford, Ireland, 14th-16th September 2011, p.42.

Sarah-Louise McManus, Per-Erik Mellander, Catherine E. Coxon, and Karl G. Richards (2011) *Pesticide leaching from diffuse agricultural sources to groundwater in the Republic of Ireland*. In proceedings of the XIV Symposium in Pesticide Chemistry: Pesticides in the Environment: fate, modelling and risk mitigation. 30th August - 1st September 2011, Università Cattolica del Sacro Cuore, Piacenza, Italy.

Sarah-Louise McManus, Karl G. Richards, Jim Grant, Anthony Mannix and Catherine E. Coxon (2011) *Physical characteristics & pesticides in groundwater across Ireland: results of*

the EPA groundwater survey 2007-2008. International Association of Hydrogeologists – Irish Group conference proceedings Tullamore, Co. Offaly, 12th & 13th April.

Sarah-Louise McManus, Karl G. Richards, Jim Grant, Anthony Mannix and Catherine E. Coxon (2011) *Are physical site characteristics allowing pesticide products to leach to groundwater in Ireland?* Geophysical Research Abstracts Vol. 13 EGU2011-8259-4, EGU General Assembly, Vienna

S-L, McManus, K.G. Richards, J. Grant, A. Mannix and C.E. Coxon (2011) *Which physical site characteristics are associated with pesticide detections in groundwater across Ireland?* Agricultural Research Forum, 14th & 15th March, Tullamore, Co. Offaly, p.7.

2009

McManus, S-L., Coxon, C.E & Richards, K.G (2009) *Pesticide loss to groundwater in Ireland*. Environ '09, 9th – 11th February, Waterford Institute of Technology, Book of abstracts, C14.

McManus, S-L., Richards, K.G & Coxon, C.E (2009) *Pesticide occurrence in Irish groundwaters*. GSI groundwater newsletter, December 2009, p.12.

McManus, S-L., Coxon, C.E & Richards, K.G (2009) *Case studies of Pesticide loss to groundwater in Ireland*. Conference Proceedings from Pesticide behaviour in soils, water and air, York, England 14th – 16th September, Food and Environment Research Agency, book of abstracts, A33.

McManus, S-L., Richards, K.G & Coxon, C.E (2009) *Investigating pesticide occurrence in groundwater in Ireland*. Ireland's rural Environment: Research Highlights from Johnstown Castle, August 2009, Teagasc, Wexford. Edited by: S.T.J. Lalor and D. Ó hUallacháin. ISBN: 1-84170-543-8, P.51.