LEABHARLANN CHOLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE LIBRARY DUBLIN
Ollscoil Átha Cliath | The University of Dublin

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.

PHOSPHORUS EXPORTS FROM AGRICULTURAL GRASSLAND IN OVERLAND FLOW AND SUBSURFACE DRAINAGE WATER

Volume 1

A thesis submitted to the University of Dublin in fulfilment of the requirements for the degree of Doctor of Philosophy

by Isabelle Kurz, M.Sc.

Department of Geology, Trinity College Dublin

and

Teagasc, Johnstown Castle, Wexford

Supervised by Dr. C.E. Coxon, Trinity College Dublin

October 2002

TRINITY COLLEGE LIBRARY DUBLIN

TRINITY COLLEGE
12 JUN 2003
LIBRARY DUBLIN
THESIS
~~7890.1~~
7277.1

Declaration

I declare that this thesis is my own work except where otherwise stated. It has not been submitted for a degree at any other university. The library may lend a copy of this thesis upon request.

Isabelle Kurz

Isabelle Kurz

Summary

On the background of increasing phosphorus (P) concentrations in Irish rivers and lakes, this project set out to investigate several aspects of the potential of agricultural grassland to lose P to water. All study sites were located at Johnstown Castle Research and Development Centre, Wexford, Ireland. Water samples were collected from field sites, from an artificial subsurface drainage network (at the Beef Unit), and from a small stream (at the Dairy Farm).

To study the effects of soil P levels on P exports in overland flow from grassland, the quantity and quality of overland flow from a low soil P (4 mg P/l Morgan's) and a high soil P (17 mg P/l Morgan's) field were measured for 16 consecutive months. Additionally, a medium soil P (8 mg P/l Morgan's) site was monitored for 5 of the 16 months. A combination of open trenches and berms were used to hydrologically isolate the surface of the overland flow monitoring sites. To investigate the possibility of P losses along subsurface flow pathways, the artificial subsurface drainage network at the Beef Unit was monitored as an example of an existing subsurface drainage system. The measurements of flow and composition of the discharge from the artificial subsurface drainage network were complemented by a soil water sampling programme of limited extent. To study the combined effects of fields of different site and management characteristics on stream water quality, the stream running through the Dairy Farm was monitored continuously at the upstream and the downstream boundary of the Dairy Farm sub-catchment. Additionally, a grab sampling programme provided information on changes of the stream water quality along the channel. Measurements of flow and quality of water in the artificial subsurface drainage network at the Beef Unit and in the Dairy Farm stream were carried out for 5 and 6 months, respectively, in consecutive years. Dissolved reactive P (DRP) and total dissolved P (TDP) were determined in most water samples from the overland flow and the subsurface flow monitoring sites. Total P (TP) was measured in a subset of samples. DRP was the main P fraction analysed in water from the Dairy Farm stream but some TDP and TP determinations were also carried out.

The P concentrations in overland flow were elevated in comparison to the P levels measured in rainfall. P in overland flow was extremely variable during and between events. Nevertheless P export in overland flow clearly increased from the low to the medium and the high soil P monitoring sites. The annual DRP exports and the flow-weighted average annual DRP concentrations amounted to 698 g P/ha and 0.090 mg P/l, respectively, at the low soil P site, compared to 4,764 g P/ha and 1.076 mg P/l, respectively, at the high soil P site. Exports and concentrations for the 5 winter months of monitoring at the medium soil P site were estimated as 111 g P/ha and 0.028 mg P/l, respectively, at the low soil P site; 300 g P/ha and 0.069 mg P/l, respectively, at the medium soil P site; and 1,162 g P/ha and 0.354 mg P/l, respectively, at the high

soil P site. The inter-site variability of the P concentrations in overland flow by far exceeded the variability of the amounts of overland flow from the different sites. Thus the P concentrations had a larger impact than the volume of overland flow on the differences in P exports measured at the three sites. Saturation excess overland flow was determined to be the main mechanism of overland flow production and the occurrence of overland flow was assessed to be unevenly distributed throughout a field.

Some of the P concentrations in water running through the artificial subsurface drainage network were high during peak flow conditions. The maximum DRP concentrations measured during the events monitored ranged from 0.087 to 1.650 mg P/l. These elevated P levels were reflected in soil water samples from zero-tension samplers, which are thought to mainly sample macropore flow. The application of liquid manure to fields contributing flow to the artificial subsurface drainage network monitored led to an increase of P concentrations in artificial subsurface drain flow. The P is thought to have reached the artificial subsurface drainage network via preferential flow pathways down the soil profile.

Data from the Dairy Farm stream suggest that, overall, the Dairy Farm sub-catchment acted as a sink for P during the monitoring period. The Dairy Farm sub-catchment had a buffering effect on storm flow and P concentration peaks. A small area of wetland along the course of the stream was assumed to be largely responsible for this effect.

The greatest proportion of the P found in overland flow and in water from the artificial subsurface drainage network was in dissolved form. In reference to total P (TP), particulate P (PP = TP – TDP) amounted to about 23% in overland flow and about 30% in water from artificial subsurface drains. Most of the dissolved P was molybdate reactive. However, incidences of elevated levels of unreactive (i.e. organic and condensed) forms of dissolved P in overland flow were discovered. These were probably an effect of the presence of grazing animals at the overland flow sites.

From the data presented it was concluded that P losses in overland flow from gley soils were of environmental and, at high soil P, also of economic significance. Environmental conditions and agricultural management practices, such us fertiliser applications and grazing, were found to influence phosphorus exports from agricultural grassland in overland flow, in subsurface drain flow and in stream water. Overall, the effect of agricultural grassland on water quality was shown to be the result of complex interactions between site characteristics, environmental and agricultural factors.

Acknowledgements

Many thanks to my supervisor Dr. C.E. Coxon in Trinity College and my supervisor Dr. H. Tunney in Johnstown Castle, Teagasc. Their help and encouragement throughout this project has been invaluable.

Thanks to all the staff at Johnstown Castle. I cannot think of one person there who did not take a special effort to help me during this study.

Special thanks to Joe Scott and Denis Brennan who carried out the automated analyses for me, to Michael Coffey who helped me set up the study sites, to Eddie McDonald who very patiently drew up the maps for me, to Vincent Staples who draw up the sketches of field instrumentation, and to Tommy O'Donnell and Aidan Fanning who were involved with the development of the overland flow sites and helped out with field and lab work.

Many thanks to Declan Ryan and John Bennett who collected data for SWAMP (Sustainable Waste Management Application Project) at two of my sites. The co-operation with them greatly enhanced my work.

Thanks to Dr. Karen Daly, Pamela Bartley and Dr. Karl Richard who were students at Johnstown Castle at the time the data for this study was collected. The discussions with them were always helpful and constructive.

Thanks also to Teagasc and the Environmental Protection Agency for funding this project, and to the Office of Public Works who let me use the Ordnance Survey contour information for the Dairy Farm for free.

Very special thanks to Clodagh Duffy for keeping us fed, amusing the babe, proof-reading and much more.

Loads of thanks to my family here and in Switzerland. Writing up this PhD has made many demands on them and curtailed my time with them greatly, especially during the last year. I am particularly grateful to my mother who took great efforts to give me the time to write up my work.

Table of Contents

VOLUME 1

CHAPTER 1: BACKGROUND AND OUTLINE OF THE STUDY		**1**
1.1	General Background	1
1.2	Land Related Agricultural P Losses in Ireland	3
1.3	EPA (Environmental Protection Agency) Environmental Research Priorities 1995	3
1.4	Aims of the Study on P Exports from Agricultural Grassland with Overland Flow and Artificial Subsurface Drainage Water	4
1.5	Summary of the Data Collection	7
1.6	Layout of the Thesis	7
CHAPTER 2: LITERATURE REVIEW		**9**
2.1	Introduction	9
2.1.1	Phosphorus (P) and Cultural Eutrophication	9
2.1.2	The Role of P in Surface Water Bodies (Freshwater)	10
2.1.3	Enrichment of Water Bodies with P	12
2.1.4	Sources of P	13
2.1.5	Diffuse Agricultural P Contributions	13
2.2	P in Soils	15
2.2.1	Origin and Redistribution	15
2.2.2	Forms of P in Soils	16
2.2.3	Plant Available P	17
2.3	Agricultural P Additions and Soil Properties	20
2.3.1	Benefits of P Fertilisation	20
2.3.2	P Fertilisation and Crop Requirements	21
2.3.3	Effect of P Additions	22
2.4	Storm Flow	23
2.4.1	Rainfall Events and P Transport	23
2.4.2	Overland Flow	24
	Infiltration Excess Overland Flow	24
	Saturation Excess Overland Flow and Return Flow	26
2.4.3	Subsurface Flow	26
2.4.4	Artificial Subsurface Drains	29

2.4.5	Importance of Pathways	29
2.5	Interactions Between P Sources and Hydrology	30
2.5.1	P Sources and P Mobilisation	30
2.5.2	Forms of P in Overland and Subsurface Flow	32
2.5.3	Transport of P	33
	Overland Flow	33
	Subsurface Flow	34
	Subsurface Flow: Artificial Subsurface Drains	36
2.6	Magnitude of P Losses	37
2.7	Connection Between Fields and Water Bodies	37
2.8	Measures to Reduce P Exports to Water	38
CHAPTER 3: CHARACTERISTICS AND MANAGEMENT OF THE STUDY SITES		**41**
3.1	Introduction	41
3.2	Selection of the Study Sites	42
3.3	Method of Soil Investigation	44
3.4	Overland Flow Sites	45
3.4.1	General Site Characteristics	45
3.4.2	Management	46
3.5	Artificial Subsurface Drainage Site (Beef Unit)	49
3.5.1	General Site Characteristics of the Beef Unit	49
3.5.2	Management	50
3.6	Dairy Farm (Stream)	50
3.6.1	General Site Characteristics	50
3.6.2	Management of the Dairy Farm	53
CHAPTER 4: DETERMINATION OF SOIL CHEMICAL AND HYDROLOGICAL PARAMETERS		**54**
4.1	Introduction	54
4.2	Methods	55
4.2.1	Soil P, K and pH Levels	55
4.2.2	Infiltration Capacity	56
4.2.3	Dye Studies	57
4.2.4	Water Table Levels	57
4.3	Results	59
4.3.1	Soil P, K and pH Levels	59

4.3.2	Infiltration Capacity	60
4.3.3	Dye Studies	63
4.3.4	Water Table Levels	63
4.4	Discussion	66
4.4.1	Soil P, K and pH levels	66
4.4.2	Infiltration Capacity	67
4.4.3	Dye Studies	69
4.4.4	Water Table Levels	70
CHAPTER 5: WATER QUALITY PARAMETERS		**72**
5.1	Introduction	72
5.1.1	Phosphorus	72
5.1.2	Additional Parameters Measured	74
5.2	Methods	75
5.2.1	Water Analysis at Johnstown Castle	75
5.2.2	Selection of P Fractions to be Analysed	76
5.2.3	General Laboratory Procedures	76
5.2.4	Manual Digestion and its Comparison to Automatic Digestion	77
5.2.5	Limits and Accuracy of P Analysis	77
	Dissolved Reactive P	77
	Total P and TDP	78
5.2.6	Relationships between P Fractions	79
5.3	Results	80
5.3.1	Manual Digestion and its Comparison to Automatic Digestion	80
5.3.2	Accuracy of P Analysis	80
5.3.3	Relationships between P Fractions	81
	Regressions Based on Full and Partial Datasets	82
	Dissolved Reactive P and Total Dissolved P	84
	Total Dissolved P and Total P	86
5.3.4	Turbidity and pH	87
5.4	Discussion	88
5.4.1	Quality of P Data	88
5.4.2	Relationships between the P fractions	90
5.4.3	Turbidity and pH	92
CHAPTER 6: RAINFALL AND ITS P CONTENT		**93**
6.1	Introduction	93

6.2	Methods	93
6.3	Results	94
6.3.1	Amount of Rain	94
6.3.2	Rainfall Intensity	94
6.3.3	Phosphorus in Rainwater	95
6.4	Discussion	95
6.4.1	Amount and Intensity of Rain	95
6.4.2	Phosphorus in Rainwater	96
CHAPTER 7: PHOSPHORUS IN OVERLAND FLOW		**98**
7.1	Introduction	98
7.2	Methods	100
7.2.1	Installation and Instrumentation of Sites	100
7.2.2	Water Level Recording	103
7.2.3	Sampling Programme	103
7.2.4	Data Treatment and Calculations	105
	Water Levels, Flow and P Export	105
	Flow at the Warren 2	106
	Relationships Between Flow and P concentrations, and Between P Concentrations and Other Water Quality Parameters	106
7.3	Results	107
7.3.1	Occurrence and Quantity of Overland Flow	107
	Overland Flow Events	107
	Comparison of Overland Flow at the Three Sites	109
	Seasonal Patterns	112
	Overland flow and Water Table Levels	113
7.3.2	Phosphorus Concentrations in Overland Flow	114
	Differences between the Sites	114
	P Concentrations throughout the monitoring periods	116
	P Concentrations in Overland Flow During the Course of Events	117
	Relationships between Flow and P Concentrations	118
	Springs	118
7.3.3	Other Water Quality Parameters in Overland Flow and Their Relationship to P	119
7.3.4	Phosphorus Export in Overland Flow	120
7.4	Discussion	122

7.4.1	Occurrence and Quantity of Overland Flow	122
	Overview of the Differences Between Sites	122
	Mechanisms of Overland Flow Production	123
	Hydrology of the Sites Throughout the Monitoring Period	124
	Management and Overland Flow	126
7.4.2	P Concentration in Overland Flow	126
	Land as a Diffuse Source of P	126
	Management Influences on P Levels in Overland Flow	127
	Seasonal Influences on P Levels in Overland Flow	132
	P Concentrations During the Course of Events	133
	Influences on P in Overland Flow: Summary	135
7.4.3	P Export	135
CHAPTER 8: P IN SUBSURFACE DRAINAGE WATER		**143**
8.1	Introduction	143
8.2	Methods	144
8.2.1	Type and Location of Study Sites at the Beef Unit	144
8.2.2	Instrumentation and Installation of the Site	145
8.2.3	Flow Recording and Sampling Programme	147
8.2.4	Data Treatment and Calculations	148
8.3	Results	149
8.3.1	Flow	149
	Subsurface Drainage Network	149
8.3.2	Phosphorus Concentrations	150
	Subsurface Drainage Water Samples	150
	Soil Water Samples	151
8.3.3	Other Water Quality Parameters and Their Relationships to P in Artificial Subsurface Drainage Discharge	153
	Subsurface Drainage Water Samples	153
	Soil Water Samples	154
8.3.4	Phosphorus Export	154
8.4	Discussion	156
8.4.1	Rainfall and Subsurface Drain Flow	156
8.4.2	Nutrient Concentrations and Shallow Subsurface Flow Pathways	157
8.4.3	P in Relation to Rates of Flow	159
8.4.4	P in Relation to Other Chemical Parameters	159

8.4.5 P Exports and Concentrations 160

CHAPTER 9: P LOSS AT THE SMALL CATCHMENT SCALE: THE DAIRY FARM STREAM **162**

9.1 Introduction 162
9.2 Methods 163
9.2.1 Instrumentation at the Dairy Farm Stream 163
9.2.2 Flow Recording and Sampling Programme 164
9.2.3 Data Treatment and Calculations 166
9.3 Results 166
9.3.1 Flow 166
9.3.2 Concentrations 168
DRP Concentrations at the Monitoring Stations (M1, M2) During Events 168
Grab Samples During Events 169
Low Flow (i.e. Non-Event) Sampling 171
Pollution Incident 171
Other Water Quality Parameters and their Relationships to P 172
9.3.3 P Exports 174
9.4 Discussion 174
9.4.1 Overview of Stream Flow and DRP Concentrations in the Dairy Farm Stream 174
9.4.2 Management Practices and Water Quality 177
9.4.3 Site Characteristics and Water Quality 178

CHAPTER 10: CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH **181**

10.1 Introduction 181
10.2 Aim 1: P Export with Overland Flow from Agricultural Grassland of Different Soil P Levels 181
10.3 Aim 2: P Exports from Agricultural Grassland via Artificial Subsurface Drains 183
10.4 Aim 3: The P loss Potential of an Intensive Dairy Farm 184
10.5 Aims 1.4, 2.3 and 3.3: Effects of Agricultural Management Practices on P Losses to Water 185
10.6 Aim 4: The Different Forms of P Lost 185
10.7 Suggestions for Further Research 186

REFERENCES 188

VOLUME 2

FIGURES 1

PLATES 292

APPENDIX 1: Soil Profiles 299

APPENDIX 2: DRP, TDP and TP Concentrations in Spring/Subsurface Water Samples from Warren 1 301

APPENDIX 3: TDP CONCENTRATIONS IN SAMPLES FROM TEFLON SUCTION CUPS 302

List of Figures

Figure 1.1 Sampling sites at Johnstown Castle.

Figure 3.1 Beef Unit contour lines (Teagasc), approximate location of the artificial subsurface drains and estimated subsurface drainage cathment boundary.

Figure 3.2 Beef Unit soils (Culleton and Diamond, in print).

Figure 3.3 Beef Unit soil P levels (mg P/l Morgan's).

Figure 3.4 Dairy Farm soils (Culleton and Diamond, in print).

Figure 3.5 Dairy Farm soil P levels (mg P/l Morgan's).

Figure 3.6 Dairy Farm contour lines (Ordnance Survey), approximate location of the artificial subsurface drains and estimated sub-catchment boundary.

Figure 3.7 Water quality sampling stations.

Figure 3.8 Experimental treatments at the Dairy Farm.

Figure 4.1 Soil P levels (mg P/l Morgan's) at the Warren 1 (1), the Warren 2 (2) and the Cowlands (3). Samples taken in 1997 are to the left and samples taken in 1998 to the right.

Figure 4.2 Infiltration rates (mm/h) measured on the two days of the trial in ring system 2 at the Warren 1.

Figure 4.3 Infiltration rates (mm/h) measured on two days of the trial in ring system 2 on soil type C3 at the Beef Unit.

Figure 4.4 Percolation rates (mm/h) measured in 5 cm and 10 cm holes at the Cowlands.

Figure 4.5 Map of the water table levels at the Warren 1 on 12th December 1996. (Figure drawn up by SWAMP personnel.)

Figure 4.6 Map of the water table levels at the Cowlands on 12th December 1996. (Figure drawn up by SWAMP personnel.)

Figure 4.7 Mean water table levels (cm) above 120 cm below the ground at the Cowlands.

Figure 4.8 Mean water table levels (cm) above 120 cm below the ground at the Warren 1.

Figure 4.9 Water levels (cm) in reference to the ground in the water table tubes of line 1 at the Cowlands.

Figure 4.10 Water levels (cm) in reference to the ground in the water table tubes of line 2 at the Cowlands.

Figure 4.11 Water levels (cm) in reference to the ground in the water table tubes of line 3 at the Cowlands.

Figure 4.12 Water levels (cm) in reference to the ground in the water table tubes of line 1 at the Warren 1.

Figure 4.13 Water levels (cm) in reference to the ground in the water table tubes of line 2 at the Warren 1.

Figure 4.14 Water levels (cm) in reference to the ground in the water table tubes of line 3 at the Warren 1.

Figure 4.15 Water levels (cm) in reference to the ground in the water table tubes of line 4 at the Warren 1.

Figure 4.16 Water levels (cm) in reference to the ground in the water table tubes C4 and at the spring at the Warren 1.

Figure 4.17 Water levels (cm) in reference to the ground in the subset of water table tubes which was monitored after July 1997 at the Cowlands.

Figure 4.18 Water levels (cm) in reference to the ground in line 2 of the subset of water table tubes which was monitored after July 1997 at the Warren 1.

Figure 4.19 Water levels (cm) in reference to the ground in line 3 of the subset of water table tubes which was monitored after July 1997 at the Warren 1.

Figure 4.20 Water levels (cm) in reference to the ground in line 4 of the subset of water table tubes which was monitored after July 1997 at the Warren 1.
Figure 4.21 Water levels (cm) in reference to the ground in water table tubes 1, 2 and 3 at the Warren 2.
Figure 4.22 Water levels (cm) in reference to the ground in water table tubes 4, 5 and 6 at the Warren 2.
Figure 4.23 Water levels (cm) in reference to the ground in water table tubes B4 and C2 at the Warren 1 compared to negative soil moisture deficit (mm) curve and rainfall (mm).
Figure 4.24 Water levels (cm) in reference to the ground in water table tube B2 at the Cowlands compared to negative soil moisture deficit (mm) curve and rainfall (mm).
Figure 4.25 Water levels (cm) in reference to the ground in water table tube 2 at the Warren 2 compared to negative soil moisture deficit (mm) curve and rainfall (mm).
Figure 5.1 Phosphorus analysis techniques and products (based on Anon, 1995). Dashed boxes indicate procedures and drawn out boxes products of the analyses. Yellow boxes indicate types of P analysed in this project.
Figure 5.2 Differences (mg P/l) between mean laboratory recovery rates and true DRP values plotted against true DRP values.
Figure 5.3 TDP concentrations (mg P/l) of the full data set at the Warren 1 plotted against DRP concentrations. Separate trend indicated by red colour. Note that samples with TDP below the limit of detection were omitted (see Section 5.2.6).
Figure 5.4 Residuals of the DRP/TDP regression of the full data set at the Warren 1 plotted against DRP concentrations (mg P/l). Separate trend indicated by red colour.
Figure 5.5 TDP concentrations (mg P/l) of the full data set at the Cowlands plotted against DRP concentrations (mg P/l). Separate trend indicated by red colour.
Figure 5.6 Residuals of the DRP/TDP regression of the full data set at the Cowlands plotted against DRP concentrations (mg P/l). Separate trend indicated by red colour.
Figure 5.7 TP levels (mg P/l) plotted against TDP (mg P/l) concentrations measured at the Warren 1. Note that samples below the limit of detection were omitted (see Section 5.2.6).
Figure 5.8 TP (mg P/l) levels plotted against TDP (mg P/l) concentrations measured at the Beef Unit. Note that samples below the limit of detection were omitted (see Section 5.2.6).
Figure 5.9 Log(10) TP levels plotted against log(10) TDP concentrations measured at the Cowlands.
Figure 5.10 TP levels (mg P/l) plotted against TDP (mg P/l) concentrations measured at the Warren 2. Note that samples below the limit of detection were omitted (see Section 5.2.6).
Figure 5.11 Turbidity (NTU (Nephelometer turbidity units)) plotted against TP (mg P/l) levels.
Figure 5.12 Turbidity (NTU (Nephelometer turbidity units)) plotted against TP (mg P/l) levels in samples from the Warren 1.
Figure 5.13 Turbidity (NTU (Nephelometer turbidity units)) plotted against TP (mg P/l) levels in samples from the Cowlands.
Figure 5.14 Turbidity (NTU (Nephelometer turbidity units)) plotted against TP (mg P/l) levels in samples from the upstream monitoring station at the Dairy.
Figure 5.15 Turbidity (NTU (Nephelometer turbidity units)) plotted against TP levels (mg P/l) in samples from the downstream monitoring station at the Dairy.
Figure 6.1 Cumulative rainfall (mm) at the Johnstown Castle meteorological station and the Cowlands.
Figure 6.2 Monthly rainfall (mm) at Johnstown Castle meteorological station from January 1950 to March 1998.

Figure 6.3 Comparison of average monthly rainfall from 1950 to 1995 and the monthly rainfall November 1996 to March 1997.
Figure 6.4 Estimates of hourly rainfall (mm) values at Johnstown Castle meteorological station (automatic rain gauge).
Figure 6.5 DRP concentrations (mg P/l) in rainwater collected at the Cowlands. (Note that samples below the limit of detection were plotted as zero.)
Figure 6.6 TDP concentrations (mg P/l) in rainwater collected at the Cowlands. (Note that samples below the limit of detection were omitted.)
Figure 6.7 TP concentrations (mg P/l) in rainwater collected at the Cowlands. (Note that samples below the limit of detection were omitted.)
Figure 7.1 Site map of the Warren 1 (adapted from Ryan, 1998).
Figure 7.2 Site map of the Cowlands (adapted from Ryan, 1998).
Figure 7.3 Site map of the Warren 2.
Figure 7.4 One minute logging interval at the Cowlands.
Figure 7.5 Five minutes logging interval at the Cowlands.
Figure 7.6 Overland flow (l/s) and DRP (mg P/l) concentrations of samples taken at 15 minute (crosses) and longer (circles) (30 minute to 8 hour) intervals at the Cowlands.
Figure 7.7 Water level in the tank below the weir crest at the end of event 18.4 at the Warren 2.
Figure 7.8 Rate of loss (l/s) at the end of event 18.4 in the weir tank at the Warren 2 plotted against time (minutes).
Figure 7.9 Monthly rainfall and monthly overland flow (mm) at the Warren 1 and the Cowlands.
Figure 7.10 Monthly rainfall and monthly overland flow at the Warren 1, the Cowlands and the Warren 2.
Figure 7.11 Daily overland flow at the Cowlands (mm) plotted against the daily overland flow at the Warren 1 (mm).
Figure 7.12 Difference between cumulative rainfall and cumulative flow (mm) at the Warren 1.
Figure 7.13 Difference between cumulative rainfall and cumulative flow (mm) at the Warren 2.
Figure 7.14 Overland flow (l/s) and DRP (mg P/l) concentrations for event 1 at the Warren 1.
Figure 7.15 Overland flow (l/s) and DRP (mg P/l) concentrations for event 2 at the Warren 1.
Figure 7.16 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 3 at the Warren 1.
Figure 7.17 Overland flow (l/s) and DRP (mg P/l) and TDP (mg P/l) concentrations for event 4 at the Warren 1.
Figure 7.18 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 5 at the Warren 1.
Figure 7.19 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 6 at the Warren 1.
Figure 7.20 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 7 at the Warren 1.
Figure 7.21 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 8 at the Warren 1.
Figure 7.22 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 9 at the Warren 1.
Figure 7.23 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 10 at the Warren 1.
Figure 7.24 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 11 at the Warren 1.

Figure 7.25 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 12 at the Warren 1.
Figure 7.26 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 13 at the Warren 1.
Figure 7.27 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 14 at the Warren 1.
Figure 7.28 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 15 at the Warren 1.
Figure 7.29 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 16 at the Warren 1.
Figure 7.30 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 17 at the Warren 1.
Figure 7.31 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 18 at the Warren 1. (Excessively high P concentrations at beginning of event omitted. See table 7.2.)
Figure 7.32 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 19 at the Warren 1.
Figure 7.33 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 20 at the Warren 1.
Figure 7.34 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 21 at the Warren 1.
Figure 7.35 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 22 at the Warren 1.
Figure 7.36 Overland flow (l/s) and DRP (mg P/l) concentrations for event 1 at the Cowlands.
Figure 7.37 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 2 at the Cowlands.
Figure 7.38 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 5.1 at the Cowlands.
Figure 7.39 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 5.2 at the Cowlands.
Figure 7.40 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 7 at the Cowlands.
Figure 7.41 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 8 at the Cowlands.
Figure 7.42 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 9.1 at the Cowlands.
Figure 7.43 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 9.2 at the Cowlands.
Figure 7.44 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 10.1 at the Cowlands.
Figure 7.45 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 10.2 at the Cowlands.
Figure 7.46 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 12 at the Cowlands.
Figure 7.47 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 13 at the Cowlands.
Figure 7.48 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 14.1 at the Cowlands.
Figure 7.49 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 14.2 at the Cowlands.

Figure 7.50 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 15 at the Cowlands.
Figure 7.51 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 16 at the Cowlands.
Figure 7.52 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 17 at the Cowlands.
Figure 7.53 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 18.1 at the Cowlands.
Figure 7.54 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 18.2 at the Cowlands.
Figure 7.55 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 18.3 at the Cowlands.
Figure 7.56 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 18.4 at the Cowlands.
Figure 7.57 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 19.1 at the Cowlands.
Figure 7.58 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 19.2 at the Cowlands.
Figure 7.59 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 19.3 at the Cowlands.
Figure 7.60 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 21 at the Cowlands.
Figure 7.61 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 22 at the Cowlands.
Figure 7.62 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 18.2 at the Warren 2.
Figure 7.63 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 18.3 at the Warren 2.
Figure 7.64 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 18.4 at the Warren 2.
Figure 7.65 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 19.1 at the Warren 2.
Figure 7.66 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 19.2 at the Warren 2.
Figure 7.67 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 19.3.1 at the Warren 2.
Figure 7.68 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 19.3.2 at the Warren 2.
Figure 7.69 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 21 at the Warren 2.
Figure 7.70 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 22.1 at the Warren 2.
Figure 7.71 Overland flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event 22.2 at the Warren 2.
Figure 7.72 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 1, and curve of the difference between the percentages of cumulative flow at the two sites.
Figure 7.73 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 2, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.74 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 5, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.75 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 9, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.76 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 10, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.77 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 13, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.78 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 14, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.79 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 15, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.80 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 16, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.81 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 17, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.82 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 18.1-18.3, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.83 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 18.4, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.84 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 19, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.85 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 21, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.86 Rainfall (mm), percentage of cumulative flow at the Warren 1 and the Cowlands during event 22, and curve of the difference between the percentages of cumulative flow at the two sites.

Figure 7.87 Rainfall (mm) and curves of the differences between the percentages of cumulative flow at the overland flow sites for event 18.2-18.3: Percentage cumulative flow Warren 1 minus percentage cumulative flow Warren 2, percentage cumulative flow Warren 1 minus percentage cumulative flow Cowlands, percentage cumulative flow Cowlands minus percentage cumulative flow Warren 2.

Figure 7.88 Rainfall (mm) and curves of the differences between the percentages of cumulative flow at the overland flow sites for event 18.4: Percentage cumulative flow Warren 1 minus percentage cumulative flow Warren 2, percentage cumulative flow Warren 1 minus percentage cumulative flow Cowlands, percentage cumulative flow Cowlands minus percentage cumulative flow Warren 2.

Figure 7.89 Rainfall (mm) and curves of the differences between the percentages of cumulative flow at the overland flow sites for event 19: Percentage cumulative flow Warren 1 minus percentage cumulative flow Warren 2, percentage cumulative flow Warren 1 minus percentage cumulative flow Cowlands, percentage cumulative flow Cowlands minus percentage cumulative flow Warren 2.

Figure 7.90 Rainfall (mm) and curves of the differences between the percentages of cumulative flow at the overland flow sites for event 21: Percentage cumulative flow Warren 1 minus percentage cumulative flow Warren 2, percentage cumulative flow Warren 1 minus percentage cumulative flow Cowlands, percentage cumulative flow Cowlands minus percentage cumulative flow Warren 2.

Figure 7.91 Rainfall (mm) and curves of the differences between the percentages of cumulative flow at the overland flow sites for event 22: Percentage cumulative flow Warren 1 minus percentage cumulative flow Warren 2, percentage cumulative flow Warren 1 minus percentage cumulative flow Cowlands, percentage cumulative flow Cowlands minus percentage cumulative flow Warren 2.

Figure 7.92 Monthly overland flow totals at the Warren 1, the Cowlands and the Warren 2 expressed as a percentage of monthly rainfall.

Figure 7.93 Monthly overland flow totals at the Warren 1 expressed as a percentage of monthly rainfall plotted against monthly rainfall (mm).

Figure 7.94 Monthly overland flow totals at the Cowlands expressed as a percentage of monthly rainfall plotted against monthly rainfall (mm).

Figure 7.95 Monthly overland flow totals at the Warren 1 expressed as a percentage of monthly rainfall plotted against net monthly rainfall (i.e. monthly rainfall minus monthly potential evapotranspiration) (mm).

Figure 7.96 Monthly overland flow totals at the Cowlands expressed as a percentage of monthly rainfall plotted against net monthly rainfall (i.e. monthly rainfall minus monthly potential evapotranspiration) (mm).

Figure 7.97 Overland flow (mm) at the Warren 1 and net monthly rainfall (i.e. monthly rainfall minus monthly potential evapotranspiration (PE)) (mm).

Figure 7.98 Overland flow (mm) at the Cowlands and net monthly rainfall (i.e. monthly rainfall minus monthly potential evapotranspiration (PE)) (mm).

Figure 7.99 Daily rainfall (mm), daily overland flow (mm), water table levels (cm) in tubes B4 and C2 at the Warren 1, and negative daily soil moisture deficit (SMD) values (mm).

Figure 7.100 Daily rainfall (mm), daily overland flow (mm), water table levels (cm) in tube B2 at the Cowlands, and negative daily soil moisture deficit (SMD) values (mm).

Figure 7.101 Daily rainfall (mm), daily overland flow (mm), water table levels (cm) in tube 2 at the Warren 2, and negative daily soil moisture deficit (SMD) values (mm).

Figure 7.102 Overland flow (l/s) for event 1 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.

Figure 7.103 Overland flow (l/s) for event 5 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.

Figure 7.104 Overland flow (l/s) for event 7 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.
Figure 7.105 Overland flow (l/s) for event 8 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.
Figure 7.106 Overland flow (l/s) for event 9 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.
Figure 7.107 Overland flow (l/s) for event 10 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.
Figure 7.108 Overland flow (l/s) for event 13 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.
Figure 7.109 Overland flow (l/s) for event 14 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.
Figure 7.110 Overland flow (l/s) for event 15 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.
Figure 7.111 Overland flow (l/s) for event 16 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.
Figure 7.112 Overland flow (l/s) for event 17 at the Warren 1 and overland flow values at the Cowlands, which were adjusted to the area of the Warren 1.
Figure 7.113 Overland flow (l/s) for event 18 at the Warren 1 and overland flow values at the Cowlands and the Warren 2, which were adjusted to the area of the Warren 1.
Figure 7.114 Overland flow (l/s) for event 19 at the Warren 1 and overland flow values at the Cowlands and the Warren 2, which were adjusted to the area of the Warren 1.
Figure 7.115 Overland flow (l/s) for event 21 at the Warren 1 and overland flow values at the Cowlands and the Warren 2, which were adjusted to the area of the Warren 1.
Figure 7.116 Overland flow (l/s) for event 22 at the Warren 1 and overland flow values at the Cowlands and the Warren 2, which were adjusted to the area of the Warren 1.
Figure 7.117 Minimum, maximum and flow weighted average DRP (mg P/l) concentrations at the Warren 1. (Excessively high P concentrations at beginning of event 18 not considered in working out maximum for that event. See Table 7.2 and Section 7.3.2.)
Figure 7.118 Minimum, maximum and flow weighted average DRP (mg P/l) concentrations at the Cowlands.
Figure 7.119 Minimum, maximum and flow weighted average DRP (mg P/l) concentrations at the Warren 2.
Figure 7.120 Marker for the start of events and DRP, TDP and TP concentrations (mg P/l) at the Warren 1. (DRP not measured for some samples taken July/August 1997 and in December/January 1997/98. See Section 5.2.3. Excessively high P concentrations at beginning of event 18 omitted. See table 7.2.)
Figure 7.121 Marker for the start of events and DRP, TDP and TP concentrations (mg P/l) at the Cowlands. (DRP not measured for some samples taken July/August 1997 and in December/January 1997/98. See Section 5.2.3.)
Figure 7.122 Marker for the start of events and DRP, TDP and TP concentrations (mg P/l) at the Warren 2. (DRP not measured for some samples taken in December/January 1997/98. See Section 5.2.3.)
Figure 7.123 Ratios of maximum to minimum DRP concentrations per event and maximum rates of flow (l/s) per event at the Cowlands.
Figure 7.124 Ratios of maximum to minimum DRP concentrations per event and maximum rates of flow (l/s) per event at the Warren 1.
Figure 7.125 Ratios of maximum to minimum DRP concentrations per event and maximum rates of flow (l/s) per event at the Warren 2.
Figure 7.126 Rates of flow (l/s) plotted against P concentrations (mg P/l) at the Warren 1.

Figure 7.127 Rates of flow (l/s) plotted against P concentrations (mg P/l) at the Cowlands.
Figure 7.128 Rates of flow (l/s) plotted against P concentrations (mg P/l) at the Warren 2. Results of the two samples taken during excessively high flow on 8th (event 19.3.1) and 13th January (event 19.3.2) 1998 were omitted.
Figure 7.129 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event 18.2 at the Warren 2.
Figure 7.130 Total ammonia (TA), total oxidised nitrogen (TON) (mg N/l) and DRP (mg P/l) in overland flow from the Cowlands.
Figure 7.131 Total ammonia (TA), total oxidised nitrogen (TON) (mg N/l) and DRP (mg P/l) in overland flow from the Warren 1.
Figure 7.132 Total ammonia (TA), total oxidised nitrogen (TON) (mg N/l) and DRP (mg P/l) in overland flow from the Warren 2.
Figure 7.133 Potassium (K) (mg/l) and DRP (mg P/l) in overland flow from the Warren 1.
Figure 7.134 Potassium (K) (mg/l) and DRP (mg P/l) in overland flow from the Cowlands.
Figure 7.135 Potassium (K) (mg/l) and DRP (mg P/l) in overland flow from the Warren 2.
Figure 7.136 Conductivity (µS/cm) and DRP (mg P/l) in overland flow from the Warren 1.
Figure 7.137 Conductivity (µS/cm) and DRP (mg P/l) in overland flow from the Cowlands.
Figure 7.138 Conductivity (µS/cm) and DRP (mg P/l) in overland flow from the Warren 2.
Figure 7.139 Suspended solids (ss) (mg/l) and DRP (mg P/l) in overland flow from the Warren 1.
Figure 7.140 Suspended solids (ss) (mg/l) and DRP (mg P/l) in overland flow from the Cowlands.
Figure 7.141 Suspended solids (ss) (mg/l) and DRP (mg P/l) in overland flow from the Warren 2.
Figure 7.142 Potassium (K) levels (mg/l) plotted against DRP concentrations (mg P/l) at the Warren 1.
Figure 7.143 Suspended solids (ss) levels (mg/l) plotted against DRP concentrations (mg P/l) at the Warren 1 (two values in excess of 400 excluded).
Figure 7.144 Potassium (K) levels (mg/l) plotted against DRP concentrations (mg P/l) at the Cowlands.
Figure 7.145 Suspended solid (ss) levels (mg/l) plotted against DRP concentrations (mg P/l) at the Cowlands.
Figure 7.146 TA levels (mg N/l) plotted against DRP concentrations (mg P/l) at the Warren 2.
Figure 7.147 Monthly DRP (g P/ha) exports in overland flow from the Warren 1 and the Cowlands.
Figure 7.148 Monthly DRP (g P/ha) exports in overland flow from the Warren 1, the Warren 2 and the Cowlands.
Figure 7.149 Cumulative daily flow (mm) and DRP (g/ha) export from the Warren 1.
Figure 7.150 Cumulative daily flow (mm) and DRP export (g/ha) from the Cowlands.
Figure 8.1 Beef Unit plot boundaries, soil water sampling sites, dye study sites and soil P levels (mg P/l Morgan's).
Figure 8.2 Daily rain and daily drain flow during events at the Beef Unit.
Figure 8.3 Drain flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event BU1 at the Beef Unit.
Figure 8.4 Drain flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event BU2 at the Beef Unit.
Figure 8.5 Drain flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event BU3 at the Beef Unit.
Figure 8.6 Drain flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event BU4 at the Beef Unit.

Figure 8.7 Drain flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event BU5 at the Beef Unit.
Figure 8.8 Drain flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event BU6 at the Beef Unit. (DRP concentrations at the end of the event calculated (Section 5.2.3)).
Figure 8.9 Drain flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event BU7 at the Beef Unit (DRP concentrations at the beginning of the event calculated (Section 5.2.3)).
Figure 8.10 Drain flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event BU8 at the Beef Unit.
Figure 8.11 Drain flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event BU9 at the Beef Unit.
Figure 8.12 Minimum, maximum and flow-weighted average DRP concentrations (mg P/l) at the Beef Unit.
Figure 8.13 DRP concentrations (mg P/l) and flow rates (l/s) at the time of sampling for all events at the Beef Unit.
Figure 8.14 Rates of flow (l/s) plotted against P concentrations (mg P/l) at the Beef Unit.
Figure 8.15 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event BU1 at the Beef Unit.
Figure 8.16 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event BU2 at the Beef Unit.
Figure 8.17 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event BU3 at the Beef Unit.
Figure 8.18 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event BU4 at the Beef Unit.
Figure 8.19 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event BU5 at the Beef Unit.
Figure 8.20 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event BU6 at the Beef Unit.
Figure 8.21 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event BU7 at the Beef Unit.
Figure 8.22 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event BU8 at the Beef Unit.
Figure 8.23 Rates of flow (l/s) plotted against P concentrations (mg P/l) for event BU9 at the Beef Unit.
Figure 8.24 DRP concentrations (mg P/l) of soil water samples from the Beef Unit (Note that T indicates Teflon suction cup and Z indicates zero-tension sampler – see Table 8.2 for details).
Figure 8.25 DRP and TDP (mg P/l) concentrations in zero-tension samples taken during events BU1, BU3 and BU5.
Figure 8.26 TA, TON (mg N/l) and DRP (mg P/l) in artificial subsurface drainage water at the Beef Unit for all monitored events (BU1 to BU9).
Figure 8.27 K (mg /l) and DRP (mg P/l) in artificial subsurface drainage water at the Beef Unit for all monitored events (BU1 to BU9).
Figure 8.28 Conductivity (µS/cm) and DRP (mg P/l) in artificial subsurface drainage water at the Beef Unit for all monitored events (BU1 to BU9).
Figure 8.29 Suspended solids (mg/l) and DRP (mg P/l) in artificial subsurface drainage water at the Beef Unit.
Figure 8.30 K (mg/l) levels plotted against DRP concentrations (mg P/l) in artificial subsurface drainage water at the Beef Unit.
Figure 8.31 TON (mg N/l) levels plotted against DRP concentrations (mg P/l) in artificial subsurface drainage water at the Beef Unit.

Figure 8.32 Conductivity (µS/cm) levels plotted against DRP concentrations (mg P/l) in artificial subsurface drainage water at the Beef Unit.
Figure 8.33 Conductivity (µS/cm) levels plotted against rates of flow (l/s) when samples of water in the artificial subsurface drainage system at the Beef Unit were taken.
Figure 8.34 TON (mg N/l) levels plotted against rates of flow (l/s) when samples of water in the artificial subsurface drainage system at the Beef Unit were taken.
Figure 8.35 TA, TON (mg N/l) and DRP (mg P/l) in soil water from zero-tension samplers at the Beef Unit.
Figure 8.36 TA, TON (mg N/l) and DRP (mg P/l) in soil water from Teflon suction cup samplers at the Beef Unit.
Figure 8.37 K (mg K/l) and DRP (mg P/l) in soil water from zero-tension samplers at the Beef Unit.
Figure 8.38 K (mg/l) and DRP (mg P/l) in soil water from Teflon suction cup samplers at the Beef Unit.
Figure 8.39 Conductivity (µS/cm) and DRP (mg P/l) in soil water from zero-tension samplers at the Beef Unit.
Figure 8.40 Conductivity (µS/cm) and DRP (mg P/l) in soil water from Teflon suction cup samplers at the Beef Unit.
Figure 8.41 Cumulative daily flow (m3) and DRP export (g) via artificial subsurface drains at the Beef Unit (Nov. 97 to March 98).
Figure 9.1 One minute flow measurements at the upstream monitoring site (M1) at the Dairy Farm (24th November –2nd December 1996).
Figure 9.2 Five minute flow measurements at the upstream monitoring site (M1) at the Dairy Farm (24th November –2nd December 1996).
Figure 9.3 One minute flow measurements at the downstream monitoring site (M2) at the Dairy Farm (24th November –2nd December 1996).
Figure 9.4 Five minute flow measurements at the downstream monitoring site (M2) at the Dairy Farm (24th November –2nd December 1996).
Figure 9.5 Flow per event at the upstream (M1) and the downstream (M2) monitoring stations of the Dairy Farm sub-catchment, and % of downstream (M2) flow measured upstream (M1).
Figure 9.6 Flow (l/s) and DRP concentrations (mg P/l) at the upstream (M1) and downstream (M2) monitoring stations for event D1.
Figure 9.7 Flow (l/s) and DRP concentrations (mg P/l) at the upstream (M1) and downstream (M2) monitoring stations for event D2.
Figure 9.8 Flow (l/s) and DRP concentrations (mg P/l) at the upstream (M1) and downstream (M2) monitoring stations for event D3.
Figure 9.9 Flow (l/s) and DRP concentrations (mg P/l) at the upstream (M1) and downstream (M2) monitoring stations for event D4.
Figure 9.10 Flow (l/s) and DRP concentrations (mg P/l) at the upstream (M1) and downstream (M2) monitoring stations for event D5.
Figure 9.11 Flow (l/s) and DRP concentrations (mg P/l) at the upstream (M1) and downstream (M2) monitoring stations for event D6.
Figure 9.12 Daily flows (m3) at the downstream monitoring station (M2) plotted against daily flows (m3) at the u/s monitoring station.
Figure 9.13 Daily amounts of rain (mm), flow (m3) at the upstream (M1) and downstream (M2) monitoring station and the daily negative soil moisture Deficit (SMD) (mm) value.
Figure 9.14 Minimum, maximum and flow-weighted average DRP concentrations (mg P/l) at the upstream (M1) and downstream (M2) monitoring stations of the Dairy Farm sub-catchment.

Figure 9.15 Daily flow-weighted average DRP concentrations (mg P/l) at the upstream (M1) and downstream (M2) monitoring stations.

Figure 9.16 Daily flow-weighted average DRP concentrations (mg P/l) at the downstream (M2) monitoring station plotted against daily flow-weighted average DRP concentrations (mg P/l) at the upstream (M2) monitoring station.

Figure 9.17 DRP concentrations (mg P/l) plotted against rates of flow (l/s) measured at the upstream monitoring station (M1).

Figure 9.18 DRP concentrations (mg P/l) plotted against rates of flow (l/s) measured at the downstream monitoring station (M2).

Figure 9.19 DRP concentrations (mg P/l) plotted against rates of flow (l/s) measured at the upstream monitoring station (M1) during event D5.

Figure 9.20 DRP concentrations (mg P/l) plotted against rates of flow (l/s) measured at the downstream monitoring station (M2) during event D2.

Figure 9.21 DRP concentrations (mg P/l) plotted against rates of flow (l/s) measured at the downstream monitoring station (M2) during event D5.

Figure 9.22 Event D1: DRP concentrations (mg P/l) of stream grab samples taken at the weir (G2) and of corresponding samples at the upstream (M1) and downstream (M2) monitoring stations, and DRP concentrations (mg P/l) of grab samples of overland flow (G3O) and flow from subsurface drains (G3D1 and G3D2) running into the stream access hole in the middle of the Dairy Farm.

Figure 9.23 Event D4: DRP concentrations (mg P/l) of stream grab samples taken at the tank at the Beef Unit (A2), at the stream access hole at the castle wall (A3), at the weir (G2) and at the stream access hole in the middle of the Dairy Farm (G3), and of corresponding samples at the upstream (M1) and downstream (M2) monitoring stations. DRP concentrations (mg P/l) of grab samples taken at the drain catching the spring north of the Bogwood (G1) and at the subsurface drains (G3D1 and G3D2) running into the stream access hole in the middle of the Dairy Farm (G3).

Figure 9.24 Event D4: DRP concentrations (mg P/l) of stream grab samples (days when tank at the Beef Unit (A2) not sampled) taken at the weir (G2) and at the stream access hole in the middle of the Dairy Farm (G3), and of corresponding samples at the upstream (M1) and downstream (M2) monitoring stations. DRP concentrations (mg P/l) of grab samples taken at the drain catching the spring north of the Bogwood (G1) and at the subsurface drains (G3D1 and G3D2) running into the stream access hole in the middle of the Dairy Farm (G3).

Figure 9.25 Event D6: DRP concentrations of grab samples taken at drain at the Beef Unit (A1) and at the tank at the Beef Unit (A2), and of corresponding samples at the upstream (M1) and downstream (M2) monitoring stations.

Figure 9.26 Low flow grab sampling December 1996 to end of January 1997: DRP concentrations (mg P/l) of samples taken at the stream access hole at the castle wall (A3), at the end of the Bogwood (A4) at the weir (G2), at the stream access hole in the middle of the Dairy Farm (G3), at the upstream (M1) and at the downstream (M2) monitoring stations.

Figure 9.27 Low flow grab sampling March 1997 to 2nd May 1997: DRP concentrations (mg P/l) of samples taken at the drain at the Beef Unit (A1), at the tank at the Beef Unit (A2), at the upstream (M1) and at the downstream (M2) monitoring stations.

Figure 9.28 Rates of flow at the u/s monitoring station at the Dairy Farm 7th March to 21st April.

Figure 9.29 Flow (l/s) and DRP (mg P/l), TDP (mg P/l) and TP (mg P/l) concentrations for event D6 at the upstream monitoring station (M1).
Figure 9.30 Pollution incident: DRP concentrations (mg P/l) of stream samples taken at the drain at the Beef Unit (A1), at the tank at the Beef Unit (A2), at the access hole (X) to the underground pipe leading from A2 to A3, at the stream access hole at the castle wall (A3), at the end of the Bogwood (A4), at the upstream (M1) and downstream (M2) monitoring stations. DRP concentrations (mg P/l) in samples from a drain discharging into to the underground pipe leading from A2 to A3 at X, of overland flow from the road (XR) and at the discharge pipe from the peat filter beds.
Figure 9.31 Total oxidised nitrogen (TON), total ammonia (TA) (mg/l) and DRP (mg P/l) concentrations at the upstream monitoring station (M1).
Figure 9.32 Total oxidised nitrogen (TON), total ammonia (TA) and DRP (mg P/l) concentrations at the downstream monitoring station (M2).
Figure 9.33 Potassium (K) (mg/l) and DRP (mg P/l) concentrations at the upstream monitoring station (M1).
Figure 9.34 Potassium (K) (mg/l) and DRP (mg P/l) concentrations at the downstream monitoring station (M2).
Figure 9.35 Conductivity (µS/cm) and DRP (mg P/l) levels at the upstream monitoring station (M1).
Figure 9.36 Conductivity (µS/cm) and DRP (mg P/l) levels at the downstream monitoring station (M2).
Figure 9.37 Suspended solids (ss) (mg/l) and DRP (mg P/l) levels at the upstream monitoring station (M1).
Figure 9.38 Suspended solids (ss) (mg/l) and DRP (mg P/l) levels at the downstream monitoring station (M2).
Figure 9.39 Potassium (K) (mg/l) plotted against DRP (mg P/l) levels at the upstream monitoring station (M1).
Figure 9.40 Potassium (K) (mg/l) plotted against DRP (mg P/l) levels at the downstream monitoring station (M2).
Figure 9.41 Total oxidised nitrogen (TON) (mg N/l) plotted against DRP (mg P/l) levels at the downstream monitoring station (M2).
Figure 9.42 Conductivity (µS/cm) plotted against DRP (mg P/l) levels at the downstream monitoring station (M2).
Figure 9.43 Total oxidised nitrogen (TON) (mg N/l) plotted against DRP (mg P/l) levels at the upstream monitoring station (M1).
Figure 9.44 Conductivity (µS/cm) plotted against DRP (mg P/l) levels at the upstream monitoring station (M1).
Figure 9.45 DRP loads at the upstream (M1) and downstream (M2) monitoring stations.
Figure 9.46 Net DRP exports (load downstream (M2) minus load upstream (M1)) from the Dairy Farm sub-catchment: absolute figures and % in reference to the sum of DRP loads upstream (M1) and downstream (M2).
Figure 9.47 Daily DRP loads (g) at the upstream (M1) and downstream (M2) monitoring stations.

List of Plates

Plate 4.1 Dye distribution down the soil profile at site Dye 1.

Plate 4.2 Evenly coloured topsoil at site Dye 1.

Plate 4.3 Vertical coloured tongues divided by uncoloured areas below the topsoil at site Dye 1.

Plate 4.4 Bleached zones penetrated by roots at site Dye 1.

Plate 4.5 Dye distribution down the soil profile at site Dye 2.

Plate 4.6 Unevenly coloured topsoil at site Dye 2.

Plate 4.7 A large macropore forms the centre of a coloured finger extending down the soil profile.

Plate 4.8 Double ring infiltrometer (from Diamond and Shanley, in print).

Plate 8.1 Teflon suction cup installed as specified in Section 8.2.2.

Plate 8.2 Zero-tension sampler installed as specified in Section 8.2.2.

List of Tables

Table 3.1 Overview of study sites and types of investigations carried out.

Table 3.2 Site characteristics and monitoring periods of the overland flow sites.

Table 3.3 Land use characteristics of the overland flow sites.

Table 3.4 Management of the Dairy Farm sub-catchment.

Table 4.1 Morgan's P levels at overland flow sites.

Table 4.2 Morgan's K levels at the overland flow sites.

Table 4.3 Last recorded infiltration rates (stable on all soils but BU-C3) on day 2, means and standard deviations (stdev) of measurements at the Warren 1 (W1), the Warren 2 (W2), the Cowlands (C), soil types A2 (BU-A2), A3 (BU-A3) and C3 (BU-C3) at the Beef Unit.

Table 4.4 Last recorded percolation (holes) and infiltration (ring) rates (unstable) in 5 and 10 cm holes and the adjacent ring system at the Warren 1 (W1), the Warren 2 (W2), the Cowlands (C), soil types A2 (BU-A2), A3 (BU-A3) and C3 (BU-C3) at the Beef Unit.

Table 5.1 Numbers of samples analysed for the various fractions, numbers of samples above the limit of detection and numbers of samples with differences greater than or equal to 0.05 mg P/l between two fractions.

Table 5.2 R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the full and partial TDP/DRP datasets of the sites at the Warren, the Cowlands and the Beef Unit (TDP dependent, DRP independent variable).

Table 5.3 R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the full and partial TP/TDP datasets of the sites at the Warren, the Cowlands and the Beef Unit (TP dependent, TDP independent variable).

Table 5.4 R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the main and secondary trends in the full DRP/TDP datasets of the Warren 1 and the Cowlands (TDP dependent, DRP independent variable).

Table 5.5 R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the full DRP/TDP datasets of the upstream and downstream sites at the Dairy Farm (TDP dependent, DRP independent variable).

Table 5.6 R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the full TDP/TP datasets of the upstream and downstream sites at the Dairy Farm (TP dependent, TDP independent variable).

Table 5.7 Minimum and maximum pH values at the Warren 1, the Cowlands and the Dairy Farm sites.

Table 7.1 Numbers allocated to the overland flow events at the Warren 1 and the corresponding events at the other sites.

Table 7.2 Special occurrences during events.

Table 7.3 The range of flow-weighted average and maximum DRP concentrations at the Warren 1, the Cowlands and the Warren 2.

Table 7.4 Amounts of TDP and DRP exported in overland flow from the Warren 1 and the Cowlands during the monitoring periods of 493 and 144 days, and from the Warren 2 during the monitoring period of 144 days.

Table 7.5 Summaries of methods and results of studies on edge-of-field measurements of overland flow and P losses from grassland areas.

Table 7.6 Yearly and 144 day (8th November 1997 to 31st March 1998) amounts of overland flow and P export from the three overland flow sites. Average flow-weighted DRP concentrations for the two periods.

Table 8.1 Dates and numbers of events at the Beef Unit and corresponding events at the Cowlands.

Table 8.2 Identifications, locations (12 mg P/l and 4 mg P/l fields) and types of soil water samplers, and sampled events for which data are missing.

Table 8.3 DRP and TDP export (g/ha) between November 1997 and March 1998 from the artificial subsurface drainage system at the Beef Unit and the overland flow sites at the Warren 1 and the Cowlands.

Table 9.1 Rates of flow at the weir (G2), the upstream (M1) and downstream (M2) monitoring stations.

Table 9.2 Dates and numbers of events at the Dairy Farm and corresponding events at the Warren 1.

Table 9.3 TON, TA and K concentrations in samples taken of peat filter bed effluent and overland flow from the road.

Abbreviations

Adj.	Adjusted
AFPS	Air filled pore space
Al	Aluminium
BU	Beef Unit
C	Cowlands
Ca	Calcium
CAN	Calcium ammonium nitrate
Cond.	Conductivity
Cum	Cumulative
Diff.	Difference
DO	Dissolved oxygen
D/s	Downstream
DRP	Dissolved reactive phosphorus
E	Evapotranspiration
EPA	Environmental Protection Agency
Ev.	Event
F	Flow
Fe	Iron
Floww av.	Flow-weighted average
HCl	Hydrochloric acid
ID	Identification
K	Potassium
Log	Base 10 logarithm
LU	Livestock unit
Mg	Magnesium
Max	Maximum
Min	Minimum
MRP	Molybdate reactive phosphorus
N	Nitrogen
Neg.	Negative
No.	Number
NTU	Nephelometer turbidity units
P	Phosphorus
PE	Potential evapotranspiration
PP	Particulate P
PR	Precipitation
REPS	Rural Envrionment Protection Scheme
SMD	Soil Moisture Deficit
Ss	Suspended solids
SWAMP	Sustainable Waste Management Application Project
TA	Total ammonia
TON	Total oxidised nitrogen
TP	Total phosphorus
TDP	Total dissolved phosphorus
TRP	Total reactive phosphorus
U/s	Upstream
W1	Warren 1
W2	Warren 2

CHAPTER 1: BACKGROUND AND OUTLINE OF THE STUDY

1.1 General Background

The over-fertilisation, or eutrophication, of water bodies, and its negative impacts on aquatic ecosystems (McGarrigle, 1998; Vollenweider, 1971) and on water as a resource for domestic, industrial, agricultural and recreational usage (Caffrey and Allison, 1998; Gill, 1996; Hayes and Greene, 1984) have been a serious concern for a number of years in many countries. In Ireland about 30% of river channel surveyed by the Environmental Protection Agency (EPA) showed signs of eutrophication in the late 1990s (McGarrigle et al., 2002). As phosphorus (P) was recognised to be the main nutrient limiting primary production in most freshwater ecosystems (Levine and Schindler, 1989; Vollenweider and Kerekes, 1980), many efforts to identify and quantify the sources of the P in water bodies have been undertaken (e.g. Caraco, 1995; Hayes and Greene, 1984; Witmer, 1984).

In accordance with differences in natural and anthropogenic catchment characteristics, the origin of P in water bodies varies greatly among areas. Elevated P concentrations have often been associated with centres of population (Hirose and Kuramoto, 1981; MacDonald et al., 1995; Muscutt and Withers, 1996) but, increasingly, significant P contributions from agricultural sources are also being noted (Castillo et al., 2000; Foy et al., 1995; Stamm, 1995). Advances in wastewater treatment technology and more stringent legal requirements for industrial and domestic discharges to water bodies to be of higher quality (e.g. Council Directive Concerning Urban Wastewater Treatment (91/271/EEC)) have started the process of reducing P losses from domestic and industrial sources. The issue of agricultural P exports to water bodies, on the other hand, is still further away from being resolved. A variety of potential agricultural sources of P has been identified (Dils and Heathwaite, 1996; Loehr, 1979) but little is known about their relative importance and the yearly amounts of P they contribute to water bodies. Both of these issues are complicated by the enormous spatial and temporal variability expected with such figures.

Phosphorus lost from agriculture generally stems either from farmyards with their buildings, tanks and associated farming operations, or from land and the practices carried out to manage it. To turn P available for loss into an actual P export to a water body, a medium to mobilise and transport P and a transport pathway must be provided. In climates comparable with that of Ireland, water is the main transport medium. Thus, surface or sub-surface hydrological pathways are necessary for P from agricultural sources to be delivered to rivers and lakes (Heathwaite, 1997). Phosphorus from farmyards can be delivered to water bodies via overland and subsurface flow, whereas land related P losses from most soil types are thought to occur predominantly via surface hydrological pathways

(i.e. overland flow) (Heathwaite, 1997; Sharpley and Syers, 1979). Exports via sub-surface pathways are assumed to be less important because P tends to adsorb strongly to all but sandy soils (Morgan, 1997; Ozanne et al., 1961). Thus, unless a large proportion of the P binding sites of a soil are occupied (Holford et al., 1997), P in water percolating down a soil profile via matrix flow is largely removed (Logan and McLean, 1973). However, downward flow of water through the soil matrix is more and more found to be complemented by water movement through large pores (Flury et al., 1994). The soil matrix is thus bypassed in the latter case. Phosohorus adsorption therefore tends to be limited, which can result in preferential P transport down the soil profile (Stamm et al., 1998).

The effect of an individual farmyard on water quality tends to be localised. A farmyard acting as a source of P is thus generally identifiable and the reason(s) and mechanism(s) of P loss are usually easy to understand. For example, P can be exported to a water body with overland flow from a dirty collecting yard or with subsurface flow owing to a leak in a slurry storage tank. The technology and know-how to rectify situations which lead to P losses from farmyards are available. Depending on the circumstances, solutions may, however, be expensive. Because land related P losses can occur over wide areas, they may reach rivers and streams along extended sections of the channels. The occurrence and effects of such sources are, therefore, difficult to assess. Many of the characteristics and mechanisms which determine the potential of land to act as a source of P are not well understood, and effective measures to reduce the losses are generally hard to prescirbe.

In most situations, the P prone to be lost from land to water is located at or near the soil surface (Ahuja et al., 1981). It is contained in soil (Schreiber, 1988), in dead and live vegetation (Havis and Alberts, 1993; Miller et al., 1994), in faeces of grazing animals (Heathwaite, 1993), and in chemical and organic fertilisers (Heathwaite, 1997). Phosphorus near the soil surface can be mobilised by rain and/or overland flow. The amount of P transferred from the land surface to water is governed by the size of the P pools mentioned above and by their interactions with rain and/or overland flow. Soil P levels and soil type (Pote et al., 1999), the amount and the type of fertilisers used (Austin et al., 1996; Heathwaite, 1997) and the length of the time interval between nutrient applications and the onset of rainfall and/or overland flow (Misselbrook et al., 1995) have been found to have a large bearing on the quantity of P which can be mobilised by water. The proportion of this P that ends up as edge-of-field loss is then determined by all the factors influencing the ability of rain and/or overland flow to mobilise and transport P. These factors include soil hydrology (Pote et al., 1999), land use (Daniel et al., 1993), topography (Ahuja et al., 1982) and climate as well as present and antecedent weather conditions (Cooke and Dons, 1988). The availability of an active hydrological link between a field and a water body determines whether an edge-of-field loss reaches the water body.

To reduce land related P exports to surface water it is important to identify which of the influences on edge-of-field losses can be altered by management practices. Land use and soil hydrology can both be influenced to some degree but they are usually largely determined by site characteristics and climate. Greatly affected by management decisions are the soil P levels and the amount, type and timing of fertiliser usage.

1.2 Land Related Agricultural P Losses in Ireland

Most of the slight and moderate pollution observed in Irish rivers and streams is suspected to be caused by agriculture (McGarrigle et al., 2002). Agricultural pollutants originate from both farmyards and land (Torpey and Morgan, 1999; McGarrigle et al., 2002) and, as stated above, the relative importance of these sources is unknown and variable. Of the land related losses, it is reasonable to assume that most stemmed from grassland because this comprises about 90% of the total area farmed in Ireland (Fingleton and Cushion, 1999).

Most studies investigating P losses from agricultural grassland in Ireland have measured P exports from catchments in rivers and streams and attributed a relevant proportion of the P losses to the grassland areas of the catchments (Anon, 1996; Jordan et al., 2000), or they monitored P losses from small plots to assess the effects of specific management operations (fertiliser and/or slurry spreading) (Burke et al., 1974; Sherwood, 1990b). Nutrient exports from pasture in artificial subsurface drainage water have been described for a variety of management practices throughout the seasons in Northern Ireland (Jordan and Smith, 1985). In order to assess the P loss potential of agricultural land, measurements of edge-of-field P exports of different land uses on varying soil types and at several management intensities need to be carried out across the range of environmental conditions which usually occur during the year. To study the effects on water quality of the spatial integration of different land uses, soil types and management intensities it is, as a next step, necessary to estimate the proportion of potential P losses that actually reach water bodies in a given situation.

1.3 EPA (Environmental Protection Agency) Environmental Research Priorities 1995

With their 1995 environmental monitoring research and development programme, the Irish EPA supported several projects on subjects relevant to freshwater eutrophication. One of these projects had the overall objective of quantifying phosphorus loss from soil to water. The study in hand represents a part of this overall project, which furthermore encompassed work on P desorption from Irish soils, the development of a national 'P model', and the effects of nutrient management

planning on water quality (Tunney et al., 2000). Teagasc (Agriculture & Food Development Autrhority), Trinity College Dublin and University College Cork were partners in the overall project, and these organisations and the EPA co-funded the work.

The research on which this thesis is based was carried out at Johnstown Castle Research and Development Centre, Wexford, Ireland. All the study sites were located within the boundaries of the 388 ha estate (Figure 1.1).

1.4 Aims and Objectives of the Study on P Exports from Agricultural Grassland in Overland Flow and Artificial Subsurface Drainage Water

Aim 1: To quantify P exports with overland flow from agricultural grassland on soils of different P levels.

The main aim of the study in hand was to quantify P losses from grassland fields on soils of different P contents. The P level of a soil is thought to have a strong influence on edge-of-field P losses (Pote et al., 1999). Furthermore, because the soil can act as a P store, the soil P level generally reflects how intensively a site is managed. This parameter was thus the main management issue looked at and sites were otherwise managed as required by the soil P level. To negate the influence of soil type and other site specific and environmental factors on P concentrations in overland flow, all overland flow sites were established on the same soil type (gley), on land of similar topography and within the boundaries of Johnstown Castle Research and Development Centre, Wexford, Ireland (Figure 1.1). The investigations described in this study focussed on grazed grassland because this is the most important agricultural land use in Ireland (Fingleton and Cushion, 1999) and monitoring of overland flow was prioritised because P losses with overland flow usually exceed subsurface losses (Brookes et al., 1996; Burke et al., 1974; Haygarth et al., 1998).

The P export is the product of the amount of water leaving a site and the P concentration of that water. The soil P level is thought to mainly affect the P concentration in overland flow. The amount of overland flow produced may be slightly influenced by soil P level (see Section 2.4.2) but it is probably most strongly affected by the hydrological characteristics of the site. To document the effect of soil P level rather than site hydrology on the potential of pasture to lose P to water, the first aim was:

Aim 1.1: To assess whether differences in soil P levels of grassland on gley soils are reflected in P concentrations of overland flow.

TRINITY COLLEGE LIBRARY DUBLIN

The types of overland flow commonly described are infiltration excess overland flow, saturation excess overland flow and return flow (Cooke and Dons, 1988; Pionke et al., 1986). The overland flow mechanism prevalent at a site will determine the environmental conditions under which overland flow is expected to occur. For example, infiltrations excess overland flow will only arise at times when the rainfall intensity exceeds the infiltration capacity of the soil. This aspect of soil hydrology, together with the spatial distribution of the occurrence of overland flow, can influence P exports greatly, and the next aim was therefore:

Aim: 1.2 To identify the most important overland flow mechanism(s) on the type of soils used in this study, and gain information on the hydrological homogeneity of the sites.

Land-related P losses are known to vary during storms, throughout the year and due to management operations (Cooke, 1988; Sharpley and Syers, 1976; Sharpley et al., 1976). The fluctuations in P exports integrate the changes that occur in amount and quality of overland flow. Hence further aims were:

Aim: 1.3 To understand and compare the dynamics of overland flow rates, P concentrations and P losses at different sites during overland flow producing rainfall events.

Aim: 1.4 To gain information on overland flow quantity and quality across environmental conditions and as affected by management practices typical for pasture of given soil P levels.

Aim 2: To find out whether P exports with artificial subsurface drainage water occur from pasture areas at Johnstown Castle, and if they do, how the P reaches the artificial subsurface drainage network.

Because of the increasing international evidence that P contributions to water bodies with artificial subsurface drainage can be substantial enough to give rise to eutrophication (Haygarth et al., 1998; Stamm et al., 1998), the work reported on here aimed to establish whether such subsurface losses are an issue that needs to be further investigated in Ireland. This subject area can be organised into a number of themes which were to achieve the following aims:

Aim 2.1: To gain information on P concentrations in subsurface drainage water during rainfall events.

Aim 2.2: To estimate the extent and establish the mode of P movement down the soil profile.

Aim 2.3: To describe the effects of site management on P movement down the soil profile.

Aim 2.4: To understand the dynamics of flow rates, P concentrations and P losses during events and throughout the monitoring period.

Aim 3: To assess the P loss potential of the land of a farm unit representative of intensive dairy farming: the Dairy Farm at Johnstown Castle.

The Dairy Farm sub-catchment at Johnstown Castle contributes both overland and artificial subsurface flow to the stream running through it. The sub-catchment comprises land of various soil types and soil P levels and the combined effect of these is to be assessed. Again, a number of aims can be defined:

Aim 3.1: To gain information on the effect of the land of the farm unit on stream water quality, quantity and P exports during rainfall events.

Aim 3.2: To identify source areas of P loss and the flow pathways involved in land-related P exports.

Aim 3.3: To describe the effects of site management on P losses to the stream.

Aim 3.4: To understand the dynamics of flow rates, P concentrations and P losses during overland flow producing rainfall events and throughout the monitoring period.

Aim 4: To assess the importance of different forms of P in contributing to P losses via different flow pathways and due to varying site and management characteristics.

P in overland flow, subsurface flow and stream water has been shown to occur in organic and inorganic form. Both types can be dissolved or associated with particles (Anon, 1995). The different forms of P vary in their availability to aquatic life (Ekhlom, 1998). Their individual contribution to the P exports from an area, and the possible effects of flow pathway, site and management characteristics on P forms are, therefore, of interest.

1.5 Summary of the Data Collection

To address issues connected to P exports with overland flow, pasture areas on soils of low, medium and high P levels were hydrologically isolated so that surface water originated from a precisely defined area. The amount of overland flow from those sites was gauged and frequent samples were collected and analysed for P content and other chemical parameters. Soil profile descriptions for the overland flow sites were obtained. Water table levels were recorded at regular intervals.

Information on the subsurface movement of P was gained by sampling and analysing water from existing artificial subsurface drains, by using dye to elucidate the water movement down the soil profile and by obtaining and analysing samples both of preferential flow and of water mainly representative of matrix flow.

An intensive automatic flow recording and sampling programme was operated upstream and downstream of the Dairy Farm sub-catchment (Figure 1.1). To complement the water quality information collected at these two points, grab samples were taken at several locations along the stream running through the Dairy Farm.

Water samples were analysed for different forms of P and for ancillary water quality parameters. Rainfall records, topographical data and information on soil P levels and on management practices carried out on the land occupied by the study sites were collected.

1.6 Layout of the Thesis

The general introduction provided by this chapter (Chapter 1) is followed by a review of the literature on P exports from agricultural land, including an outline of the context of research into this subject (Chapter 2). In Chapter 3, an account of the general site and management characteristics of all the study areas is given. Soil chemical and hydrological aspects, including information on flow pathways, are discussed in Chapter 4. Chapter 5 deals with the methods of measuring water quality parameters. It also addresses the accuracy of those measurements and explores the relationships between the different forms of P in water samples from the various study sites.

Rainfall chemistry and distribution during the study period are described in Chapter 6. Chapters 7-9 contain detailed water quantity and quality information on overland flow from a low, a medium and a high soil P site (Chapter 7), on artificial subsurface drainage discharge from a network at Johnstown Castle (Beef Unit) (Chapter 8) and on a stream draining the Dairy Farm sub-catchment. The hydrological and water quality information are discussed in relation to site characteristics,

environmental conditions and management factors. Even though measurements in the stream at the Dairy Farm were taken the year before the artificial subsurface drainage was monitored, the subsurface drainage data are reported in Chapter 8 and the stream data in Chapter 9. A logical succession of contents was given preference over adherence to chronological order of data collection. The stream running through the Dairy Farm is a mix of overland flow and subsurface drainage water, and the way the chapters are organised allows for a discussion of data on the separate flow pathways before their mixed effect is considered. The Dairy Farm sub-catchment is furthermore located downstream of the artificial subsurface drainage monitoring point at the Beef Unit (Figure 3.7) and the artificial subsurface drainage water represents a large proportion of the stream water at the point where the stream enters the Dairy Farm sub-catchment.

The main findings of the study are then drawn together in Chapter 10, and areas where more research is needed are identified.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

2.1.1 Phosphorus (P) and Cultural Eutrophication

Eutrophication is the enrichment of water with nutrients followed by an increase of primary production (Vollenweider, 1971). In some water bodies this can be a natural process (Sharpley et al., 1987). Due to human activities, eutrophication nowadays often happens at an accelerated pace (cultural eutrophication), and it also affects water bodies which otherwise would remain oliogotrophic. The ill effects cultural eutrophication can have on aquatic ecosystems were recognized decades ago (Vollenweider, 1971). Yet, due to the multitude of ways in which cultural eutrophication can develop, and the complex nature of the processes involved, research on how to best reduce nutrient inputs to water bodies is ongoing and many rivers, lakes and coastal and marine ecosystems are still eutrophic (Carr and Goulder, 1990; David and Gentry, 2000; Descy, 1991; Foy et al., 1995; McGarrigle et al., 2002; Moog et al., 1993).

In Ireland, Bowman and Clabby (1998) considered cultural eutrophication to be the '...most significant threat to the quality of freshwater in the Republic of Ireland...'. The process is thought to jeopardize the survival of species reliant on oligotrophic conditions (Champ, 1998; McGarrigle et al., 1993; McGarrigle, 1998; Moorkens and Costello, 1994), to compromise recreational activities such as navigation (Caffrey and Allison, 1998), angling (Caffrey and Allison, 1998), bathing (Owens and Wood, 1968), and to impact on the use of water for drinking (Hayes and Greene, 1984; Reynolds, 1998), for agriculture and for industrial (Gill, 1996) purposes.

Phosphorus (P) is most commonly - but not always (Chessman et al., 1992; Jones, 1990; Koblenz, 1980; Winterbourn, 1990) - the nutrient limiting production in freshwater bodies (Koblenz, 1980; Levine and Schindler, 1989; Massik and Costello, 1995; Vollenweider and Kerekes, 1980; Winterbourn, 1990). The paramount importance of the phosphate ion disappears in coastal waters and N often becomes the limiting nutrient (Brennan et al., 1998; Service et al., 1998). Coastal and marine ecosystems will therefore not be discussed here.

The role of P in the spread of freshwater eutrophication led to the issue of legislation to limit the P concentration in Irish waters (S. I. No. 258 of 1998, Local Government (Water Pollution) Act, 1977; (Water Quality Standards for Phosphorus) Regulations, 1998). Thus, the legal basis and requirement to combat eutrophication has been in place since 1998, but the measures required to achieve the set standards are still being debated (Clenaghan et al., 2001).

What has, however, been recognized is that water quality issues are best addressed at catchment scale (Anon, 1997). The composition of water contributing to e.g. a stream or lake is a result of conditions and substances encountered on the way from the clouds to the water body. Water borne inputs to a water body are therefore affected by atmospheric processes and by catchment characteristics, inclusive of human activities. The quality of a body of water is then also influenced by non-water borne inputs (e. g. dry deposition). It is furthermore modified by processes within the water body, such as exchange reactions between water and suspended sediments, and by interactions of the water with the overlying air and with the bottom sediments. Water quality thus reflects recent and/or historic interactions between the atmosphere, the terrestrial and aquatic ecosystems in a catchment, and the processes within the water body.

In order to combat eutrophication by reducing P concentrations, it is advisable to identify, on a catchment basis, where the P in a water body comes from, by which processes it is mobilized, via which pathways it reaches a water body, and what happens to the P once it has entered the water body. An assessment and quantitative estimate of the magnitude of these pools and fluxes will help to focus strategies to lower P concentrations in water, and lead to efficient measures for achieving this.

2.1.2 The Role of P in Surface Water Bodies (Freshwater)

As mentioned above, P is generally the nutrient limiting primary production in freshwater ecosystems. The trophic status of a freshwater body is thus greatly influenced by the amount of available P in the water (Vollenweider and Kerekes, 1980). However, the relationship between the P concentration and the productivity of a freshwater ecosystem is not simple. Instead, P cycles through the system, taking part in various internal processes, undergoing long and/or short-term storage in components of the ecosystem and often being re-mobilized and used all over again (Ball and Hooper, 1963). The P inputs to the ecosystem greatly influence the level of productivity (Jones and Lee, 1982) at which P cycling takes place, and the level of productivity modifies the components and processes involved.

Phosphates make up the bulk of the P in freshwater bodies. Orthophosphates, condensed phosphates (oxidised organic compounds and inorganic polyphosphates (Ron Vaz et al., 1993)) and phosphates associated with organic matter are the three main types, and they all occur in dissolved and particulate form (Anon, 1995). Aquatic plants and algae utilize P as orthophosphate (Levine and Schindler, 1980) but, in time, at least a proportion of the other forms can be transformed and become bioavailable (Borström et al., 1988; Fitzgerald, 1970; Sonzogni et al., 1982; Viner, 1988). The relative importance of the various forms of P changes between and within water bodies, with

TRINITY COLLEGE LIBRARY DUBLIN

time and with environmental conditions (Hooda et al., 1997; House et al., 1997; Svendsen et al., 1995).

Free orthophosphate is removed from the water column in a surface water body as inorganic material by precipitation (Broberg, 1984; House et al., 1995a) and it is adsorbed to organic and inorganic suspended and deposited particles (Green et al., 1978; House and Denison, 1998; House et al., 1995b). Orthophosphate is also taken up by autotrophic organisms (algae, macrophytes and some bacteria) (Broberg, 1984). P in autotrophs is released to the water or transferred to the dead organic matter pool either directly or via one or more elements of the food net (Ball and Hooper, 1963; Newbold et al., 1983). There is direct P exchange between the surface of organic material and the water column. However, P bound by organic matter may also pass through saprotrophic organisms before it is returned to water or it may, at least temporarily, become unavailable (e.g. buried in the sediment (Borström et al., 1988; Foster et al., 1987)). P associated with inorganic matter will keep taking part in exchange reactions with the water (Sharpley and Syers, 1979) until it becomes physically (e.g. buried in sediment (Foster et al., 1987; Logan et al., 1979)) or chemically unavailable for varying periods of time (Furumai and Ohgaki, 1988; Green et al., 1978; Logan et al., 1979; Moore and Reddy, 1994).

The phosphate buffer concept suggests that suspended and deposited solids have a stabilizing influence on the phosphate concentration in water (Froehlich, 1988; Koski-Vähälä and Hartikainen, 2001; Oloya and Logan, 1980; Ruan and Gilkes, 2000). This means that the net release to water of P bound by particles happens in response to a drop of the P concentration in water, and that the net removal of P from water by solids is a consequence of an increase of the P concentration in water (Froehlich, 1988; Lennox, 1984). The amount of P available for these reactions makes up the exchangeable (between sediment and water) or bioavailable P pool (Sharpley, 1993). The P buffering mechanism usually only compensates for a part of a drop/increase of the P concentrations in water. Thus new equilibrium concentrations, at which the exchange reactions between sediment and water take place, are established (Froehlich, 1988; Ruan and Gilkes, 2000). These concentrations are also influenced by fluctuations of the ionic strength, the pH and the redox potential of the water (Koski-Vähälä and Hartikainen, 2001).

In reality, equilibrium concentrations are probably only rarely achieved because of the strong effect changes of the environmental conditions tend to have on P reactions (Casey and Farr, 1982; Fox et al., 1989; House et al., 1986; Istvanovics, 1988; McCallister and Logan, 1978). The release of P from solids, for example, is generally furthered by biotic or abiotic disturbances of the sediment (Johnson et al., 1976; Jones, 1990; Kronvang, 1992; Svendsen et al., 1995). Rainfall events and the resulting high flow conditions then represent a major disruption of the aquatic environment, and furthermore often go together with sediment movement and dissolved and particulate P inputs and

outputs (Balls et al., 1997; Brink, 1968; Brunet and Astin, 1998; Cullen and Rosich, 1979; D'Angelo and Webster, 1991). They thus change the whole foundation of the P reactions in an ecosystem (House and Denison, 1998).

2.1.3 Enrichment of Water Bodies with P

International and Irish evidence suggests that P enrichment in rivers often starts to become manifest at P levels around 0.02-0.03 mg/l P (Bowman et al., 1996; Dodds et al., 1997; McGarrigle, 1998). The corresponding concentrations for lakes is thought to vary between <0.01 and 0.02 mg/l P, depending on the trophic status of the lake (Champ, 1998; Sawyer 1947; Vollenweider, 1971). However, based on his comprehensive review of the eutrophication research available in the late 1960s Vollenweider (1971) points out that ballpoint figures for the onset of signs of eutrophication are not of general validity. Complex processes and conditions within and outside a water body govern its trophic status, and each water body therefore reacts differently to rising nutrient concentrations (Vollenweider, 1971).

An increase in the amount of algae and aquatic plants is generally the first effect of the enrichment of freshwater with P (Bowman and Clabby, 1998; Levine and Schindler, 1989; McGarrigle, 1998). This increase of primary production is often accompanied by a change of the overall species composition and of the abundance of many plant and animal species (McGarrigle, 1998; Levine and Schindler, 1989). Thus, triggered by rising P concentrations, far-reaching changes of the aquatic environment can take place. Symptoms such as increase in turbidity (McGarrigle, 1998) and sedimentation (Champ, 1998), increased occurrence of algal/cyanobacteria blooms (Bowman and Clabby, 1998), high dissolved oxygen (DO) levels due to photosynthesis (McGarrigle, 1998) and low DO levels due to respiration and breakdown of organic matter (Lund, 1972; McGarrigle, 1998) start to manifest. These symptoms further change the aquatic habitat, the plant and animal species composition and abundance, and they may affect the taste, odour and toxin content of water (Bowman and Clabby, 1998; Champ, 1998; Hayes and Greene, 1984; McGarrigle, 1998).

Cultural eutrophication thus seriously impacts on water resources and their use. However, once sources of excessive P are identified and P levels reduced, aquatic ecosystems can recover. The timescale of recovery is extremely variable and governed by each specific set of circumstances. For example, a lake which was fertilised for research purposes on two occasions recovered within 1-2 years (Levine and Schindler, 1989), whereas a declining trend of P concentrations of several Swiss lakes started in the mid 1980s and is still ongoing (Wehrli et al., 1996).

2.1.4 Sources of P

Sources of pollution are generally divided into point and diffuse (non-point) sources (House and Warwick, 1998; Loehr, 1979). This split is often arbitrary and affected by the scale of an investigation. However, sources such as discharges from industrial or wastewater treatment plants are always classified as point sources (House and Warwick, 1998; Loehr, 1979). The core requirement for a point source is that it occurs at one particular location. The term diffuse source, on the other hand, describes pollutant inputs originating from extended areas. The pollutants are transferred to water bodies by transport media and mechanisms which are effective over large areas (e. g. overland and subsurface flow, or wind). In comparison with point sources, diffuse sources are more difficult to identify, quantify and control (Owens, 1970; Vollenweider and Kerekes, 1980). Their detrimental effect on aquatic ecosystems may, therefore, become increasingly significant as pollution from point sources is being contained (Foy et al., 1995; Moog, 1984; Smith et al., 1994).

Point and diffuse domestic, industrial and agricultural sources all contribute P to freshwater. The proportion attributable to each sector and type of source varies among catchments (Beaulac and Reckhow, 1982; Caraco, 1995; David and Gentry, 2000). For many rivers, P inputs were found to be dominated by domestic and/or industrial sources (Caraco, 1995; Castillo et al., 2000; Hirose and Kuramoto, 1981; MacDonald et al., 1995; Muscutt and Withers, 1996; Vighi et al., 1991; Witmer, 1984). The bulk of these inputs often originates from point sources (Caraco, 1995; Loehr, 1979; Muscutt and Withers, 1996; Osborne, 1988). In areas which are chiefly affected by agricultural P losses, the relative contribution of point and diffuse sources is extremely variable and hard to assess (Gleeson and Kiely, 1995; McGarrigle et al., 1997; Mitchell, 1990; Schofield et al., 1990). Land related losses are generally regarded as diffuse agricultural sources of P, and farmyards and associated facilities, manure heaps, feedlots and areas around drinking troughs and gateways as agricultural point sources of P (Cooke and Williams, 1970; Dils and Heathwaite, 1996; Gleeson and Kiely, 1995; Loehr, 1979). However, a separation of P sources into point and diffuse is particularly vague in an agricultural context.

It is worth noting that the impact particular P inputs will have is variable for different water bodies (Moog et al., 1993), seasons (Correll et al., 1999; Duda and Finan, 1983; Heathwaite and Burt, 1991; Heathwaite et al., 1989; Hooda et al., 1997) and according to fluctuations of other environmental parameters (House, 1990).

2.1.5 Diffuse Agricultural P Contributions

Elevated P levels in freshwater bodies fed by predominantly agricultural catchments free from obvious point sources of pollution have been described often (Foy and Withers, 1995; Kronvang,

TRINITY COLLEGE LIBRARY DUBLIN

1990; 1992; Nelson et al., 1996). More specifically P enrichment of freshwater bodies has been attributed to the use of organic (Misselbrook et al., 1995) and inorganic fertilisers (McColl et al., 1975;), the subsequently augmented soil and plant P levels (McDowell et al., 2001), the presence of livestock and the livestock density in catchments (Johnes et al., 1996) and to features which encourage erosion (Steegen et al., 2001). All but the last one of these factors are linked inseparably. Generally, the soil P level represents a long-term integration of the efficiency of agricultural production systems because it is greatly affected by the balance of P inputs and removals (Culleton et al., 1999a; Tunney, 1990).

Due to the fact that transport of P from a source area to a water body is chiefly mediated by water in humid temperate climate zones, an active hydrological link between the P source and the water body is required for P transfer. As hydrological links are often activated by rainfall, P losses from land to water are driven by precipitation events (Heathwaite, 1997; McDowell et al., 2001). However, the response of an area to the precipitation determines whether P from a particular source will reach a water body (Duda and Finan, 1983; McColl, 1979; McDowell et al., 2001). That is to say, the hydrological characteristics of a source area determine whether P becomes mobilised in the first instance, and the existence and quality of a hydrological link decide whether mobilised P is merely repositioned or whether it reaches a water body.

Agricultural activities can impact on the hydrological responses and pathways in an area (Foster and Dearing 1987), and they can furthermore turn land into potential sources of P loss. This usually happens when P inputs to a production system are greater than P outputs in produce, i. e. when the amount of P imported in fertilisers and feedstuffs is greater than the amount of P exported in crops (Korevaar and den Boer, 1990; Tunney, 1990; Withers, 1996). In order to prevent P depletion of soils from affecting crops (Tiessen et al., 1983) and livestock (Culleton et al., 1999b), and to maximise production (Karlovsky, 1958; Mattingly and Penny, 1968), the use of P fertilisers has become a widespread agricultural practice (Hanley, 1965).

P fertilisation and the build–up of soil P levels are thus a feature of agricultural intensification. Frequently coupled with other practices capable of enhancing P loss, they can but do not always lead to cultural eutrophication. It is therefore necessary to identify the factors which further P transfer from land to water, and describe and implement a way of farming which allows optimum (from an economic point of view) production without leading to the degradation of water resources. In Ireland, about 30% of the river channel surveyed by the EPA is eutrophic (McGarrigle et al., 2002). Diffuse agricultural sources of pollution are held largely responsible for the eutrophication (McGarrigle et al., 2002). As grassland by far dominates agricultural land use in Ireland (Fingleton and Cushion, 1999) this type of land use is likely to be responsible for a considerable portion of the

TRINITY COLLEGE LIBRARY DUBLIN

land related P loads in freshwater bodies. The control of P losses from agricultural grassland may therefore be particularly relevant to achieving a reduction of the P levels in Irish freshwater ecosystems.

2.2 P in Soils

2.2.1 Origin and Redistribution

The primary sources of P in soils are the P rich minerals in parent material (solid rock and deposits) (Ahl, 1988; Froehlich, 1988; Hanley, 1965). Larsen (1967) describes all other P inputs into soils as a part of a redistribution process, which encompasses all P imports other than those from the primary source, and all P exports. Water, wind, animals (wild and cultivated) and the farmer, when he/she removes crops and applies organic and inorganic fertilisers, are the agents in the redistribution process.

P is released from minerals (mainly apatite) to the soil solution through the process of weathering (Holtan et al., 1988). It can then precipitate out of solution again, adsorb onto organic or inorganic particles, be incorporated into soil fauna and flora or be taken up by higher plants. The plants are then either eaten by herbivores, removed from the system by harvesting or they die, decay and the P in them is recycled into the soil P pool. Some of the P taken up by herbivores will also be returned to the soil P pool more or less immediately by defecation or, in the longer term, by the death of animals. Exports of P from a particular area do not only occur by crop (plant and animal) removal but also via water running out of the area and, to a small degree in humid temperate climate zones, by wind erosion. P imports as a part of the redistribution process occur by fertiliser applications (chemical and organic), with seeds, by wet and dry atmospheric deposition and by water that carries P running into the area.

In natural ecosystems, the recycling of P from dead plants, animals and from faeces leads to a gradual accumulation of plant available P in the topsoil (Syers et al., 1969; Tiessen et al., 1983). Nowadays, this process is usually exacerbated in agricultural ecosystems where fertilisers, manures (liquid and solid), soiled water and crop residues represent significant P additions (Johnes and Hodgkinson, 1998; Ryan, 1990; Young and Mutchler, 1976) to the top few centimetres of the soil. These P inputs often exceed P removed by crops (Smith et al., 1997) and thus lead to a considerable increase of P levels near the soil surface (Humphreys et al., 1998; Murphy and Culleton, 1997).

2.2.2 Forms of P in Soils

P in soils generally occurs as phosphate, which is in organic and inorganic form (Holtan et al., 1988). The percentage of organic P in soils is assumed to vary between 20 and 80 (Larsen, 1967; Vaithiyanathan and Correll, 1992; Williams, 1959). Schachtschabel et al.(1992) group soil P into defined inorganic phosphate, defined organic P compounds and sorbed phosphate. The defined inorganic phosphates include calcium (mono-, di- and octa-) phosphates, iron and aluminium phosphates (Chang and Jackson, 1957; Larsen et al., 1965). In his review of organic P in soils Dalal (1977) lists inositol phosphates, phospholipids, nucleic acids, phosphoproteins and sugar phosphates as the defined organic forms of P which have been identified. Phosphates bound to Fe (iron) and Al (aluminium) ions in humic and fulvic acid complexes have also been observed (Martin and Molloy, 1971; Schachtschabel et al., 1992). The last group, sorbed phosphates, comprises phosphates sorbed to Fe and Al oxides and hydroxides, to clay minerals, to Ca (calcium) and Mg (magnesium) carbonates and to organic matter complexes with Fe and Al (Bowman et al., 1998; Holford, 1997; Holford and Mattingly, 1975; Mozaffari and Sims, 1994; Schachtschabel et al., 1992). This group encompasses physically as well as chemically sorbed phosphates (He et al., 1994; Hsu, 1964; Ryden et al., 1977). These phosphates are sorbed to the surface of particles or they can be sorbed phosphates which have diffused beneath the surface (occluded P) (Barrow, 1983a; 1983b; Chang and Jackson, 1957; Hanley, 1965; Ryden et al., 1977).

Nutrient additions (Fransson and Bergquist, 2000) and soil physical and chemical characteristics like texture (Olsen and Watanabe, 1970), structure (Higgs et al., 2000), drainage (Khalid et al., 1977; Williams, 1959), mineral composition (Bowman et al., 1998; Römkens and Nelson, 1974), organic matter contents (Barberis et al., 1996; Larson et al., 1972) and alkalinity and acidity (Anderson et al., 1974; Daniel et al., 1994; Herlihy et al., 1996) largely determine the type and abundance of P species in soils. These characteristics are influenced by interdependent factors such as parent material (Williams, 1959), soil development (Syers et al., 1969), climate and season (Tate et al., 1991; Weaver et al., 1988a), topography (Fransson and Bergkvist, 2000), vegetation and management (He et al, 1995; Ogaard, 1996; Vaithiyanathan and Correll, 1992).

The development and changes of the plant available soil P pool illustrates the interplay of many of these factors. During the course of soil development, the proportion of P in the form supplied by parent material (mainly apatite) decreases and the percentages of secondary inorganic and organic forms of P increase (Bowman et al., 1998; Syers et al., 1969; Tiessen et al., 1983). Secondary forms of P contribute to a transitional, more or less plant available soil P pool before they are converted to forms of P of negligible plant availability (Bowman et al., 1998). Vegetation and crop production then are affected by and influence the size and composition of the transitional soil P pool. Vaithiyanathan and Correll (1992), for example, measured nearly 70% of the P as organic P

in the topsoil of a forest and about 25% organic P in the topsoil of arable land. They attributed the higher proportions and amounts of inorganic P in arable soil to fertiliser additions and to mineralisation of organic matter during cultivation. In comparison with arable land, grassland leads to higher levels of organic matter (He et al., 1995), and therefore to higher percentages of organic P in soils (Cooke and Williams, 1970). Organic matter and organic P also tend to accumulate when mineralisation is impeded, e. g. in very dry or waterlogged soils, or at cold temperatures (Cooke and Williams, 1970; Hanley, 1965). A rise in temperature, improved oxygen supply due to drying, or the restoration of adequate soil moisture increase microbial breakdown of organic matter and thus the release of P to the plant available soil P pool (Cooke and Williams, 1970; Hortenstine and Forbes, 1972). Such releases are, therefore, common in spring and autumn (Cooke and Williams, 1970). Magid and Nielsen (1992) also measured a decrease of organic soil P in spring, but claim that it is too marked to be attributable to biological processes alone.

2.2.3 Plant Available P

The P in soil solution at a given time amounts to a very small fraction of the annual P needs of plants (Morel et al., 2000). Plant P requirements are thus mainly met by P bound to soil (Frossard et al., 2000; Morel et al., 2000; Munk and Rex, 1990; Saarela, 1992). Growth is affected by the amount of P that will be released from the solid phase to the soil solution, because this is the P that can be taken up by plants (available P) (Holford, 1997). The rate of P release is the other important factor influencing the plant available P in soil solution (Cooke, 1966).

The fraction of the soil P which is available for replenishing the soil solution is often called the labile or exchangeable P pool (Holford, 1997; LeMare, 1981). This pool is mainly made up of the part of the sorbed P pool held at sites of low bonding strength (Holford, 1983; Holford et al., 1974). However, contributions of the defined organic (Dalal, 1977; Macklon et al., 1997; Tarafdar and Claasen, 1988) and defined inorganic soil P pools are also reported to occur (Chang and Jackson, 1957; Holford, 1983; Holford, 1988). Over time, labile P can become non-labile by incorporation into biomass, occlusion into minerals (Froehlich, 1988; Ryden et al., 1977) and micoraggregates and precipitation as sparingly soluble compounds (McCollum, 1991, Tiessen et al., 1983). Conversely non-labile P can become a part of the exchangeable soil P pool (Holford, 1988) through the processes of mineralisation (Garbouchev, 1966) and weathering (Rubaek and Sibbesen, 1995), which includes dissolution (Schachtschabel et al., 1992). Mineralisation is of prime importance in soils which are high in organic matter (Zou et al., 1992) and have enough air to support the breakdown processes (Hortenstine and Forbes, 1972) (see above).

There is a continuous exchange of P between the labile soil P pool and the soil solution (Schofield, 1955). The direction and magnitude of the sum of all exchange reactions are mainly governed by

TRINITY COLLEGE LIBRARY DUBLIN

the degree to which a soil can resist changes of the P concentration in soil solution (buffering capacity) (Holford, 1988; Kamprath, 1999), but also by the contact time between soil and water (Hsu, 1964; Sharpley et al., 1981b), by temperature (White and Taylor, 1977a.) and by the composition of the soil solution (Bolan and Barrow, 1984; Geelhoed et al., 1999). Changes of the P concentration in soil solution are for example induced by plant uptake of P or P fertiliser additions (Hortenstine and Forbes, 1972; Ron Vaz et al., 1993). The buffering capacity of a soil will then govern the replenishment of solution P from solid P and the transfer of solution P to soil matrix P respectively (Holford, 1988; Holford and Mattingly, 1976a). The buffering capacity is dependent on the soil's capacity to remove P from solution and on the strength with which P is held by the soil (Holford, 1997). As soil releases P more easily with increasing P saturation (Fried et al., 1957; Hooda et al., 2000; Hsu, 1964; Sharpley, 1995a), the buffering capacity is affected by the size of the labile soil P pool (Kamprath, 1999; Morel et al., 2000). The effect of the buffering capacity of a soil on plant available P decreases with increasing root development of the crop (Holford and Mattingly, 1976b). However, at a given available soil P level and stage of growth, the plant uptake of P, and therefore the decrease in labile soil P, were shown to be greatest on the soil with the lowest buffering capacity (Holford and Mattingly, 1976b; Kamprath, 1999). In time and in the absence of more changes, the P concentration in soil solution will approximate an equilibrium P concentration at which soil P fixation equals soil P release (Logan and McLean, 1973).

The mechanisms by which the P in soil solution is assumed to be replenished are desorption and, to a smaller degree, dissolution (Holford, 1988; Leinweber et al., 1997; Webber and Mattingly, 1970) and mineralisation (Dalal, 1977). The importance of dissolution often increases towards the later stages of plant growth when the defined inorganic P pool is more likely to be drawn on (Holford, 1988). Dissolution also tends to be of enhanced significance shortly after fertilisation (Holford, 1997; White and Taylor, 1977b) and with decreasing pH (Holford, 1983).

As sorption and desorption processes are generally considered to be the main P transfer mechanisms between soil matrix and solution, the P sorption and desorption properties of soils are commonly used to characterise the plant availability of P (Holford, 1997). Soil P sorption is determined by measuring the amount of P removed by soils from solutions of a range of P concentrations (Holford, 1997; Nair et al., 1984). To assess P desorption, the quantity of P released from soil suspended in distilled water or solution is determined (Barrow, 1983b; Oloya and Logan, 1980; Sharpley et al., 1981a). Laverdière and Karam (1984) point out that the P removal from solution in such experiments occurs via sorption and precipitation. Strictly speaking, sorption studies report on the sum of P fixed by sorption and precipitation. Similarly, desorption estimates

may include a proportion of P dissolution. P release due to biological activity, on the other hand, is inhibited in most experiments (Nair et al., 1984).

Regardless of the release/immobilisation mechanisms assessed by sorption/desorption experiments, such studies help to identify parameters which influence the P release or fixation characteristics of soils. Sorption studies are commonly used to measure the capacity of the soil to retain added P (P sorption capacity) (Mozaffari and Sims, 1994). The number of unsatisfied P sorption sites (P sorption index) can be estimated by measuring the amount of P fixed from a single addition (Laverdière and Karam, 1984). Mozaffari and Sims (1994) recommend the P sorption index as a quick way of appraising the sorption capacities of soils. Sorption data fitted to models yield soil P sorption maxima (Laverdière and Karam, 1984; Holford et al., 1974; Mozaffari and Sims, 1994), which are used to calculate the percentage of extractable soil P (various extractants) in reference to the P sorption maximum (P sorption saturation) (Sharpley, 1995a). This is commonly called the degree of P saturation.

Relationships between sorption data and other soil properties revealed that amorphous iron and aluminium oxides and hydroxides and clay minerals are the most important soil constituents involved in the exchange of inorganic and organic P between the labile soil P pool and soil solution (Anderson et al., 1974; Dorich et al., 1985; Laverdière and Karam, 1984; McCallister and Logan, 1978; Mozaffari and Sims, 1994; Vaithiyanthan and Correll, 1992). Additional sorption sites are known to be provided by calcium carbonate surfaces in calcareous soils (Holford and Mattingly, 1975; McKercher and Anderson, 1989). The role of organic matter is ambivalent. It sorbs P very strongly (Laverdière and Karam, 1984) but has also been observed to enhance the release or decrease the fixation of inorganic P from soils (Dalton et al., 1952; Habib et al., 1994) due to organic anions competing with P for sorption sites (Geelhoed et al., 1999; Holford et al., 1997; Leinweber et al., 1999). Elevated (> 5) solution pH is also said to depress P sorption (Anderson et al., 1974), which explains reports of increasing soil P release after liming (McConaghy, 1965; Webber and Mattingly, 1970a). Reduced conditions were found to further the release of native soil P, while at the same time enhancing the amount of sites which can adsorb added P (Khalid et al., 1977).

In summary it can be said that the amount of plant available P in soils is affected by the size of the soil P pools, the soil type, by biological, chemical and physical soil processes, by the vegetation and its developmental stage and by management practices. Plant available P is, therefore, also influenced by the climate (Hanley, 1965), the weather and the time of year (Garbouchev, 1966; Rubaek and Sibbesen, 1995; Saunders and Metson, 1971; Shand et al., 1994; Simpson, 1965; Tate et al., 1991).

2.3 Agricultural P Additions and Soil Properties

2.3.1 Benefits of P Fertilisation

Agricultural production relies on adequate amounts of plant available P in soils. Soils are said to be deficient in P when application of P results in better growth of plants (Schofield, 1955). For animal nutrition is furthermore advantageous if plant P levels are sufficiently high to support healthy stock (Culleton et al., 1999b) without the need of P supplementation. Sub-optimal P supplies to crops were widespread in Ireland until relatively recently (Tunney, 1990) and they are still a cause for concern world-wide (Brown et al., 2000; Holford, 1997; García-Rodeja and Gil-Sotres, 1997; Haynes and Williams, 1992). As P fertilisation is known to lead to increased plant growth in many soils (Johnston et al., 1986; Kaila and Hänninen, 1961; Karlovsky, 1958; Mattingly and Penny, 1968), it has become common practice in modern agriculture and has thus led to widespread changes in the amounts and fractions of P in soils (see Section 2.2.2).

Apart from environmental losses and gains, P is exported from agricultural systems by crop removal (plants, milk, animals), it is recycled from crop residues and animal excreta and imported into systems through the purchase of chemical fertilisers, foodstuffs, animals and seeds. Without P additions, agricultural land use tends to deplete the labile soil P pool because of the P export in produce (Dalal, 1997; Haynes and Willliams, 1992; Tiessen et al., 1983).

The application of P fertilisers on P deficient soils not only increases crop production (Hera, 1996) but generally also increases the P contents and cycling of agricultural systems (Haynes and Williams, 1992; Tate et al., 1991). The use of easily soluble chemical P fertilisers enhances the amount of plant available P temporarily (Munk, 1985; Sharpley et al., 1978) but the level of easily available P then decreases exponentially (Larsen et al., 1965; Logan, 1982). Unless a soil is overfertilised, increases of the labile soil P pool are often only measurable for 1 to 4 months after fertilisation (Garbouchev, 1966; Logan and McLean, 1973; Sharpley et al., 1977). Merely 1-25% of applied P is normally utilised by crops in the first growing season (Dalton et al., 1952; Greenwood et al., 1980; Hera, 1996; Higgs et al., 2000; Ozanne et al., 1961; Strong et al., 1997). The remainder becomes a part of the general soil P pool (Garbouchev, 1966; Haynes and Williams, 1992; Larsen et al., 1965), which therefore supplies most of the P utilised by plants (Munk and Rex, 1990; Reith et al., 1987). This is very important because it explains why, on low P soils, not even heavy fertiliser additions will result in production equal to that achieved on high P soils (Johnston et al., 1986). Increasing levels of available P in soil then also enhance the P concentration in plants (Dalal, 1997; Kaila and Hännien, 1961; Tate et al., 1991). Elevated P levels in feed in turn lead to a higher P content of animal faeces (Barnett, 1994; Culleton et al., 1999a).

The amount of P which will be exported or recycled is, therefore, greater the higher the level of plant available soil P.

Fertiliser P fixed by soils can become available to plants in subsequent years (Russell, 1965; Strong et al., 1997; Williams, 1965). The addition of P fertilisers in excess of crop requirements also increases the proportion of soil P which is easily available to plants (Barberis et al., 1996; Holford et al., 1974; Logan and McLean, 1973). The higher the amount of plant available P in a soil then, the smaller will be the response of crops to further P additions (Johnston et al., 1986). There is a critical soil P level above which crop response to P can no longer be observed (Kamprath, 1999). At this critical level, which is the level between deficiency and sufficiency (Cox, 1992), the soil supplies adequate amounts of P for maximum crop production (McCollum, 1991). Due to the differences in buffering capacities of soils and P requirements of crops, the critical soil P level varies according to soil (Kamprath, 1999) and crop type (Cox, 1992). The volume of soil explored by roots and thus soil structure, soil moisture (Higgs et al., 2000) and weather conditions (Cox, 1992) also have an effect on the critical soil P level.

2.3.2 P Fertilisation and Crop Requirements

From the above it becomes clear that the soil is an important store for plant available P. However, information on the amounts that will be supplied to a crop from the soil at a particular site is often not easily available to a farmer, and accurate P fertilisation is therefore quite difficult. The critical soil P level and P requirements may not have been established for a particular soil type or crop (Cox, 1992). Even if the soil P level to best aim for is known, advice on P application rates may not be very reliable due to the spatial (Schepers et al., 2000), temporal (Friesen et al., 1985) and seasonal (Childs and Jencks, 1967) effects on soil P contents and P supply from soils to crops, due to differences in plant P usage as a result of the supply of other nutrients (Heckrath et al., 1995; Terman et al., 1977) and environmental conditions, and due to the inaccuracies inherent in soil sampling and analysis (Gallagher and Herlihy, 1963).

Agricultural soil P tests measure the amount of P extractable from a soil sample at a given time. The test result can then serve as an indicator of the amount of soil P which will be available for crop production during the year (Holford and Mattingly, 1979). Soil tests tend to measure the amount of labile and, thus, the easily desorbable P (McCallister and Logan, 1978; Oloya and Logan, 1980; Sharpley et al., 1984). As P desorption characteristics are affected by soil properties, so are the soil tests (Fernandes et al., 1999; Foy et al., 1997; Holford, 1980). The test results are therefore not always comparable across soil types (Wolf et al., 1985) and the usefulness of a test at a given site may depend on the existence of a satisfactory crop response curve for that particular soil. Finally, as P removed by chemical extractants is merely an estimate of the plant available P

reserves, it is likely that a soil test either misses a plant available P fraction (Culleton et al., 1999b) or extracts P which is not available to plants (Sibbesen, 1983). To ensure that crops receive enough P despite the insecurities associated with soil testing, recommendations and applications are often greater than crop demand (Cox, 1992).

Despite all this, excessive soil P levels are more likely to occur if soil testing is not carried out on a regular basis. Soil P also tends to accumulate if the P content of applied organic fertilisers is unknown and/or not taken into account when chemical P is added, or if organic fertilisers are applied at rates necessary to meet the N requirements of a crop (Maguire et al., 2000; Pote et al., 1996; Randall et al., 2000; Whalen and Chang, 2001). Excessive soil P levels as a consequence of the over use of organic fertilisers are of course more common in areas of high livestock densities, and thus significant P imports in feed (Leinweber et al., 1997; Sims et al., 2000).

2.3.3 Effect of P Additions

The total amount of P in soils is increased by the addition of chemical fertilisers (Haynes and Williams, 1992), liquid and solid organic manures rich in P (Rubaek and Sibbesen, 1995; Smith et al., 1998) and crop residues (Larson et al., 1972). Fresh animal faeces are also high in inorganic and organic P (Barnett, 1994; Sharpley and Moyer, 2000). They usually contain P ingested close to the point of faeces deposition and thus represent a redistribution of P rather than an addition. Agricultural P additions are also known to further the development of a vertical P gradient in the soil profile, where higher P levels occur at the surface (see above).

All the aforementioned types of P additions enhance the organic and the inorganic soil P pools. However, chemical fertiliser applications predominantly increase the inorganic fractions and of these mainly sorbed P and calcium phosphates (Haynes and Williams, 1992; Oloya and Logan, 1980).

The majority of the chemical fertiliser applied in excess of crop requirements has been shown to be transferred into the non-labile soil P pool in the long term (McCollum, 1991). In the short term, however, excessive P is easily available (Ogaard, 1996). It tends to be associated with fine material (Maguire et al., 1998; Ogaard, 1996) or to be precipitated as P rich particles (Pierzynski et al., 1990). Apart from its effect on soil P levels and P fractions, the application of organic and inorganic P has, furthermore, been shown to increase infiltration and soil moisture (Lambert et al., 1985; Rubaek and Sibbesen, 1995; Wendt and Corey, 1980) and to change the microflora of soils (Tate et al., 1991).

2.4 Storm Flow

2.4.1 Rainfall Events and P Transport

In humid temperate climate zones, water is the main medium to transport P from land to water bodies. This is especially true in connection with P from diffuse agricultural sources of pollution, which predominantly reaches water bodies during storms (Cooke, 1988; Heathwaite et al., 1989; Heathwaite et al., 1990a; Pionke et al., 1996). Transfer of P is, therefore, linked to the hydrological cycle, which describes the circulation of water from the atmosphere, to and through terrestrial and/or aquatic ecosystems, and back to the atmosphere. The amount of water available to transport P depends on the local characteristics with influence on the hydrological cycle. The proportion and fractions of P mobilised from source areas and delivered to water bodies are greatly influenced by the path the water follows on its way to the water body (Dils and Heathwaite, 1996).

Precipitation can fall as rain, snow, sleet or hail (Rohan, 1986). The mild temperatures prevailing in Ireland ensure that the amount of rainfall by far exceeds the amounts of other forms of precipitation (Rohan, 1986). The role of snow, sleet and hail in the hydrological cycle and in P transport will, therefore, not be considered here.

In the long term, flow from a catchment area generally equals precipitation minus evapotranspiration. Water reaches e. g. a stream as precipitation falling directly into it, as overland flow, throughflow (shallow subsurface flow) and groundwater flow (Ogunkoya and Jenkins, 1993). Overland flow and throughflow normally make up the bulk of storm flow, but substantial contributions from groundwater have also been reported (Ogunkoya and Jenkins, 1993). Evaporative losses occur from all wet surfaces (water bodies, wet soils, plants, concrete surfaces, etc.) as long as the air above the surface is not saturated with water (Ling, 1982). A considerable proportion of the rain intercepted by vegetation and litter (Petch, 1988; Smith, 1992), and of the rain that reaches the ground, evaporates (Church and Woo, 1990). Transpiration then returns water taken up by plants back to the atmosphere. Evaporation and transpiration are controlled by climatic factors but also by plant species, surface and soil characteristics and conditions. They influence and are influenced by soil moisture (Hendrickx, 1990; Ling, 1982) and, therefore, by each other.

The rainwater that reaches the ground either infiltrates the surface or stays on top of it and, depending on topography, becomes overland flow or is stored in surface depressions (Horton, 1933). The partitioning of rainwater into the infiltrating and non-infiltrating components is controlled by the infiltration characteristics (Bouma and Dekker, 1978; Römkens et al., 1990) and the moisture contents (Baker and Laflen, 1982; Philip, 1957) of a soil.

TRINITY COLLEGE LIBRARY DUBLIN

Overland flow can reach a surface water body, evaporate, be held back in surface depressions or infiltrate downslope, often into a soil of higher infiltration capacity, and thus become subsurface flow (Chevallier and Planchon, 1993; Gburek, 1983). Subsurface flow has been observed to re-surface as overland flow (Eshleman et al., 1993; Pionke and DeWalle, 1994; Pionke et al., 1986; Sklash and Farvolden, 1979), travel to water bodies as throughflow (shallow subsurface flow) or travel down the soil profile until reaching a groundwater body (deep subsurface flow) (Germann, 1990). Hence, a clear separation between overland and subsurface flow is not possible. As contact with the often P rich soil surface tends to affect the P levels in water, all flow which travels on the surface before it enters a water body is classified as overland flow here.

2.4.2 Overland Flow

The amount of overland flow in general is influenced by soil type (Gardiner, 1986), land cover (Dunne, 1983) and management (see below), amount of rainfall (Van Keuren et al., 1979), rainfall intensity (McColl, 1979), antecedent soil moisture (Henninger et al., 1976; Taylor and Pearce, 1982), in some instances slope (Liu et al., 1997) and artificial subsurface drainage (see below). How far overland flow travels is largely dependent on soil type but also on slope (Gburek, 1983) and storm size (McColl, 1979). During storms which give rise to a lot of overland flow, the water is inclined to travel further along the surface. Large overland flow producing rainfall events can also pick up water which had been stored in depressions since a previous event (Dils and Heathwaite, 1996).

Infiltration Excess Overland Flow

Infiltration excess overland flow occurs if the rate of rainfall exceeds the infiltration capacity of a soil (Cooke and Dons, 1988; Horton, 1933). The infiltration capacity usually decreases as more and more water is added to a soil (Diamond and Shanley, 1998; Horton, 1933; Philip, 1957). This is partly due to the fact that there is a reduction in matric suction as the soil wets up (Bodman and Colman, 1943). Some of the clay minerals can furthermore swell up and the size of pores and cracks can be reduced (Bouma et al., 1979; Freeze, 1974). At field capacity, infiltration has decreased to a constant infiltration capacity (Diamond and Shanley, 1998; Shaw, 1994). This value is typical for each soil and independent of initial soil moisture (Diamond and Shanley, 1998; Philip, 1957). As it is mainly a measure of the volume and the connectivity of the soil pore network (Arya and Paris, 1981; Hills, 1970) and, in some soils, of the swelling potential of clays, the infiltration capacity is to a large degree determined by the texture, organic matter content and structure of a soil (Bache et al., 1981; Chambers et al., 2000; Reynolds and Zebchuk, 1996), and the biological activity (Ehlers, 1975). Changes of soil particle sizes and packing, of organic matter content, soil structure, or the biological activity will, therefore, also affect the infiltration capacity. Knapp

(1978), for example, claims that low pH can weaken soil structure and therefore lower the infiltration capacity.

Infiltration capacity is known to be different in winter than in summer (Cooke and Dons, 1988; Diamond and Shanley, 1998). This is commonly attributed to increased viscosity and surface tension of cooler water (Lehmann and Ahuja, 1985), and to changes in bulk density due to lower biological activity (Lehmann and Ahuja, 1985).

The permeability of the soil surface can be reduced by a variety of factors. The impact of raindrops can increase the packing density of soil particles (Freeze, 1974; Horton, 1933; Knapp, 1978). Rain can, furthermore, wash material into open soil pores and they can become sealed (Angulo-Jaramilo et al., 1997; Le Bissonnais and Singer, 1993). These processes affect exposed soil surfaces to a much larger degree than surfaces protected by dense vegetation. It is, therefore, not surprising that greater amounts of overland flow were found to be associated with reduced vegetation cover (Daniel et al., 1993; Heathwaite et al., 1990a; Van Keuren et al., 1979). Surface sealing and thus an increase in the volume of overland flow has also been shown to result from the application of some liquid manures (Smith et al., 1998).

Especially on wet soils, the presence of grazing animals and the use of heavy machines can reduce the porosity of the topsoil, lower infiltration capacity and increase the risk of overland flow (Heathwaite and Johnes, 1996; Robinson and Naghizadeh, 1992). Surface applied farmyard manure (Sharpley and Withers, 1994) and high rates of chemical P fertilisation in combination with increased stocking density (Lambert et al., 1985), on the other hand, were observed to suppress the amount of overland flow. The lower volumes were attributed to increased infiltration capacity. Enhanced numbers of earthworms due to the availability of more organic matter (straw and dung) were named as a reason for the greater infiltration (Lambert et al., 1985). The addition of crop residues in no-till systems can also increase earthworm activity and, therefore, infiltration (Ehelrs, 1975; Kladivko et al., 1986; Zachmann and Linden, 1989). Greater macroporosity, the interception of rainwater by litter and reduced surface sealing can explain lower volumes of overland flow measured from no-till than from conventionally cultivated land (Dick et al., 1989; Klausner et al., 1974; Stoltenberg and White, 1953). Note though that Mueller et al. (1984) observed higher volumes of overland flow from no-till than conventionally cultivated soils and Heathwaite et al. (1990b) found that ploughing increased infiltration capacity.

The infiltration characteristics are not just a feature of the soil surface. Ward and Robinson (1990) describe that the infiltration capacity at a given time is limited by the soil layer with the lowest hydraulic conductivity encountered by the wetting front.

Saturation Excess Overland Flow and Return Flow

Once a soil is fully saturated with water, no more can infiltrate (Pearce et al., 1986). Rain falling on such areas turns into saturation excess overland flow (Pionke et al., 1988) at an overland flow to rainfall ratio of nearly 1:1 (Dunne and Black, 1970b). These areas are generally characterised by a high groundwater table or they become saturated due to layers of low permeability close to the soil surface (Cooke and Dons, 1988; Eshleman, 1993). Once enough rain has infiltrated to fill up the pores above a saturated layer, further rain will turn into overland flow (Dunne and Black, 1970a). Water from upslope areas flowing along a layer of low permeability (throughflow) can contribute to the saturation of surface soil further down (Anderson and Burt, 1990). If the layer of low permeability intersects the soil surface or an already saturated area, the upslope water can re-surface as overland flow (return flow) (Anderson and Burt, 1990; Sklash and Farvolden, 1979).

These variable overland flow source areas are permanently or temporarily saturated (McColl et al., 1985). They are often found along stream channels (Pionke et al., 1996), in hollows (Burt et al., 1983), on concave slopes (Petch, 1988), at the bottom of slopes or where soil water storage is reduced (Anderson and Burt, 1990) e.g. due to thin soil cover. The extent of saturated areas changes seasonally (Zollweg et al., 1995), during rainfall events (Pionke et al., 1988), according to days since rain (McColl et al., 1985) and due to agricultural management practices (Duda and Finan, 1983).

2.4.3 Subsurface Flow

Surface and subsurface water are not separate. Instead, there is a dynamic exchange of water between the surface, the unsaturated and the saturated subsurface zones. Ward and Robinson (1990) split subsurface water into shallow and deep subsurface water. The deep component corresponds to groundwater and the shallow to soil water, which moves as saturated (perched water table) and unsaturated throughflow. During a rainfall event, infiltrated water percolates down the soil profile until it reaches the groundwater or a perched water table due to a restricting layer (see above). The infiltrated water can furthermore move downslope as unsaturated flow (Bosch et al., 1994). Throughflow can reach the groundwater, and throughflow and groundwater flow both discharge into a water body or re-surface as return flow (Bosch et al., 1994; Pionke and DeWalle, 1994; Pionke et al., 1986; 1988).

The movement of infiltrated water follows differences in soil water potential (Shaw, 1994), which is affected by the number and sizes of pores, the connection between them, the changes of the pore network after wetting (Knapp, 1978), and by water content and position. The characteristics of the pore network are a result of the texture and the structure of the soil (Hendrickx, 1990), and the

biological activity. The textural voids are commonly called micropores and continuous openings which are not due to texture are called macropores (Beven and Germann, 1982; Bouma, 1982) and mesopores (Wilson and Luxmoore, 1988). There have been several attempts made to classify pores according to their size. Luxmoore (1981), for example, suggested size ranges of <10 μm, 10-1000 μm and > 1000 μm for micro-, meso- and macropores respectively. From a water movement viewpoint, Germann's (1990) split according to the dominant forces working on water in pores is useful. Pores in which water is mainly drained by gravity he calls macropores and he defines micropores (soil matrix) as pores in which capillary and gravitational forces are effective. Radulovich et al. (1992) specify that micropores are pores still filled with water at field capacity.

The reasons for the development of macropores are manifold: plant roots (Edwards et al., 1988), soil fauna (Beven and Germann, 1982), and more specifically worms (Shipitalo et al., 1990) have been named, and soil processes give rise to cracks (Flury et al., 1994), fissures (Grant et al., 1996), natural soil pipes and channels (Bouma et al., 1977; White et al., 1986; Wild and Babiker, 1976).

As the soil matrix is comparable with a porous medium, matrix flow can approximately be described by Darcy's Law. This concept suggests that the rate of flow through a porous medium is proportional to the hydraulic gradient (Ward and Robinson, 1990). However, even in homogeneous coarse textured soils the flow of water can be more complex (Netto et al., 1999). A texture change (Magid et al., 1992; Starr et al., 1978) or soil disturbance (Ghodarti and Jury, 1990) can split the wetting front up into fingers. The meso- and macropore space tends to be irregular and is, therefore, not comparable to the voids in a porous medium. Meso- and macropore networks can go to considerable depth. Stamm et al. (1998) observed active macropores at a depth of 1 m. To make them effective in transporting water, meso- and macropores need to be connected (Germann et al., 1984) and continuous (Beven and Germann, 1982; Bootlink and Bouma, 1991; Edwards et al., 1988), and a minimum moisture content is necessary to grant continuity (Germann, 1990).

Flow through meso- and macropores is called bypass (Flury et al., 1994), non-matrix (Germann, 1990), or preferential flow. Such flow bypasses a portion of the soil matrix (Flury et al., 1994). It occurs in a small portion of the soil volume (Simard et al., 2000) through few large pores (Trojan and Linden, 1992) or through sequences of water conducting pores (Seyfried and Rao, 1987). With preferential flow water moves rapidly (Bouma and Wösten, 1979) either vertically (Bouma and Dekker, 1978) or laterally downslope (Beven and Germann, 1982; Stamm et al., 1998). During a rainfall event, preferential flow moves faster (Beven and Germann, 1982; McCoy et al., 1994) and further down the soil profile (Shipitalo et al., 1990) than matrix flow. This suggests that the soil matrix as a whole does not need to be saturated before flow in macropores can occur (Armstrong

and Garwood, 1991; Kirkby et al., 1997; Wilson et al., 1991). This assumption was confirmed by the observation that localised saturated conditions are sufficient to initiate macropore flow (McCoy et al., 1994; Mosley, 1982). Seyfried and Rao (1987), however, measured significant bypass flow only under saturated conditions.

Bypass flow has been described in a wide variety of soils (Larsson and Jarvis, 1999; Kung, 1990; Schoen et al., 1999). Soil structure, texture and management affect the number of macro- and mesopores and, therefore, also the significance of preferential flow for water movement through a soil (Flury et al., 1994; Mosely, 1982; Shipitalo and Edwards, 1993; Singh and Kanwar, 1991). The shape, direction, and surface characteristics of the pores also influence the occurrence of non-matrix flow (Radulovich et al., 1992; Trojan and Linden, 1992). Additionally, more intense rainfall (Germann et al., 1984; McCoy et al., 1994; Trojan and Linden, 1992) and events of longer duration (Bouma and Dekker, 1978; Radulovich et al., 1992; Shipitalo et al., 1990) can further the importance of preferential flow, and most studies measured a higher proportion of the percolation volume as non-matrix flow at low rather than high initial soil moisture (Larsson et al., 1999; McCoy et al., 1994; Shipitalo et al., 1990; White et al., 1986). However, Flury et al. (1994) did not detect a large effect of initial soil moisture on preferential flow.

Because of the pronounced differences in water movement through the micropore and the meso- and macropore systems, it is tempting to separate pores into two different pore space domains (Rao et al., 1980; Steenhus and Muck, 1988; White et al., 1984): the soil matrix and the meso- and macropore space. This separation exists temporarily (Germann, 1990; Jensen et al., 2000; Lennaretz et al., 1999) but in time there is usually water and solute exchange between pore spaces (Bouma and Dekker, 1978; Rao et al., 1980; Shipitalo et al., 1990; Steenhus and Muck, 1988). Infiltrating water may also encounter and mix with water from a previous event. This is, for example, the case when water reaches the groundwater table. There it is said to mix with and displace the water of the capillary fringe (Germann, 1990). Such a mechanism is often considered to operate in the case of subsurface storm flow. Water contributing to storm flow in e.g. a stream, has frequently been shown to originate from an earlier event. The assumption is that infiltrating water from a monitored event recharges the soil water and pushes pre-storm water out into the stream (DeWalle et al., 1988; Pearce et al., 1986) or to the soil surface as return flow (Eshleman et al., 1993). This can happen at great speed (Germann, 1990), but Wilson et al. (1991) describe that the fastest water stems from the monitored event. This water is thought to bypass the soil matrix via macro- (Chapman et al., 1997) and/or mesopores (Wilson et al., 1991) and then dominate the early subsurface contribution to storm flow (Laubel et al., 1999; Wilson et al., 1991). Storm flow contribution from a current event seems to become more important the bigger the event (DeWalle and Pionke, 1994).

2.4.4 Artificial Subsurface Drains

Artificial subsurface drainage networks are installed to achieve improved drainage and lower the water table (Rose et al., 1991). Thus the grazing season on wet sites (Armstrong and Garwood, 1991) can, for example, be extended and/or the risk of impeded growth due to high water tables reduced (Brereton and Hope-Cawdery, 1988). Subsurface drainage networks can hugely alter the hydrology of a field (Foster and Dearing, 1987; Newson and Robinson, 1983). Drains encourage quick movement of water away from the surface into the subsurface zone (Addiscott et al., 2000; Rose et al., 1991). They thus reduce the occurrence of overland flow (Bottcher et al., 1981; Simard et al., 2000; Turtola and Paajanen, 1995). As management practices which loosen the soil and increase hydraulic conductivity are often used in combination with artificial subsurface drainage, the water content of the soil can be increased as a consequence (Bottcher et al., 1981; Kuntze, 1975; Reid et al., 1990), and the water yield of a catchment may be lowered (Bottcher et al., 1981).

Artificial subsurface drains also provide for a special type of subsurface flow. They intercept both matrix and macropore flow (Stamm et al., 1998). They have been described as stable large and well connected macropores, which provide a quick route from agricultural land to a water body (Dils and Heathwaite, 1996; Lowrance et al., 1984). They can establish a direct hydrological connection to areas at a distance from e. g. a stream (Duda and Finan, 1983).

2.4.5 Importance of Pathways

The relative importance of different hydrological pathways in contributing to stormflow varies with climate and catchment characteristics such as land use and management, soil type, geology and topography (Anderson and Burt, 1990; Burt and Butcher, 1985; Cooke and Dons, 1988; Derby and Knighton, 2001; Foster and Dearing; 1987; Heathwaite et al., 1990a). At a given site, the relative importance of pathways is furthermore affected by season, the size of the rainfall event (Cooke and Dons, 1988; Pionke et al., 1993) and antecedent soil moisture (Dils and Heathwaite, 1996). Often, overland flow is thought to be the main contributor to peak stormflow in rivers and streams (Cooke and Dons, 1988; Dunne and Black, 1970b; Eshleman et al., 1993; McColl et al., 1985; Ogunkoya and Jenkins, 1993), but subsurface flow can also dominate storm flow (Burt and Butcher, 1985; Culley et al., 1983; DeWalle et al., 1988; Heathwaite et al., 1989f; Pearce et al., 1986; Sklash and Farvolden, 1979). Overland flow travels very fast (Dunne and Black, 1970b) and is likely to give rise to early peak flow (DeWalle and Pionke, 1994; Pionke et al., 1986). Even if subsurface flow contributes significantly to storm flow it tends to reach the stream later than overland flow and thus become more important as the storm goes on (Burt and Butcher, 1985; Burt et al., 1983; Harris et al., 1984; Pionke et al., 1988). However, the time lag between water arriving via the different pathways can be small if subsurface flow moves close to the surface (Beven and Germann, 1982;

Harris et al., 1984), if an effective macropore network transmits water rapidly to depth (Beven and Germann, 1982), or if the capillary fringe reaches to near the soil surface (Beven and Germann, 1982; Pionke et al., 1988) and allows for a rapid rise in groundwater table and the fast initiation of translatory flow towards the stream (Anderson and Burt, 1990).

Again it is important to remember that there is an exchange of water between surface and subsurface pathways. A particular 'parcel' of water can travel along different types of pathways, and activities in one type of flow path can influence movement in another. It is, therefore, not surprising that the variable source area concept described above for overland flow is also relevant for subsurface stormflow. Like overland flow, subsurface stormflow does not arise evenly distributed over the catchment area but it is contributed by distinctive shrinking and expanding areas within a catchment (Duda and Finan, 1983). If such a hydrologically active area intersects a P source area (e. g. field with high soil P), the P losses from the source area can be important for freshwater quality.

2.5 Interactions Between P Sources and Hydrology

The forms and the amount of P that land releases to or removes from rain/overland flow depend on the rainfall/overland flow characteristics, soil conditions, on the nature of the land surface and the amount and forms of P present. During the progress of a particular volume of water to a water body, the interactions between the land and the water, and the reactions between solid and dissolved substances in the water continue. The amounts and forms of P mobilised and thus contained in the volume of water are, therefore, likely to change many times (Heathwaite, 1993; Sharpley and Smith, 1990). The incessant P mobilisation and immobilisation reactions are modified according to the flow pathway but as P mobilisation/immobilisation and P transport are neither temporally nor spatially separated, their effects on P concentrations in overland and subsurface flow are difficult to identify. Still, some general features of the P in shallow subsurface and overland flow have been described.

2.5.1 P Sources and P Mobilisation

During a rainfall event the water which falls onto a grassland field, for example, will interact with the ground and may become enriched with P. Basically, the same is true for overland flow, which may be rain after falling on upstream areas or it may be return flow and, therefore, not fresh rain water. However, in the case of rain there is the added effect of the raindrop impact on the soil surface (Ghadiri and Rose, 1991), and rainwater is furthermore typically of lower dissolved salt content than return flow (Pionke et al., 1988). Shallow subsurface flow is usually made up of water which has passed through the land surface. If there are P sources at or near the soil surface, this

water will have interacted with them. It may thus have acquired P as rainwater reaching the ground and/or as overland flow.

P can be mobilised by rain or overland flow from fresh and decomposing plant material (Schreiber and McDowell, 1985; Sharpley and Smith, 1989; Timmons et al., 1970), from deposited faeces (Chichester et al., 1979), from the top layer of soil (Logan, 1982; Pionke et al., 1988), which is commonly enriched with P (Sharpley et al., 1978), and from organic and inorganic fertilisers (Misselbrook et al., 1995) applied shortly before rainfall/overland flow (Haygarth and Jarvis, 1997; Misselbrook et al., 1995).

The timing of storm events in relation to the availability of P for mobilisation is of prime significance. The application of organic and inorganic fertiliser in reference to rainfall events and soil water conditions have, for example, a considerable influence on P transfer to rainfall/overland flow (Burke et al., 1974; Haygarth and Jarvis, 1997; Misselbrook et al., 1995; Sherwood, 1990). But the high P losses shown to occur during rainfall events following fertiliser applications, decrease markedly with time (McColl, 1979; McColl and Gibson, 1979; Nash et al., 2000; Roberts et al., 1989; Sharpley and Syers, 1976). Soil and plant material, on the other hand, represent a constant and significant supply of P to water at the soil surface (Havis and Alberts, 1993; Ketcheson and Onderdonk, 1973; Pote et al., 1999).

The P transfer usually happens in one of three ways. First, rain can mix with soil solution and thus acquire the P dissolved therein (Ingram and Woolhiser, 1980; Logan 1982). Second, P can be removed from stationary soil matrix (Ekholm, 1998; Magid et al., 1992; Yli-Halla et al., 1995), and third, from eroded soil particles suspended in rainwater/overland flow (Ekholm, 1998; Ogaard, 1996) by the processes of dissolution and/or desorption (Logan, 1982). Sorption/desorption reactions dominate the exchange between the soil particles and rainwater/overland flow (Yli-Halla et al., 1995; Sharpley et al., 1981b). P release by dissolution occurs mainly in connection with P fertilisation (Sharpley et al., 1981b).

Mixing of water and stationary soil at the land surface is mainly confined to the top 2 cm and is most intense in the top 1 cm of the soil (Ahuja et al., 1981; Nash and Murdoch, 1997; Ogaard, 1996; Sharpley et al., 1988). This zone is called the mixing zone (Ingram and Woolhiser, 1980) or effective average depth of interaction (Ahuja et al., 1981). It varies with rainfall intensity, duration, slope of the soil surface, soil type and crop cover (Ahuja et al., 1981; 1982; Ingram and Woolhiser, 1980; Sharpley, 1985a).

In general, the P release to water is furthered by prolonged contact between soil and water (Nash and Murdoch, 1997; Sharpley et al., 1988), by greater water:soil ratios (Sharpley et al., 1981a; Yli-Halla et al., 1995), by larger amounts of P for release in the soil (Logan, 1982; Pote et al., 1996; Yli-Halla and Hartikainen, 1996), by higher temperatures (Yli-Halla and Hartikainen, 1996), lower ion contents of the water (McDowell and Sharpley, 2001; Yli-Halla et al., 1995) and reducing conditions (Grant et al., 1996). Because of their influence on the extent of the interaction between soil and water, factors such as the depth of the mixing zone, the length (Froehlich, 1988) and steepness (Sharpley et al., 1981c) of a slope and the rate of flow will have a bearing on the P released to rainwater/overland flow.

Soil particles suspended in water are an effective means of mobilising and removing P from an area. Usually the smaller and lighter particles, which also tend to be enriched with P, are eroded preferentially (Massey and Jackson, 1952; Maguire et al., 1998; Sharpley, 1985b; Stoltenberg and White, 1953). Erosion due to the impact of rainwater and/or overland flow is furthered by lack of crop cover (Chambers et al., 1992; 2000; Daniel et al., 1993), by topographical features which concentrate overland flow (Chambers et al., 2000), by compacted tramlines and wheelings (Chambers et al., 1992; 2000) and by rolling of late sown crops (Chambers et al., 2000). Maintenance of a good topsoil structure and a reduction of the area of exposed soil surface, on the other hand, are said to combat erosion (Chambers et al., 2000).

Suspended solids are also able to remove dissolved P from solution (Sharpley et al., 1981b) and interaction with the vegetated soil surface can lead to a decrease in the amount of particulate and/or dissolved P in overland flow (Alberts et al., 1981). This is the principle upon which many filter strip designs are based. Whether there is a net P release or a net P fixation by the soil is determined by the relative magnitude of the levels of available P in soil and overland flow. Rainwater, on the other hand, usually contains very little P (Jordan, 1997) and therefore normally acquires P when mixing with the soil surface. Once in solution, the exchange reactions between the dissolved and particulate forms of P have been described as a dynamic equilibrium (Sharpley, 1993).

2.5.2 Forms of P in Overland and Subsurface Flow

The forms of P in water are commonly distinguished according to the analytical methods used to quantify them. The 'Standard Methods for the Examination of Water and Wastewater' (Anon, 1995) describe the analysis of total and total dissolved P, of total and dissolved reactive and acid-hydrolyzable P. Other types of P, like organic and suspended P, are assessed by summation or subtraction of the measured fractions. A filter size of 0. 45 μm is defined to separate dissolved and particulate types of P. This criterion is widely used. However, 0. 45 μm filtration is an arbitrary distinction of dissolved and particulate P because there are colloids which are smaller than 0. 45

μm. Analysis of the total and dissolved reactive P measures the amount of P which reacts with molybdate in unfiltered and filtered samples. Molybdate reactive P is considered to be an estimate of the orthophosphate, and therefore the most readily available P (Anon, 1995; Flanagan, 1992). (For details on P forms and analyses used in this study, see Section 5.1.1.)

Acid-hydrolyzable P approximates the amount of condensed P (oxidised organic compounds and inorganic polyphosphates (Ron Vaz et al., 1993)) in a sample and total P the concentration of P in all forms. The difference between the total and the dissolved measurements are an estimate of P associated with suspended matter. Organic P (dissolved and suspended) is calculated by subtracting the relevant reactive and acid-hydrolyzable concentration from the total or total dissolved P concentration (Anon, 1995).

The forms of P that are immediately available to algae are often considered to be the most important. The DRP fraction is usually immediately bioavailable (Herve and Kauppi, 1986; Rigler, 1964; Stainton, 1980). Ekholm (1998) and Stevens and Stewart (1982a) estimated that 0 to 23% of particulate P also tend to be immediately available. This is the portion of particulate P that takes part in the exchange reactions between particulate and dissolved P (Sharpley, 1993). Condensed and organic forms of P are less readily available than DRP (Haygarth et al., 1997). Stevens and Stewart (1982b) measured that 10 to 32% of dissolved organic P is available for growth within 10 days. The fact that most of the TP is potentially bioavailable in the long term (Lean, 1973; Logan et al., 1979) should, however, be borne in mind.

2.5.3 Transport of P

Overland Flow

Most studies found that the dissolved P fractions, and of these the inorganic P forms, dominate P concentrations in overland flow from grassland areas (Andraski et al., 1985; Cooke, 1988; Daniel et al., 1994; Liu et al., 1997; Nash and Murdoch, 1997; Nash et al., 2000; Sharpley and Syers, 1979). Overland flow from tilled land, on the other hand, tends to contain a large proportion of particulate P (Daniel et al., 1993; Olness et al., 1975; Sharpley and Smith, 1990; Turtola and Jaakkola, 1995; Uusitalo et al., 2001). During transport suspended solids originating from low P soils tend to remove P from overland flow. Thus lower concentrations of dissolved but elevated levels of particulate P were measured in such samples (Sharpley et al., 1981b). Increased amounts of particulate P are also observed as a result of heavy grazing pressure (Heathwaite, 1993; Heathwaite and Johnes, 1996; Heathwaite et al., 1990a) and winter grazing – a practice which may, furthermore, lead to elevated concentrations of dissolved organic P (Sharpley and Syers, 1976). In general, the presence of grazing animals was found to chiefly affect TP levels if overland flow occurred shortly after or while the animals were present in an area (Jawson et al., 1982; McColl,

1979). However, at low stocking rates, grazing animals are unlikely to affect local water quality (Owens et al., 1989).

The use of organic and inorganic fertilisers has frequently been sshown to lead to an increase in P (Cox and Hendricks, 2000; Powell and Taylor, 1979; Römkens and Nelson, 1974; Sauer et al., 2000; Sharpley et al., 2001), and especially DRP (Sharpley and Syers, 1979), in overland flow. A positive relationship between the amount of available soil P - as determined by a variety of methods - in the very top layer of the soil and the P concentrations in overland flow has been described for arable (Bundy et al., 2001; Yli-Halla et al., 1995) and grassland (Daniel et al., 1993). Linear (Sauer et al., 2000; Sharpley et al., 1977), curvilinear (Sibbesen and Sharpley, 1997) and linear relationships characterised by change points (McDowell and Sharpley, 2001) have been observed. The trend of rising P concentrations in overland flow with increasing soil test P levels exists across soil types (Pote et al., 1996; 1999) but the P contents of overland flow and the increase of the concentrations with rising soil P levels differ between soils (Cox and Hendricks, 2000; Sharpley, 1995a).

Seasonal effects on the amount of P in overland flow and the proportions present in the various forms have also been observed. Highest P concentrations in overland flow were often measured in summer or autumn (Higgs et al., 2000; McColl, 1979; McColl and Gibson 1979; Yli-Halla and Hartikainen, 1996), and a general decrease was observed to occur during the course of autumn and winter (Sharpley et al., 1977). There is some evidence that dissolved inorganic forms of P in overland flow from pasture are more common in summer and autumn, and that particulate forms increase in winter and spring (Cooke, 1988).

Subsurface Flow

The quantity of P delivered to water bodies in subsurface flow depends on the amount of P that travels with the infiltrating water down the soil profile and towards e. g. a stream. Whereas the P levels in shallow subsurface flow can be considerable if, for example, artificial subsurface drainage networks are involved, the P concentrations in groundwater are often reported to be low (Cooke, 1988; Daly, 1991). Even though this is not always the case (Kilroy, 2001; Kronvang et al., 1993; Novak et al., 2000), P in groundwater is not considered here.

Two very different, but not mutually exclusive, methods of P movement down the soil profile have been proposed: P movement due to oversaturation of the soil matrix with P, and P transfer with meso- and macropore flow. The first mechanism is normally used to describe P movement in free draining soils of coarse texture. P in such soils is assumed to move with infiltrated surface water which percolates through the soil matrix (Haynes and Williams, 1992; Ozanne et al., 1961;

Richards et al., 1998). As P dissolved in water tends to be adsorbed or precipitated by soil constituents (Logan and McLean, 1973), it does not usually move very far down the soil profile. There is, however, a considerable increase in P transport through the soil matrix once a high proportion of the P sorption sites have been occupied (Holford et al., 1997; Leinweber et al., 1999; Shoumans and Breeuwsma, 1997). This happens more quickly in soils with low numbers of sorption sites (e. g. organic soils or sandy soils) (Calvert, 1975; Fox and Kamprath, 1971; Leinweber et al., 1999). P sorption sites can, furthermore, be used by organic anions. Thus the application of organic fertilisers was found to reduce the sorption capacity of a soil more than can be explained by the P addition alone (Holford et al., 1974; 1997; Jensen et al., 2000).

In the case of P movement with preferential flow, P enriched water from the soil surface moves down the soil profile through meso-and macropores (Bottcher et al., 1981; Grant et al., 1996; Laubel et al., 1999; Turtola and Jaakkola, 1995; Turtola and Paajanen, 1995). Mainly due to the great velocity at which the water is flowing down the soil profile (Elliot et al., 1998; Gentry et al., 2000), and the relatively small soil surface area exposed to the flowing water (Jensen et al., 2000), there is at times little interaction between the soil and the P in solution (Shipitalo et al., 1990). P in water flowing down preferential flow pathways is, therefore, easily lost to water bodies via subsurface flow (Steenhus and Muck, 1988). A combination of the two mechanisms of P loss with drainage water may often occur but P loss due to preferential flow is likely to be dominant in soils of heavier texture (Djodjic et al., 2000).

As there is at times only limited mixing between water draining through meso- and macropores and matrix water (Shipitalo et al., 1990), differences between P in soil solution and P in drainage water do occur (Chapman et al., 1997). DRP is usually considered to be the most important form of P in drainage water (Chapman et al., 1997). In comparison with drainage water, Chapman et al. (1997) measured a higher proportion of organic but a lower proportion of DRP in soil solution. Because DRP is mainly regulated by sorption reactions (Chapman et al., 1997), elevated proportions in drainage water suggest a paramount importance of sorption processes on P concentrations. P in soil water, on the other hand, is also influenced by biological activity and therefore contains more organic and condensed P (Chapman et al., 1997). The significance of DRP in drainage water in reference to other P fractions is additionally heightened if land is fertilised (Kirkby et al., 1997). On the whole, elevated soil P levels (Holford et al., 1997; Logan and McLean, 1973) and fertiliser applications (Cooke, 1988; Djodjic et al., 2000) tend to increase the P concentrations in drainage waters, but to what degree this happens is greatly influenced by soil type (Leinweber et al., 1999; Logan and McLean, 1973).

Subsurface Flow: Artificial Subsurface Drains

Artificial subsurface drains intercept subsurface water at a usually shallow depth of <1-2 metres (Beauchemin et al., 1998; Culley et al., 1983; Djodjic et al., 2000; Grant et al., 1996; Haygarth et al., 1998; Kladivko et al., 1991; Stamm et al., 1998). In contrast to other forms of shallow subsurface flow, water in artificial subsurface drains can no longer interact with the soil matrix (Dils and Heathwaite, 1996), and normally travels at much greater speed (Lowrance et al., 1984). The P that reaches an artificial subsurface drain is thus likely to be delivered to the drain outflow (Duda and Finan, 1983).

The proportions of the different forms of P found in water running through artificial subsurface drains varies between and during rainfall events but is also affected by land cover/use. Under continuously tilled land the particulate P is often found to be of greater (Bottcher et al., 1981; Culley et al., 1983; Grant et al., 1996; Uusitalo et al., 2001) or of equal (Djodjic et al., 2000) importance as dissolved P. The dominance of dissolved P has, however, also been observed (Gaynor and Findlay, 1995). Subsurface drainage discharge from grassland has commonly been found to contain more dissolved than particulate P (Haygarth et al., 1998; Hooda et al., 1999; Stamm et al., 1998; Turner et al., 1979).

A link between increases in P concentrations in artificial subsurface drainage systems and organic (Hergert et al., 1981; Stamm et al., 1998) and inorganic (Bolton et al., 1970; Hanway and Laflen, 1974; Heckrath et al., 1995) fertiliser applications has been found in many instances. This effect is, of course, strongly influenced by the timing of rainfall events in relation to the fertiliser applications (see above). Mirroring the P dynamics in soils, fertiliser applications are reported to not only increase the amount of P but also the proportion of P that is available to plants and algae (Turner et al., 1979).

Positive relationships between soil P levels of the topsoil and P concentrations in drainage water have been described for many situations (Brookes et al., 1997; Heckrath et al., 1995; Hesketh and Brookes, 2000; Smith et al., 1995). However, Sharpley et al. (1977) determined the soil P level at the depth of the drains to be a better indicator of the P concentrations in artificial subsurface drains than the P found in topsoil. Phosphorus levels and fractions in subsurface drainage water were, furthermore, shown to be influenced by the presence/absence of grazing animals (Jordan and Smith, 1985; Turner et al., 1979), by soil type (Calvert, 1975; Cooke and Williams, 1970), by seasonal factors (Grant et al., 1996; Laubel et al., 1999; Simard et al., 2000), by lime applications (Calvert, 1975) and by the depth to the drains (Culley et al., 1983).

2.6 Magnitude of P Losses

Due to the fact that both a P source and a transport mechanism need to be available for P losses from a field to occur, the P exports fluctuate with variation of source and transport characteristics.

Land related P losses to water are generally not considered to be of economic significance for agriculture (Burke et al., 1974; Fleming and Cox, 1998). Annual P losses from agricultural areas have been estimated to range from <1% to 32% of the P applied (Burke et al., 1974; Hawkins and Scholefield, 1996; McColl, 1979; Nash et al., 2000; Powell and Taylor, 1979; Roberts et al., 1989; Sharpley and Smith, 1990; Sharpley and Syers, 1979; Sharpley and Withers, 1994; Sharpley et al., 1988), and they can, therefore, rise from negligible to excessively high levels with regard to freshwater ecology. Phosphorus inputs with rain can exceed P exports from unfertilised areas (Hirose and Kuramoto, 1981; Owens et al., 1991; Sharpley et al., 1986), even if the land is wet (Burke et al., 1974). Annual P losses of less than 0. 5 kg P/ha have been measured in farmed and fertilised areas (Hanway and Laflen, 1974; Hawkins and Scholefield, 1996; Kilmer et al., 1974; Klausner et al., 1974; Vighi et al., 1991) but P exports can also amount to several kg/ha (Bengston et al., 1988; Brookes et al., 1996; Fleming and Cox, 1998; Haygarth and Jarvis, 1997; Hooda et al., 1996; Leinweber et al., 1999; Sharpley, 1995b; Sharpley and Syers, 1979).

On sites at which P exports occur via different pathways, water flowing through artificial subsurface drains generally contained equal (Dils and Heathwaite, 1997) or more (Sharpley and Syers, 1979) P than the other shallow subsurface water. The P concentrations in overland flow have frequently been found to be considerably higher than those measured in any type of shallow subsurface flow (Brookes et al., 1996; Burke et al., 1974; Fleming and Cox, 1998; Hanway and Laflen, 1974; Hawkins and Scholefield, 1996; Hergert et al., 1981; Pionke et al., 1988; Smith et al., 1998; Zhao et al., 2001). Reducing the volume of overland flow by installing artificial subsurface drains in land prone to overland flow can, therefore, lead to a reduction in P exports (Hawkins and Scholefield, 1996). Depending on management practices, the P losses through artificial subsurface drains may, however, still be environmentally significant. Furthermore, dissolved P losses via artificial subsurface flow can equal (Uusitalo et al., 2001) or exceed (Xue et al., 1998) losses via overland flow at some sites.

2.7 Connection Between Fields and Water Bodies

As P exports from agricultural land are usually more significant from an environmental than an agronomic perspective, the potential impact of P losses from a field depends on how much of the P is delivered to water bodies. The impact is potential rather than actual because the effect of P on the aquatic ecosystem changes with the form of P delivered, other constituents of the

overland/subsurface flow and the conditions encountered in the water body (Nash and Murdoch, 1997; Wendt and Corey, 1980).

The presence and quality of a hydrological surface or subsurface link between an area and e.g. a stream usually determine if and how much of edge of field P losses reach the stream. This points to the characteristics of the near stream areas or of land beside open drains with a direct connection to the stream as an important influence on stream water quality (Dils and Heathwaite, 1996; Heathwaite et al., 1990a; 1990b; Heathwaite and Johnes, 1996; Koblenz, 1980; McDowell et al., 2001). Overland flow from such areas does not have to travel far to deliver its, often considerable, P content to the stream. In comparison with overland flow from remote areas, overland flow from near stream areas is therefore less likely to evaporate, infiltrate, be stored in depressions (Gburek, 1983; McColl, 1979) or be slowed down to such an extent that the suspended solids and thus the particulate P can settle out (Alberts et al., 1981).

The hydrological connection between remote wet areas and a water body can often be improved by the installation of artificial subsurface drainage and open drains (Duda and Finan, 1983). Improving land drainage can thus increase P delivery to water bodies even though P concentrations are usually lower in water from artificial subsurface drains than in overland flow (see above).

Hydrological connections between a water body and the land parcels of its catchment are not simply a function of distance from the water body but rather a characteristic influenced by a complexity of natural and man-made factors, which vary greatly among areas. It is, therefore, not surprising that, even though land use in near stream areas may control P concentrations in water in many areas, land use of the whole catchment can influence P levels in some water bodies (Hunsaker and Levin, 1995; Johnes and Heathwaite, 1997; Tufford et al., 1998).

2.8 Measures to Reduce P Exports to Water

The immense variability of P sources and transport factors between areas and with time makes it extremely difficult to determine management practices and fertility levels which are reconcilable with good surface water quality. The attenuation of P on the way to a water body, the mixing of water with varying levels of P and the sensitivity of a water body to P additions influence the impact P exports from land will have on a receiving water body. These issues, therefore, also need to be considered when deciding on farming practices that will safeguard a desired level of water quality.

Approaches to reduce the impact of agriculture on water bodies are normally either efforts to reduce edge of field losses or strategies which will lead to P removal from overland or subsurface flow before it reaches the water body. Both buffer strips (Alberts et al., 1981; Cooke and Dons, 1988; Kedziora et al., 1995; Lee et al., 2000; Magette et al., 1989; Peterjohn and Correll, 1984; Sanderson et al., 2001) and wetlands (Casey and Klaine, 2001) have been shown to remove P from water but the results are ambiguous (Clausen et al., 2000; Kovacic et al., 2000; Magette et al., 1989; Osborne and Kovacic, 1993).

Agricultural land can be managed with the aim of minimising P exports. Suitable measures diminish P transport, P sources and/or P mobilisation. Strategies to reduce edge of field P losses include:

- the avoidance of soil compaction (Withers and Jarvis, 1998) and surface sealing (Knapp, 1978),
- the removal of livestock and the omission of organic and inorganic fertiliser applications when land is very wet (Cooke and Dons, 1988; Chichester et al., 1979; Hooda et al., 1999),
- restrictions of the rates of fertilisation (Cooke, 1988),
- recommendations on fertiliser placement and on the timing of application relative to grass height (Baker and Laflen, 1982; Hansen et al., 2000; Kimmell et al., 2001; McColl and Gibson, 1979; Mueller et al., 1984; Withers et al., 2001),
- advice on the type of fertiliser used (Ozanne et al., 1961; Roberts et al., 1989; Tariq Siddique et al., 2000; Weaver et al., 1988b; Withers et al., 2001),
- a reduction of P levels or P solubility in organic fertilisers (Dao et al., 2001; Malmquist and Göransson, 1997; Moore and Miller, 1994; Poulson, 2000; Smith et al., 2001; Valk et al., 2000),
- the land application of compounds to reduce P mobilisation (Basta et al., 2000; Codling et al., 2000; Haustein et al., 2000; Hyde and Morris, 2000; Moore et al., 2000; Stout et al., 2000),
- the definition of maximum soil P and/or soil P saturation levels (Leinweber et al., 1999; Sharpley, 1995a; Sharpley et al., 1995) and
- the establishment of threshold stocking levels as a way of controlling the intensity of agricultural land use (Irvine et al., 2000).

Overall P losses are also reduced by minimising soil losses due to erosion (Pesant et al., 1987; Sharpley et al., 1992). This can be achieved with steps like the establishment of satisfactory vegetation cover before the wet season (Withers and Jarvis, 1998), across slope cultivation (Quinton et al., 2001) and the use of no-till cultivation practices (Pesant et al., 1987; Sharpley et al., 1995).

These measures may be recommended for all agricultural land. However, in some cases a more efficient way of controlling P exports is to first identify areas from which P is likely to be lost and then implement measures in these areas (Cooke, 1988; Pionke et al., 1996). As stated above, such areas are characterised by the presence of both a P source and an active hydrological connection to a water body. Methods to not only pinpoint sites vulnerable to P loss, but also to rank them according to their potential for P loss have been developed (Lemunyon and Gilbert, 1993) and applied successfully (Birr and Mulla, 2001; Sharpley, 1995b; Sharpley et al., 2001).

TEAGASC AGRICULTURAL COLLEGE LIBRARY

CHAPTER 3: CHARACTERISTICS AND MANAGEMENT OF THE STUDY SITES

3.1 Introduction

During this project, water samples were collected from three field sites, from an artificial subsurface drainage network at the Beef Unit at Johnstown Castle, and from a small stream at the Dairy Farm at Johnstown Castle. All study sites were located within the land of Johnstown Castle Research and Development Centre, Wexford. Johnstown Castle is the Teagasc (Agriculture and Food Development Authority) centre focusing on environmental research. Names and types of investigations carried out at the study sites are listed in Table 3.1, and the locations of the study sites are indicated in Figure 1.1.

Table 3.1: Overview of study sites and types of investigations carried out.

Name of site	Type of studies carried out
Warren 1	• Intensive automatic sampling of overland flow. • Continuous recording of the amounts of overland flow. • Measurement of water table levels.
Warren 2	• Intensive automatic sampling of overland flow. • Continuous recording of the amounts of overland flow. • Measurement of water table levels.
Cowlands	• Intensive automatic sampling of overland flow. • Continuous recording of the amounts of overland flow. • Measurement of water table levels.
Beef Unit	• Intensive automatic sampling of water from an artificial subsurface drainage network. • Continuous recording of the amount of water discharging from the artificial subsurface drainage network. • Soil water sampling with Teflon suction cups and zero-tension samplers. • Dye studies to illustrate water movement down the soil profile.
Dairy Farm stream	• Intensive automatic high flow sampling of stream water where the stream enters the Dairy Farm sub-catchment and where the stream leaves the sub-catchment. • Continuous recording of stream flow at abovementioned sites. • Grab sampling along the stream channel. • Occasional sampling of overland and flow and water from artificial sub-surface drains.

Johnstown Castle is situated approximately 6 km to the south-west of Wexford town (302404/116584 UTM), at an altitude of about 60 m above sea level. The estate covers an area of

nearly 390 ha. Almost a third of it is taken up by ornamental gardens, including three artificial lakes, and mature and recently planted woodland. The remainder of the land is organised into three experimental farming units: the Dairy Farm (83 ha), the Beef Unit (106 ha) and the Organic Farm (57 ha). All the land of the Dairy Farm and the Beef Unit is grassland, but some of the area of the Organic Farm is used for cereal production in most years.

Johnstown Castle lies in a temperate climate zone with maritime influence. The annual mean daily air temperature is about 10° C, the mean annual rainfall approximately 1000 mm and the estimated mean annual evapotranspiration 571 mm (Rohan, 1986).

The bedrock geology at Johnstown Castle was assigned to the Cambrian and Lower Carboniferous periods of the Lower Palaeozoic and Upper Palaeozoic eras respectively. A Cambrian formation of sandstone, slaty mudstone and siltstone (Culleton Formation) underlies the main part of the farm. Red silt- and sandstone conglomerates (Duncormick Conglomerate Formation) of early Carboniferous age form the solid geology of the south-southeast corner of the Dairy Farm (Tietzsch-Tyler et al., 1994).

The Quaternary deposits on the estate are mainly glacial tills of loam to clay loam texture. The depth of the deposits ranges from 1 to 20 m and, in some areas, they are covered by a layer of sand of varying thickness (Culleton, 1976). The soils at Johnstown Castle Estate predominantly consist of well to moderately drained brown earths, moderately to poorly drained gleys, and areas of well drained brown podzolics/brown earths (Culleton and Diamond, in print). Culleton and Diamond (in print) compiled a detailed soil map of the estate. Due to that fact that the soils at Johnstown are so variable (J. Diamond, pers. comm.) detailed soil investigations to confirm the information on the soil map were carried out at all study sites except the Dairy Farm.

3.2 Selection of the Study Sites

The overland flow sites (designated Warren 1, Warren 2 and Cowlands) were chosen to have the same soil type, similar topography and land use, but different soil P levels. The Warren 1 was the low, the Warren 2 the medium and the Cowlands the high soil P site. The main site characteristics are summarised in Table 3.2 and the locations of the sites are indicated in Figure 1.1.

Table 3.2: Site characteristics and monitoring periods of the overland flow sites.

Name	Area ha	Mean (range) Morgan's P mg/l	Soil type	Average Slope	Monitoring period
Cowlands	0.46	17 (14.1 – 21.3)	Gley	2°	24.11.96 to 31.3.98
Warren 1	1.54	4 (3.3 – 4.4)	Gley	2°	24.11.96 to 31.3.98
Warren 2	1.09	8 (5.3 – 10.3)	Gley	3°	8.11.97 to 31.3.98

A 24.4 ha area within the Beef Unit was selected as the main site for work on P in artificial subsurface drainage water because the subsurface drains serving this area are all led into a single collector pipe, which was uncovered and instrumented for sample collection and flow measurement. Within this area there were also sites of comparable soil type but contrasting soil P contents, which were used for soil water sampling under grassland of contrasting soil P levels. Monitoring of the artificial subsurface drainage water from this area of the Beef Unit also provided information on the P sources affecting the upstream (u/s) monitoring station at the Dairy Farm stream (see below).

At the beginning of the overall EPA project on 'Quantification of phosphorus loss from soil to water' (see Section 1.3) an area of the Dairy Farm was deemed suitable for monitoring the impact of P exports from an area having medium soil P content on stream water quality. Therefore this area, the Dairy Farm sub-catchment, along with the low soil P and the high soil P overland flow sites (Warren 1 and Cowlands) were added to the contractual research agreement with the EPA. However, there were reservations about the suitability of the Dairy Farm site from the beginning of the study. The Dairy Farm sub-catchment is located downstream (d/s) of some of the land and the farmyard of the Beef enterprise (Beef Unit) at Johnstown Castle. There was, therefore, a recognised risk of elevated P concentrations occurring in the stream before it even entered the Dairy Farm. Elevated P levels in the stream upstream of the Dairy Farm could render the task of detecting an effect of the Dairy Farm sub-catchment on stream quality more laborious.

As Teagasc had named the Dairy Farm site in the contract document, they were reluctant to discard it until it was proven to be unsuitable. It was, therefore, decided to monitor the Dairy Farm stream for a winter (96/97), and use the results to decide whether to stop or continue using the site. By spring of the following year, however, construction on two large office complexes (EPA and Department of Agriculture, Food and Rural Development headquarters) within the Dairy Farm sub-catchment had started. The stream was clearly affected by the building work (very high suspended

solids levels at high and low flow) and there were plans to discharge the roof and other water running off clean areas from the finished complexes into the Dairy Farm stream.

With agreement of the EPA, the Dairy Farm site was abandoned at the end of May 1997. To replace it, plans were made to set up a medium soil P overland flow site (Warren 2, see above). Furthermore, the measurement at the u/s site of the Dairy Farm stream had raised some questions about the sources contributing P to the stream. Dirty water, which had been passed through peat filtering systems (see Section 9.2.2), and overland flow from some of the land of the Beef Unit and from the main road were identified as possible contributors of P but the role of the artificial subsurface drainage system at the Beef Unit was unclear. It was thus decided to look into the likelihood and possible mechanisms of P losses to the stream via artificial subsurface drainage from the Beef Unit (see above).

By the conclusion of this study, overland flow from the high and low soil P sites was monitored for about 16 consecutive months and overland flow from the medium soil P site for about 5 consecutive months (Table 3.2). Water flow and composition for selected constituents at two points in the Dairy Farm stream at Johnstown Castle were gauged from 24th November 1996 to 31st May 1997, and water from artificial subsurface drains at the Beef Unit was monitored from 4th November 1997 to 31st March 1998. Figure 1.1 gives an overview of the locations of the various sites and Figure 3.7 shows the course of the stream that was monitored.

3.3 Method of Soil Investigation

Overland flow data from the Warren 1 and the Cowlands were used by the Sustainable Waste Management Application Project (SWAMP)[1] to develop a model to identify land that is prone to overland flow (Ryan et al., 1999). The soils at the Warren 1 and the Cowlands sites were described as a part of SWAMP. As a part of the study in hand, the textural classification was confirmed by mechanical analysis of the samples taken by SWAMP.

Soil profiles (Appendix 1) were described at the Warren 2 and at the dye study sites at the artificial subsurface drainage site (Beef Unit) (Table 3.1, Figure 8.1). The profiles were described following the recommendations of Hodgson (1976). A Dutch auger was used to gather some soil information on the low soil P soil water study site at the Beef Unit (Figure 8.1).

[1] Optimal Use of Animal Slurries for Input Reduction and Protection of the Environment in Sustainable Agricultural Systems, AIR-CT94-1276, Teagasc, Oak Park Research Centre Carlow and Johnstown Castle Research and Development Centre, Wexford.

A micro-pipette method mainly based on Miller and Miller (1987), Burt et al. (1993), Doesburg (1996), Anon (1986) and adapted by D. Brennan (unpublished) was employed to determine soil texture. According to their percentages of sand, silt and clay, the samples were assigned to the soil texture classes used by the staff of the Soil Survey of Ireland (Gardiner and Radford, 1980). The soil texture analysis was carried out on duplicate samples. If the two results did not agree on a soil textural class, the analysis was repeated until duplicate sub-samples agreed.

3.4 Overland Flow Sites

3.4.1 General Site Characteristics

The main site characteristics are summarised in Table 3.2.

The sites vary in size but are of similar slope. The soil profiles at the Cowlands (high soil P site) showed a sandy loam topsoil overlying a loam. Embedded in the loam, a loamy sand lens of varying magnitude and distance from the surface runs from the top to near the bottom end of the site. At the Warren 1 (low soil P site), a sandy loam topsoil of 10-20 cm depth overlies a layer of sandy loam (magnitude of 20-50 cm) and a loam. Several lenses of more sandy material were detected at this site (T. D. Ryan, pers. comm.). The topsoil at the Warren 2 (medium soil P site) is a loam of about 20 cm depth. Below it, there is first a sandy loam of extremely variable size (2-20 cm) and finally a loam (see Appendix 1 for profile description). All horizons at the sites in the Warren are heavily gleyed. Gleying is also evident in the Cowlands. The high water tables which were observed at all sites are likely to have given rise to gleying, but Diamond and Sills (1998) also found evidence of a temporary saturation of the soil with surface water at the Cowlands.

Artificial subsurface drainage was installed at both sites at the Warren between 1975 and 1979. There are no records of the design of the drainage systems put in place at that time. Attempts were made to find the drains by making use of their magnetic characteristics (Magnetic Gradiometry), and by looking for evidence of a change in moisture distribution due to drains (Electrical Resistivity). However, trial runs of the two methods showed that neither of them worked (Kevin Barton, pers. comm.). The artificial drainage system at Johnstown Castle was superimposed onto a very old network of box shores (old drains constructed using stones). Based on anecdotal evidence, it could be determined that tile drains are arranged in a herring bone design. The main drains have a diameter of 15 cm and the branches a diameter of 10 cm. The distance between the branching drains is generally 17 to 19 m. On average, the drains are at a depth of 80 cm and were covered with 30 cm of gravel. A drain about 3 m below the surface catches the spring contained within the area of the Warren 1. This drain leads to one of the branching drains and thus joins the drainage

network. A spring also surfaces in the area of the Warren 2. A subsurface drain at a depth of 80 cm captures it. This drain leads the spring water into an open trench.

There is no knowledge of the existence of an artificial subsurface drainage system at the site in the Cowlands. However, box shores were found in an adjacent field and the excavations carried out to set up the site revealed the presence of tile drains nearby.

All the sites are in permanent grassland. Rushes are common at the Warren 1.

3.4.2 Management

The management practices carried out at the sites are listed in Table 3.3. The site at the Cowlands is a part of a long-term grazing trial, which started in 1968. The aim of this trial is to study the effect of different P application rates on soil P and sward composition (Culleton et al., 1999a). The site at the Cowlands was therefore managed according to the requirements of that experiment and included in the rotational grazing system operated on the plots of that trial. The overland flow site was grazed by 6.6 LU (livestock units)/ha for 27 days between the end of March and the end of October each year. The exact dates of entry and removal of the animals to the site were not recorded. The site received 30 kg P/ha per year in a single application towards the end of March. In 1998, the P application was delayed (and thus carried out after overland flow monitoring had stopped) because of the wet weather conditions prevailing in March. Close to the time of the P application, the site also received 57 kg N (Nitrogen)/ha and 31 kg K (potassium)/ha each year. Additional nitrogen was applied as detailed in Table 3.3.

The Warren 1 has been in permanent grassland since the 1970s (Tunney et al., 1997). Up to, and including, year 1996 the site was cut for hay in summer. The field received very little chemical fertiliser or slurry until 1991, when 33 m^3/ha of slurry were spread in summer. From autumn 1991 to spring 1996 the site was again unfertilised. Since summer 1996, N and K fertiliser was applied each summer. In order to make the management of the Warren 1 more comparable to the management of the site at the Cowlands, grazing animals were introduced in summer 1997. The availability of grass and the occurrence of sufficiently dry conditions to avoid poaching governed grazing.

Before the Warren 2 was converted to an overland flow monitoring site, it was a part of the silage and slurry spreading area of the Beef Unit at Johnstown Castle. The last application of slurry at this site occurred in March 1997. The field was cut for silage in May 1997 and then grazed for the

summer. No chemical P or K fertiliser was applied to the Warren 2 but the site received 57 kg N/ha in March 1997 and 1998.

Table 3.3: Land use characteristics of the overland flow sites

Site	**Livestock**	**Cuts**	**Fertilizer use**
COWLANDS			
Jan – Dec 1996	Grazed (6.6 LU[2]/ha) for 27 days from the end of March to the end of October.	None	**Phosphorus**: 30 kg P/ha on 25th March as superphosphate. **Potassium**: 31 kg K/ha on 27th March as muriate of potash. **Nitrogen**: 57 kg N/ha on 21st March as urea, 67 kg N/ha on 16th May as CAN and 67kg N/ha on 16th July as CAN (Calcium Ammonium Nitrate).
Jan – Dec 1997	Grazed (6.6 LU/ha) for 27 days from the end of March to the end of October	None	**Phosphorus**: 30 kg P/ha on 20th March as superphosphate. **Potassium**: 31 kg K/ha on 20th March as muriate of potash. **Nitrogen**: 57kg N/ha on 19th March as urea, 67 kg N/ha on 8th May as CAN and 67 kg N/ha as CAN in July 1997 (exact day unknown).
Jan – March 1998	None	None	**Nitrogen**: 57 kg N/ha on 5th March as urea.
WARREN 1			
Jan – Dec 1996	None	Cut for hay in June.	**Potassium**: 33 kg K/ha on 16th May as muriate of potash. **Nitrogen**: 27 kg N/ha on 16th May as CAN.
Jan – Dec 1997	Grazed (10.8 LU/ha) 2.7.97 to 14.7.97 and (5.2 LU/ha) 12.9.97 to 19.9.97.	None	**Potassium**: 33 kg K/ha on 23rd July as muriate of potash. **Nitrogen**: 27 kg N/ha on 23rd July as CAN.
Jan – March 1998	None	None	None
WARREN 2			
Jan – Dec 1997	Grazed (18.3 LU/ha) for 30 days in July and August.	Cut for silage at the end of May.	**Nitrogen**: 57 kg N/ha in March as urea. **Slurry** was spread in March (33.7 m^3/ha)
Jan – March 1998	None	None	**Nitrogen**: 57 kg N/ha on 17th March as urea.

[2] Livestock units as defined REPS (Department of Agriculture Food and Forestrey, 1996) : 1 L.U. = Cattle over 24 months old

TRINITY COLLEGE LIBRARY DUBLIN

3.5 Artificial Subsurface Drainage Site (Beef Unit)

3.5.1 General Site Characteristics of the Beef Unit

The artificial tile subsurface drainage system of about 24.4 ha of the permanent grassland used for beef production drains to a point just upstream of the farm buildings (monitoring station MB in Figure 1.1). According to anecdotal evidence, three main drains (outer diameter of 15 cm) with branching drains (outer diameter of 10 cm), which are 17 to 19 m apart, drain the area. This system was installed between 1975 and 1979 and superimposed on an existing network of stone shores. Eighty cm is the average depth of the tile drains but one of the stone shores was found at a depth of 30 cm below the surface. However, this was in a hollow (see below). The shores found when the tile drains were put into place were usually at 80 cm or deeper. The fact that the tile drains are surrounded by gravel was confirmed when one of the branching drains was accidentally disturbed during a dye study (see Chapter 4). Apart from the replacement of broken tiles, no maintenance has been carried out on the drainage network since it was installed.

The exact area drained by the network of artificial field drains cannot be determined. The catchment of the drainage system does not coincide with the surface water catchment because the network cuts through small hills that form part of the surface water catchment boundary. Based on a map of the contour lines and on anecdotal information on the location of the drains, an approximate subsurface drainage water catchment area of 24.4 ha was delimited (Figure 3.1). Only a proportion of the precipitation falling on those 24.4 ha will end up in the subsurface drains. The fields also produce considerable amounts of overland flow. Furthermore, due to the low density of drains in some parts of the area, large amounts of the infiltrating water will bypass the subsurface drains.

Some of the water in the subsurface drains is groundwater. A spring contributes to the flow in the drainage system. It is caught by one of the old stone shores. The shore is thought to originate within the area under investigation. It was known to run underneath a dip in the land well within the boundaries of the subsurface drainage catchment. In autumn 1997, the shore was excavated and was found to be 40 cm deep, 20 cm wide and covered by just 30 cm of soil. The stone shore joins the drainage network established in the 1970s upstream of the location at which samples were taken during this project.

The soil of the subsurface drainage catchment consists mainly of fine to coarse loamy poorly and imperfectly drained gleys (Figure 3.2). However, sand lenses are common throughout the area. At the dye study site 1 (Dye 1) (see Chapter 8), a sandy loam topsoil about 20 cm thick covered a loamy sand layer of 30 cm thickness and a loam subsoil. The profile at the dye study site 2 (Dye 2)

(see Chapter 8) showed a sandy loam of 30 cm depth overlying a sandy loam of 40 to 70 cm thickness and a loamy sand. Gleying was apparent throughout both profiles. The auger studies at the low P soil water sampling (see Chapter 8) site revealed a 30 to 40 cm deep loam topsoil covering a loam. Gleying was also evident in this field. The profile descriptions of the dye study sites are contained in Appendix 1.

The soil at the Dye 2 site was mapped as poorly drained gley and the soils at Dye 1 and at the low P soil water sampling site as imperfectly drained gleys (see Figures 3.2 and 8.1). The sand content is much greater in the soil at Dye 1 than in the surrounding soil. This suggests that Dye 1 is located at or near one of the sand lenses. The surrounding soil, on which both soil water sampling sites were located, is well described by the type of soil found at the low P soil water sampling site (Culleton and Diamond, in print).

The soil P levels in the subsurface drainage catchment range from 4 to 12 mg/l Morgan's (Figure 3.3) and the area weighted average is 8 mg/l.

3.5.2 Management

The catchment area of the drainage system has been in permanent grassland for the last 20 years, and was re-seeded in 1989. Between 14th April and 6th October 1997, a rotational grazing system was operated on the upper half of the area (Tower Field). Bullocks, at an average stocking rate of about 1 LU/ha, grazed the area. The lower half of the catchment was used for grazing calves and bullocks.

In February 1997, 6 kg P (as superphosphate)/ha and 35 kg K (as muriate of potash)/ha were applied to the subsurface drainage catchment. The Tower Field received no slurry in 1997 or 1998 but nitrogen was applied in March (57 kg N/ha as urea), April and May (33 kg N/ha as CAN each time) of each year. Slurry (44 m^3/ha) was applied to the lower part of the catchment in summer 1997 and February 1998 (20th/27th February 1998). Nitrogen was applied to those fields at rates of 117 kg N/ha (as urea) in March (4th March 1998) and 50 kg N/ha (as CAN) in June and August of both years.

3.6 Dairy Farm (Stream)

3.6.1 General Site Characteristics

The impact of the Dairy Farm at Johnstown Castle on stream water quality was investigated by monitoring a stream which drains most of the land of the Dairy Farm. Thus the study does not

address P losses from all of the Dairy Farm at Johnstown Castle, only from the section of it that drains to the stream monitored. This area of land is called the Dairy Farm sub-catchment. The Dairy Farm farmyard and the associated buildings and facilities are located within the Dairy Farm sub-catchment (Figure 3.7). This farmyard is not expected to contribute nutrients to the stream. The slurry and dirty water are collected in tanks and applied to the land. A deep drain, furthermore, surrounds the yards and buildings. It collects subsurface flow from the direction of the farmyard and this water is then also applied to the land. Nevertheless, the grab sampling programme (see Section 9.2.2) was designed to pick up nutrient losses from the Dairy Farm farmyard if they occurred (grab sampling station G2 in Figure 3.7).

The point at which the stream flows into the Dairy Farm was used as the upstream monitoring station. The downstream station was located at the exit of the stream from the farm (Figures 1.1 and 3.7). During the preparation of the sites and the monitoring period, construction of the headquarters of the EPA (autumn 1996) and the Department of Agriculture Food and Rural Development (spring 1997) was started. The location of those building sites within the Dairy Farm is indicated in Figure 1.1. The description and the management of the study site depict the Dairy Farm as it was in autumn 1996.

The Dairy Farm takes up an area of more than 80 ha gently sloping (average slope of 1-2°) grassland. One of the fields, the Cricket Field, is separated from the main farm unit. It was, therefore, not considered in this study. The upper soil horizon of the Dairy Farm is heterogeneous (Figure 3.4). All the soil classes mapped on the estate occur within the boundaries of this farm unit. The most areally extensive soil types on the Dairy Farm are fine loamy and coarse loamy over fine loamy, well to moderately drained brown earths and fine loamy and coarse loamy over fine loamy, moderately to imperfectly drained gleys (Culleton and Diamond, in print). The soil P levels of the land range between 2 and 25 mg P/l Morgan's (Figure 3.5) and the area weighted average soil P level is 8 mg P/l.

As on the rest of the estate, artificial subsurface drains were installed on the land of the Dairy Farm between 1975 and 1979 (Sections 3.4.1 and 3.5.1) (Figure 3.6). The system was again linked with an existing network of old stone shores. The hydrology of the dairy farm is complex and reliable information on it is sparse. This study focused on the influence of surface and shallow subsurface flow on the monitored stream because P contributions via groundwater were assumed to be negligible. The challenge was, therefore, to estimate which fields were hydrologically connected with the stream through surface or shallow subsurface pathways. This assessment was complicated by the fact that the stream was transferred underground between 1975 and 1979 and now runs in concrete pipes for most of its course.

The stream at the Dairy Farm as it is today is fed by two springs. One arises within the area of the Beef Unit and the other one within the area of the Dairy Farm. The spring at the Beef Unit is led into the subsurface drainage network of that area of the Beef Unit (see Section 3.5 and Figure 3.7). The end point of that subsurface drainage network was the monitoring station for the investigations into P loss via subsurface drains (MB in Figure 3.7). At the end of the drainage network, an underground tank (A2 in Figure 3.7) was installed to pond up the water and make it available for washing the yard and the sheds of the Beef Unit. A concrete pipe forms the outlet of the tank. The stream then runs underground in concrete pipes as far down as a small wooded area of wetland, the Bogwood (Figure 3.7). There are small open access holes to the pipe where it crosses the main road just downstream of the Beef Unit ,and there is a manhole where the stream flows into the area of the Dairy Farm. This manhole formed the upstream sampling station at the Dairy Farm (M1 in Figure 3.7).

The second spring contributing to the stream rises to the north of the Bogwood in the area of the Dairy Farm (Figure 3.7). The subsurface drainage network of the Dairy Farm catches the water of this spring and leads it down to the Bogwood. The flow from this spring is very small and the water moves very slowly through the Bogwood to a small pond. The underground pipe from the direction of the Beef Unit surfaces at the pond. The end of the concrete pipe is half submerged. Downstream of the pond, the water flows faster than before. The small stream flows out of the wetland just beside the buildings of the Dairy Farm. It flows as an open stream along the edge of the Bogwood down to the road, where it is again piped underground. The stream then remains underground to the end of the dairy farm. There is one more open access hole to it just downstream of a farm road (G3 in Figure 3.7). The water runs through a concrete pipe as far downstream as the old mill (Figure 3.7). There it flows through a system of deep stone shores, which was constructed for the mill, and then through a stone shore to the road beside the downstream monitoring station (M2 in Figure 3.7) at the end of the farm. Underneath the road, concrete pipes were inserted into the old stone shores and the downstream monitoring station (M2 in Figure 3.7) was located at the point where the concrete pipes ended and the stream was again left to flow through stone shores.

The above description elucidates that there are only two stretches of stream where overland flow can reach the monitored section of stream. The stream runs in an open channel through the area of the Bogwood and along it down to the road, and overland flow has also been observed to flow into the large access hole near the old mill (G3 in Figure 3.7). Subsurface drainage water gains access to the stream as indicated in Figure 3.6.

On the basis of contour lines and anecdotal information on artificial subsurface drains (Figure 3.6), an approximate sub-catchment drainage area of 70 ha was estimated for the monitored section of stream (stretch between M1 and M2).

3.6.2 Management of the Dairy Farm

Research on the evaluation of environmental, agronomic and economic implications of high and low input dairy systems determines the management of the Dairy Farm. Plots of high, medium and low soil P are used to study the effect of phosphorus usage on dairy output (Culleton and Murphy, 1996; Culleton et al. 1999b), and the effects of nitrogen application rates on production are investigated (Culleton and Murphy, 1996).

The basic management requirements of the different experimental treatments are summarised in Table 3.4, and Figure 3.8 shows the areas used for the different treatments. The potassium applications are not listed in the table because they were variable. The target soil potassium level was 100 mg/l and fertiliser was applied according to the requirements indicated by the potassium levels measured in the previous soil test. The P application rates in the area of the P trial were determined by the amount of P necessary in each plot to achieve the required soil P level. The target soil P levels were 2-3 mg P/l in the low P plots, 6-8 mg P/l in the medium and greater than 10 mg P/l in the high P plots.

During the monitoring period (24th November 1996 to 31st May 1997) nitrogen was applied 25th to 27th February, 31st March to 4th April and 5th to 7th May 1997. The P and potassium fertilisers were applied at the beginning of March and May 1997. On some of the fields (silage ground), slurry was spread at a rate of 23 m^3/ha between 21st and 23rd January 1997.

Table 3.4: Management of the Dairy Farm sub-catchment

Experiment	Treatments	Chemical P and N fertiliser application rates		
		P kg/ha	N kg/ha	Stocking Rate L.U./ha
P trial	Low soil P (PL)	0	250	2 to 5
	Medium soil P (PM)	0-19	250	2 to 5
	High soil P (PH)	35	250	2 to 5
N trial	Intensive (INT)	35	300	3
	REPS (RN)	26	90	2
Non-research plots	Commercial (C)	37	250	2.5

CHAPTER 4: DETERMINATION OF SOIL CHEMICAL AND HYDROLOGICAL PARAMETERS

4.1 Introduction

To assess P loss with overland and/or subsurface flow, information on the characteristics of an area as a P source, on the availability of the transport medium water and on the drainage pathways prevalent at a site was needed.

In Ireland, the most commonly used soil P test measures the amount of P extracted by Morgan's solution (Herlihy et al., 1996). The Morgan's P test was developed for agricultural purposes (Peech and English, 1944). Thus it is used to indicate the level of P supply that can be expected from soil reserves to a particular crop (Herlihy et al., 1996; Holford and Mattingly, 1979). The strong positive linear relationship between Morgan's P and water soluble soil P (Daly et al., 2001) indicates that P available for plant uptake may also be prone to be washed away by water. In the study in hand, the soil P level estimated by the Morgan's test was used to identify low, medium and high soil P sites, and to detect changes of available soil P with depth. Soil K and pH levels were determined to explain variations of these parameters in water samples (see Chapter 5), should they occur.

Apart from overland and artificial subsurface drain flow measurements (Sections 7.4.1 and 8.4.1), the soil hydrological aspects investigated in this study were the infiltration capacity, the existence of preferential flow pathways and the water table levels in the soil. The infiltration characteristics of the soil surface determine whether or not water (rain or overland flow) will pass through the soil surface or stay on it and be stored in depressions or become overland flow (Section 2.4.2) (Horton, 1933). The rate of infiltration is influenced by the soil moisture level as well as by soil physical characteristics (Philip, 1957). The maximum infiltration at field capacity is thought to be a characteristic which is unaffected by the initial soil moisture conditions. The maximum infiltration at field capacity is, therefore, a useful indicator of the risk of infiltration excess overland flow at a site (Diamond and Shanley, 1998). Winter values for infiltration capacity were found to exceed summer values considerably (Cooke and Dons, 1988; Diamond and Shanley, 1998). The winter values are thought to reflect the hydrologic regime rather than the properties of the soil (Diamond and Shanley, 1998). As the infiltration capacity as a soil characteristic was of interest here, the summer values were measured at the overland flow and artificial subsurface drain flow sites.

Another type of overland flow, saturation excess overland flow, sets in once the water table has reached the soil surface (Eshleman et al., 1993) (Section 2.4.2). Hence, by affecting the amount of pore volume available for infiltrating water, the proximity of the water table to the soil surface has a considerable bearing on how likely a site is to produce overland flow. Water table levels were therefore monitored at the three overland flow sites.

Germann and DiPietro (1996) describe two basic ways in which water moves down the soil profile: Preferential (or bypass or macropore) flow is distinguished from dispersive (or matrix) flow by the fact that it bypasses most of the soil matrix. The type of flow pathway has great implications on the P contents of subsurface water (Logan and McLean, 1973). In the case of preferential flow, water moves down the soil profile quickly through a network of meso- and macropores (Stamm et al., 1998) (Section 2.4.3). The interactions between the soil and any P dissolved or suspended in infiltrating water are thus much reduced when compared to the reactions taking place during the slow micro-filtering process of matrix flow.

The objectives of Chapter 4 are to describe the P source aspect of the soils of the study sites, to present soil hydrological information, to discuss possible sources and mechanisms of overland flow production and to investigate the likelihood and pathways of P transport down the soil profile.

4.2 Methods

4.2.1 Soil P, K and pH Levels

The topsoil P levels at the Beef Unit and the Dairy Farm were obtained from the research projects carried out in those areas. The soil P levels of abovementioned study sites are described in Sections 3.5.1 and 3.6.1. The soil samples were taken to a depth of 10 cm, which is common practice in Ireland (Culleton et al., 1996) but not necessarily in other countries (Humphreys et al., 1998). Soil sampling to determine the soil P, K and pH levels (10 cm sampling depth) at the other study sites was carried out according to the code of practice suggested by Culleton et al. (1996). Each soil sample was made up of 20 soil cores taken over the area of a field. These cores were combined and mixed to form a single soil sample. Duplicate or triplicate 10 cm soil samples, each a composite of 20 cores (see above), were taken and analysed for pH, soil P and K content in January 1997 and February 1998. In addition, single samples to a depth of 2 cm (each a composite of 20 cores) were analysed at the Warren 1 and the Cowlands in January 1997. At the Warren 1, sediment transported by overland flow before the start of this study was also sampled and analysed. The sediment had accumulated in a sediment trap over several years. The sediment trap was bypassed before the monitoring period of this project started (see Section 7.2.1).

As the movement of P down the soil profile was of interest at the artificial subsurface drainage site (Beef Unit), samples of soil horizons below the topsoil were taken in three plots and analysed for P content. In two of the plots, the samples were obtained with a trowel while describing the profiles at the dye studies. One of the dye studies was carried out in the high soil P field, which was also used for soil water studies. Deep samples in the low P field of the soil water studies were taken with a Dutch auger of 6 cm diameter.

Morgan's P and K levels in soils were measured using an automated version of the procedure described by Peech and English (1944). The method used to measure soil pH is described by Byrne (1979).

4.2.2 Infiltration Capacity

The double-ring infiltrometer method was used to measure the summer infiltration capacity of the soils at the overland flow sites (Warren 1, Warren 2 and Cowlands) and on the main three soil types (A2, A3, C3) at the artificial subsurface drainage site (Beef Unit) (Figure 3.2). The infiltration studies were carried out between the middle and the end of September 1998. The groundwater levels at the site at the Warren 1 (see Section 4.2.4) were recorded using the water table tubes the day the infiltration trials started.

Plate 4.8 shows a sketch of a double-ring infiltrometer. The diameters of the inner rings used for infiltration measurements ranged from 28 to 32 cm and the diameters of the outer rings from 54 to 58 cm. The measurements were carried out following the procedure described by Diamond and Shanley (1998). To eliminate the effect of the initial soil moisture content on the rate of infiltration (Philip, 1957), two-day infiltration measurements were undertaken. The first day mainly served to moisten the soil. The infiltration capacity was determined on the basis of the measurements taken on the second day.

The plan was to carry out two-day infiltration trials at three sites in each overland flow plot and at three or four sites on each of the three main soil types at the artificial subsurface drainage site. Because the infiltration rates at the soil surface were very low, information on percolation rates below the soil surface was obtained by removing about 14 cm by 14 cm of topsoil to a depth of 5 and 10 cm, pouring water into the resulting holes and then measuring the drop of the water level over time. In order to compare the infiltration rates at the soil surface to the percolation rates measured in the holes, the holes were dug at locations near to where one of the 3-4 replicate ring system measurements was carried out at each overland flow measurement site and on each of the

soil types studied in the Beef Unit. The holes were located in the vicinity of ring system 1 at all sites and soil types but soil type A3. On soil A3, the holes were dug near the second ring system. The percolation rates at 5 and 10 cm were measured for 60 minutes at the Warren 1, the Cowlands and at the Beef Unit on soil type A2, and for 120 minutes at the Warren 2 and at the Beef Unit on soil types A3 and C3. These measurements were only carried out on one day. They were therefore compared to the day one infiltration rates recorded in the adjacent ring system.

4.2.3 Dye Studies

In June 1997, dye studies were carried out at two locations within the subsurface drainage catchment (Beef Unit) (see Figure 8.1). As described by Ryan and Noonan (1995), acid red dye (30 g/l) was dissolved in water and poured into circular cylinders (30 cm diameter), which had been driven 5 cm into the soil surface. Pits were opened adjacent to the rings as soon as the dyed water had infiltrated into the soil. At site Dye 1 the dyed water took 6 days to infiltrate, and at site Dye 2, infiltration of dyed water was completed after 31 days. Spade and trowel were then used to carefully excavate the dyed areas below the rings. The soil and dye patterns were described and photographed.

4.2.4 Water Table Levels

To study soil water flow was a part of the brief of SWAMP (see Section 3.4). Thus SWAMP installed a network of water table tubes and nested piezometers at the Warren 1 and the Cowlands (Ryan et al., 1999) (Figures 7.1 and 7.2). Both sites were furnished with 17 water table tubes. These were arranged in a grid of vertical and horizontal transects relative to the field boundaries. The horizontal transects were assigned the letters A to E at the Warren 1 and A to F at the Cowlands from lower to upper elevations of the sites. The vertical transects were given ascending numbers from the left (upstream facing) to the right hand sides of the sites. At the Warren 1 an additional water table tube was installed at the location of a wet patch in the field. It was suspected that the spring caught by the artificial subsurface drainage network of the Warren 1 once surfaced at this location (Section 3.4.1). The water table tubes reached to a depth of 110 to 120 cm below the ground surface. Two and four sets of nested piezometers were installed at the Warren 1 and the Cowlands, respectively. At the Warren 2, 6 water table tubes were installed in autumn 1997 (Figure 7.3). Three tubes were installed in a diagonal line from the upstream corners of the field to the lowest point where the overland flow was collected. The tubes of the diagonal on the left hand side (upstream facing) were numbered from 1 to 3 from the top to the bottom of the field. The tubes in the diagonal on the right hand side were numbered from 4 to 6 from the bottom to the top

of the field. Water level monitoring at the Warren 2 was carried out from the end of October 1997 to the end of March 1998.

All tubes were fitted with rubber stoppers. Holes in the stoppers or tubes allowed air to enter. The time of response to added water was tested at all tubes and found satisfactory. An electrical water level dipper was used to determine the water levels in the tubes. Between November 1996 and July 1997 measurements were carried out by the author and by SWAMP personnel. As SWAMP required detailed water level information, the tubes were monitored frequently (daily to weekly) during the winter months. Once SWAMP had finished data collection, (July 1997) readings were taken less frequently and only from a subset of tubes at the Cowlands and the Warren 1. After July 1997, measurements were taken in tubes A to E of line 2 at the Cowlands and in tubes A, B and C in line 2 and line 4, and in tubes D and E in line 3 at the Warren 1. To indicate water levels deeper than the depth of the tubes, a value of -130 cm (lowest measured value was –120 cm) was inserted in graphs.

As an easy way of relating meteorological variables to soil water table information, the accumulated soil moisture deficit (SMD) estimation carried out by Teagasc, was graphed alongside the water table level data. Teagasc work out the SMD by first subtracting the daily precipitation (PR) from a calculated daily value for evapotranspiration (E) (Brereton and Hope-Cawdery, 1988). The difference is then added to the previous day's value (SMD_0).

$$SMD = SMD_0 + (E - PR)$$

The accumulated SMD does not achieve negative values. Once it reaches 0, negative values for (E - PR) are ignored. The Teagasc SMD calculation differs from the usual SMD approach in so far as SMD normally refers to the amount of water needed to bring soil moisture up to field capacity (amount of water in soil after gravitational drainage of excess water) (Burke et al., 1986). This makes the Teagasc SMD calculation independent of the ill-defined and soil dependent concept of field capacity (Webster and Beckett, 1972). The Teagasc SMD does not refer to any specific condition of the soil. It is a balance of evapotranspiration versus rainfall. The balance is ongoing as long as total evapotranspiration exceeds total rainfall. When this is no longer the case accounting stops until a day when daily evapotranspiration exceeds daily rainfall.

The ground surface was the reference point for the water table levels. It was assigned the value zero and water table levels below the surface were recorded as negative values. To facilitate a visual comparison of the SMD curve with trends of water levels (negative values), the SMD values were multiplied by –1 and therefore called negative SMD. In Figures 4.23 – 4.25 the water table levels

in cm are graphed on the same y-axis as the negative SMD in mm. Thus, if the two curves reach the same value, the water table level below ground is in reality 10 times greater than the SMD.

4.3 Results

4.3.1 Soil P, K and pH Levels

The soil chemistry results are compiled in Tables 4.1 and 4.2 and the soil P levels are displayed in Figure 4.1. Despite the considerable within-site variation of soil P levels (Figure 4.1), the results in Table 4.1 show that the three overland flow sites are of clearly different soil P status. Results for two years were included in the calculation of a mean soil P level per site because the ranges of samples taken in 1997 and 1998 at a particular site clearly overlapped between the years (Figure 4.1). The similarity between 1997 and 1998 soil P concentrations was great at the Warren 1 and the Cowlands but it was less pronounced at the Warren 2. However, especially because there were only 2 samples taken in 1997, the mean was still based on the pooled soil P results at the Warren 2.

The ranges and standard deviations of soil P in samples taken from the one site are considerable, especially in case of the Cowlands. Still, the ranges of the sites do not overlap (Figure 4.1 and Table 4.1), which clearly distinguishes the three overland flow sites as regards soil P levels.

Table 4.1: Morgan's P levels at overland flow sites.

Site	Morgan's P levels mg/l				
	Mean (10 cm)	Minimum (10 cm)	Maximum (10cm)	Standard deviation (10 cm)	2 cm depth core
Warren 1	3.9	3.3	4.4	0.4	6.2
Warren 2	8.0	5.3	10.3	1.9	
Cowlands	17.2	14.1	21.3	2.8	24.3

The P levels in the samples taken to a depth of 2 cm were higher than the maximum soil P values measured in 10 cm samples from corresponding sites (see Table 4.1).

The P content in samples to 2 cm depth was, however, considerably lower than the P concentrations determined in samples of eroded soil from the sediment trap at the Warren 1. The eroded soil was measured to contain 10.9 and 29.0 mg P/l (Morgan's) in the two samples taken. The layers below the topsoil, which were sampled at the artificial subsurface drainage site (Beef Unit), all contained less than 1 mg/l of P, which is the limit of detection.

Table 4.2: Morgan's K levels at the overland flow sites.

Site	Morgan's K levels mg/l				
	Mean (10 cm)	Minimum (10 cm)	Maximum (10cm)	Standard Deviation (10 cm)	2 cm depth core
Warren 1	123	110	136	9	165
Warren 2	104	86	121	15	
Cowlands	100	75	142	28	130

The soil at all overland flow sites had a pH of 6.5. The soil K levels at all these sites were similar (Table 4.2). Comparable to the soil P levels, the within-site variation was greatest at the Cowlands. The maximum K levels at the sites in the Warren were measured on the same samples as the maximum P values. At the Cowlands, the second highest K value was detected in the sample containing most P. There was a tendency for the samples taken to a depth of 2 cm to be enriched with K, but this trend was not as pronounced as in the case of P. The K concentrations in the sediment samples from the Warren 1 amounted to 114 and 116 mg K/l and were therefore of the same magnitude as the K levels in the topsoil (10 cm) at that site.

4.3.2 Infiltration Capacity

At the start of the infiltration measurements, the mean water table level at the Warren 1 was 65 cm below the ground. The highest and lowest water table levels recorded that day at this site were 35 cm and 107 cm below the surface. The soil moisture deficit (SMD), calculated according to Brereton and Hope-Cawdery (1988), on that day was 36 cm and it did not fall lower than 20 cm for the duration of the infiltration studies.

The results of the infiltration and percolation experiments are summarised in Tables 4.3 and 4.4 and select data are illustrated in Figures 4.2 to 4.4. The last recorded infiltration rates serve as an estimate of the infiltration capacities. Typically, the rate of infiltration is high at the start of a trial, and then decreases with time until it approximates a constant value. In this study, the plots of the rates of infiltration on day 2 against time did not display the usual shape. Instead, the rate of infiltration was normally very low at the beginning of day 2 and then increased and reached an approximately constant value. Figure 4.2 shows an example of this pattern. The graphs of the measurements carried out on soil type C3 at the subsurface drainage site (Beef Unit) did not approximate a constant value at the end of day 2. This is illustrated in Figure 4.3 using the measurements taken at rings system 2 as an example.

The highest infiltration capacity was achieved in one of the rings at the Warren 1. It amounted to 8.1 mm/h. Rates of 0 were found at both sites at the Warren, at the Cowlands and on soil types A2 and A3 at the subsurface drainage site (Beef Unit). The mean infiltration capacity was smaller than

or equal to 1 mm/h at the Cowlands and the subsurface drainage site (Table 4.3). It was slightly higher at the Warren 2 (1.7 mm/h) and reached 5.3 mm/h at the Warren 1.

The variability between the rates measured in different rings at the one site or soil type was considerable (Table 4.3). The standard deviation of the three (or four) measurements was greater than or equal to the mean at the Warren 2 and on soil types A2 and A3 at the subsurface drainage site (Beef Unit).

Table 4.3: Last recorded infiltration rates (stable on all soils but BU-C3) on day 2, means and standard deviations (stdev) of measurements at the Warren 1 (W1), the Warren 2 (W2), the Cowlands (C), soil types A2 (BU-A2), A3 (BU-A3) and C3 (BU-C3) at the Beef Unit.

Ring system no.	W1	W2	C	BU-A2	BU-A3	BU-C3
				mm/h		
1	0.0	4.7	1.4	0.8	0.0	1.3
2	8.1	0.0	0.2	0.0	0.6	1.0
3	7.9	0.5	1.4	0.0	0.3	0.8
4				0.2		
mean	5.3	1.7	1.0	0.3	0.3	1.0
stdev	4.6	2.6	0.7	0.4	0.3	0.3

Because the water levels in the 5 and 10 cm percolation holes were only observed for a total duration of 60 or 120 minutes, they cannot be considered to represent steady state percolation rates. However, in all cases the plots of the percolation rates in the holes against time show that the curves were clearly levelling out and tended to approximate a constant value towards the end of the trials. Figure 4.4 shows an example of this. The rates of percolation at 5 and 10 cm depth were generally quite similar to each other at the sites in the Warren and at the Cowlands. On all three soil types at the subsurface drainage site, the rate of percolation at 10 cm was considerably greater than the one at 5 cm at the beginning of the trial. On soils A2 and C3, the rates at the two depths were similar to each other towards the end of the test. On soil A3, on the other hand, the rate of infiltration at 10 cm below the surface remained higher than the one in the hole of 5 cm depth.

At the Warren 2, the last recorded percolation rates at 5 and 10cm depth were lower than the corresponding infiltration rate measured in the nearest ring system. At the Warren 1, the percolation rates at 5 and 10 cm remained only slightly higher than the infiltration rates in ring system 1 (Table 4.4). The percolation rates at 5 and 10 cm at the Cowlands and at the Beef Unit on soil type A2 were considerably higher than those measured in the adjacent rings. On soil type C2 at the Beef Unit, the percolation rates at 5 and 10 cm depth also remained higher than the infiltrations rates in the ring system, but to a lesser extent than on soil A2 and at the Cowlands. On soil type A3, the rates at 5 cm and at the surface (ring system) were nearly the same, but they were much lower than the percolation rates recorded at a depth of 10 cm.

Table 4.4: Last recorded percolation (holes) and infiltration (rings) rates (unstable) in 5 and 10 cm holes and the adjacent ring system at the Warren 1 (W1), the Warren 2 (W2), the Cowlands (C), soil types A2 (BU-A2), A3 (BU-A3) and C3 (BU-C3) at the Beef Unit.

Depth/Type	W1	W2	C	BU-A2	BU-A3	BU-C3
				mm/h		
5 cm	10.0	11.5	50.0	26.0	20.0	18.0
10 cm	12.0	10.5	48.0	45.0	70.0	12.0
Adjacent ring system	3.0	19.5	13.0	6.0	21.0	0.8

4.3.3 Dye Studies

The soil at Dye 1 consisted of a sandy loam topsoil (surface to 20cm depth), overlying a loamy sand (20 to 50 cm depth) and a loam (below 50 cm depth) (see Section 3.5.1 and Appendix 1). The dye had only travelled down about 40 cm at this site but it had also moved laterally down the slope (Plate 4.1). The topsoil was strongly and evenly coloured by dye across the area of infiltration (Plate 4.2). In the loamy sand layer, on the other hand, long vertical tongues of colour divided completely uncoloured areas (Plate 4.3). The coloured tongues turned out to be areas of soil which were bleached in comparison to the surrounding soil. These areas were penetrated by roots (Plate 4.4). The bleached zones were found throughout that layer.

Dye 2 happened to be carried out on top of an artificial subsurface drain, which was discovered when the site was excavated after the infiltration of the dye. A branching drain (clay pipe of about 10 cm outer diameter) surrounded by gravel was found at a depth of 80 cm below the surface. The soil at this site consisted of a sandy loam topsoil (0 to 30 cm depth) overlying a sandy loam (30 to 70/100cm depth) and a loamy sand (below 70/100 cm depth) (see Section 3.5.1). The bulk of the dyed water had travelled down about 40 cm (Plate 4.5) but the distribution of dye was irregular even in the topsoil (Plate 4.6). Below 40 cm depth there were only vertical fingers of dye (Plate 4.5). A macropore of 5 mm diameter formed the centre of a coloured finger (Plate 4.7) which extended down as far as the subsurface drain. This pore was probably constructed by an earthworm rather than e.g. a dock root because it was hollow and there was no decaying root material in it. In connection with the 5 mm and other pores it was noticeable that an area of micropores around the pores was also coloured.

4.3.4 Water Table Levels

The water table information collected by SWAMP personnel and the author during this project is displayed in Figures 4.5 to 4.25. Analysis of the piezometer data by SWAMP personnel showed that there generally was an upward water pressure at the Warren 1 and a downward soil water pressure at the Cowlands (Ryan et al., 1999). A comparison of the contours of the two sites (Figures 7.1 and 7.2) and the water table levels on 12th December 1996 (Figures 4.5 and 4.6, drawn up by SWAMP personnel) illustrates that the groundwater levels after a week of dry weather (see Section 6.3.1) broadly followed the contour lines.

Between November 1996 and July 1997, the average of the water table measurements was 32 cm below the surface at the Warren 1 and 53 cm below the surface at the Cowlands. The mean value at the Cowlands is a slight over- or underestimate because the water table level at tube D1 fell below 120 cm depth at several occasions and a value of 130 cm below the ground was assumed on

those days. At both sites, the mean water table below ground measured at the different tubes varied considerably. The lowest mean water table level in all lines (vertical transects) at the Cowlands occurred at tube D, but the highest mean water table levels were measured at tubes C, B, and E in lines 1, 2 and 3 respectively (Figure 4.7). The range of mean water table levels was smallest in the middle line (line 2).

The changes of water levels below ground along lines 2 and 4 at the Warren 1 are quite similar (Figure 4.8). The mean water table in those lines rises and peaks at tubes C and then falls. In line 3, on the other hand, the mean water table reaches a minimum at tube C and a maximum at tube D. The mean water table at tube D in this line is, together with the one at the tube at the spring, the highest at this site. The two tubes monitored in line 1 show a slight drop of the water table from tube B to tube C.

The plots of the water table levels against time reveal great differences in the relative variations of the water table levels measured in tubes at the same site. In line 1 at the Cowlands (Figure 4.9), the water level in tube B was the only one to reach the surface. However, the level in this tube also dropped lower than the levels of all other tubes but D. Tube D usually presented lower levels than the other tubes and tube F displayed the smallest variation in water levels. In February, the water level in line 2 reached the surface in tubes A and B and came very close to it in all other tubes (Figure 4.10). An interesting aspect of line 2 is that the highest water levels were generally recorded from tube B but only until the middle of May. The water level in line 3 (Figure 4.11) reached the surface in tubes B, E and F but not in A, C and D. Thus the water level rose to the surface in tube 2 of the horizontal transect A, in all three tubes of the horizontal transect B and in tubes 3 of E and F. The level remained below the surface on all monitoring days in the horizontal transects C and D.

At the Warren 1, the water level did not quite reach the surface in either of the two tubes (B and C) in line 1 (Figure 4.12), but it came very close. The level in tubes B and C in line 2 (Figure 4.13) was often quite near the surface. In tube C it reached ground level several times. The greatest variation of measurements in line 2 was observed in tube A. The water level in A was often below that of the other tubes but it also came up to ground level several times. The level in tubes D and E in line 3 (Figure 4.14) remained at or near the surface for extended periods, whereas the levels in tubes A and C were commonly around or below -60 cm. The water levels measured in tube E in line 4 (Figure 4.15) were noticeably lower than those of the other tubes at the Warren 1. The levels in tubes C and D reached ground level and the ones in tubes A and B came very close to it. The water table tube at the spring was located adjacent to tube C4 and the levels in those two tubes were very similar (Figure 4.16). The fact that the water level in tubes A3, C3 and E4 remained

well below ground level makes these the most distinctly different water table tubes at the Warren 1. The water levels in all the other tubes reached, or came very close to the soil surface.

To allow comparisons of the water levels of the two winters, plots of the subsets of tubes in which monitoring was continued after July 1997 were drawn up for the entire monitoring period (November 1996 to March 1998). Figure 4.17 shows that the water levels at the Cowlands were generally higher in winter 97/98 than in winter 96/97. Figures 4.18 to 4.20 confirm this trend for the Warren 1. Especially in pipes B and C of line 4, the levels remained high for extended periods. In the subset of tubes, the highest water levels were generally measure at B2 at the Cowlands and tubes B4 and C2 at the Warren 1.

In the left diagonal at the Warren 2, the water levels in the middle tube (2) (Figure 4.21) were clearly higher than the ones in the other tubes. On the right hand side of the field, the water levels of the two upper tubes (5 and 6) were similar and often near ground level. The levels in the lowest tube (4) (Figure 4.22) came close to ground level on occasion but also dropped to below 100 cm. Overall, the water levels in tube 2 were generally closest to the surface. However, the differences between the levels in this tube and tubes 5 and 6 were quite small.

To understand overland flow, the wet areas are particularly interesting. The measurements from tubes characterised by high ground water levels (B2 at the Cowlands, B4 and C2 at the Warren 1 and tube 2 at the Warren 2) were, therefore, compared with the daily rainfall at the Johnstown Castle meteorological station (see Chapter 6) and to the soil moisture deficit (SMD) estimated by Teagasc (Figures 4.23 – 4.25). The calculated negative SMD curve is remarkably similar to the plots of the water table levels in tubes B4 and C2 at the Warren 1 and B2 at the Cowlands. Both the water table levels and the negative SMD rise during rainfall events and fall during dry periods, but not always to the same extent. In January 1997 and February/March 1998 the value for water levels in the tubes at the Warren 1 and the Cowlands were considerably lower than the negative SMD (note different units of measurement, see also Section 4.2.4). Unlike the water table levels at the Warren 1, the negative SMD was not calculated to reach zero in April, May and June 1997. However, the negative SMD came closer to zero than the water levels in tube B2 at the Cowlands came to the soil surface. The negative SMD curve follows the same trend as the water table levels in tube 2 at the Warren 2, but the values for the water levels were slightly lower than those for the negative SMD (note different units). This tendency was most pronounced in March 1998.

4.4 Discussion

4.4.1 Soil P, K and pH levels

The variability between soil P measurements of samples taken at the same site was very high. At the high P site (Cowlands) the difference between the maximum and the minimum soil P measurement (7.2 mg P/l) was greater than the width of Teagasc's soil P Index classes (3 mg P/l). Within site variation of soil P levels was notably higher at the high than the low P site (Figure 4.1). The work of Daniels et al. (2001) has established increasing variability of soil P measurements with rising soil P levels in fields as a general trend.

Still, the rounded mean P levels (10 cm) of 4, 8 and 17 establishes the Warren 1 as the low, the Warren 2 as the medium and the Cowlands as the high soil P overland flow sites. The P concentrations at the sites fall into different soil P index categories as defined by Teagasc (Coulter, 2001). The soil P levels are affected by the intensity of management. At the same time they influence the production that can be achieved at a site (see Section 2.3.1). The Teagasc index categories are designed to represent and cater for different levels of production (Coulter, 2001). The overland flow sites can, thus, be taken to reflect different intensities of production. The Warren 1 at index 2 represents an under-utilised grazing area, the Warren 2 at index 3 an average grazing area and the Cowlands at index 4 stands for over-fertilised (with P) grazed land (Coulter, 2001).

The P levels of the soil samples to a depth of 2 cm confirm that the described (Murphy and Culleton, 1997) accumulation of available P in the top few centimetres of soil also took place at the Warren 1 and the Cowlands overland flow sites. Assuming an effective depth of interaction of at most 2 cm (Ahuja et al., 1981), the rain and/or overland flow water is likely to interact with soil of higher P concentrations than that measured in standard 10 cm soil samples. The P rich surface layer of the soil may be a part of the reason for the difference in P levels between the soil and the sediment at the Warren 1. The particles eroded from the soil and deposited as sediment are bound to stem from the very top of the soil, and to be high in P. However, selective erosion of fine, P rich material has also been observed to result in higher P concentrations in eroded than in source soil (Green et al., 1978; Sharpley, 1985). Despite the fact that the soil surface (2 cm) was slightly enriched with K, the enhanced K levels in eroded soil, which were observed by Sharpely (1985b), could not be detected in sediment from the Warren 1. This points to the slight surface enrichment with K having been caused by K applications in spring 1996 (see Chapter 3). The sediment had been allowed to accumulate for several years. As K fertilisation had not been carried out since the sediment trap had last been emptied (Tunney et al., 1997), the K concentrations in eroded soil

probably reflect past lower soil K levels. Overall, the K and pH values at the three overland flow sites were similar during the monitoring period.

The P concentrations in soil samples taken below the topsoil at the artificial subsurface drainage site (Beef Unit) were all very low. As P moving from the topsoil down the soil profile in matrix flow would enhance P levels in deeper layers of soil (Ozanne et al., 1961), this type of P translocation can be dismissed. Phosphorus transported with preferential flow, on the other hand, is unlikely to lead to increased soil P levels in deeper soil horizons and preferential transport of P can, therefore, not be ruled out.

4.4.2 Infiltration Capacity

Cylinder infiltrometer rates are thought to be an overestimate of the true infiltration capacity of a soil because of lateral seepage (Tricker, 1978). A double ring system with ring diameters as used in this study is thought to reduce considerably the effect of lateral flow on the infiltration rates measured in the inner ring (Swartzendruber and Olson, 1961). Bouwer (1986) claims that the issue of lateral seepage is only resolved if cylinder diameters of greater than 1 m are used. However, he confirms the usefulness of smaller ring systems to compare the infiltration characteristics at various sites (Bouwer, 1986).

The infiltration capacities were very low at all sites. As the water table level was well below the surface, the values describe a soil characteristic (Diamond and Shanley, 1998). The highest mean infiltration capacity measured in this study was equal to the summer infiltration values obtained for an impermeable gley at Castlecomer (Diamond and Shanley, 1998). The Castlecomer site was characterised by the lowest infiltration capacity measured by Diamond and Shanley (1998). In winter and summer, the infiltrations capacity at the Castlecomer site was lower than the hourly rainfall rate with a return period of 5 years (Diamond and Shanley, 1998). As the summer infiltration capacity was 3.5 times greater than the winter value, the risk of infiltration excess overland flow at the Castlecomer site was estimated to be high in winter and considerable in summer (Diamond and Shanley, 1998). The infiltration studies carried out at the sites at Johnstown Castle suggest a significant risk of infiltration excess overland flow in winter and summer. The risk appears to be smaller at the sites in the Warren than in the Cowlands and on the soils investigated in the Beef Unit, but there were great variations among measurements made at the same site.

The fact that the standard deviations were high in comparison with the means indicates that three measurements per site or soil type may not result in an infiltration capacity estimate of high

accuracy. Diamond and Shanley (1998) found that an average of six replicates was needed to determine the mean summer infiltration rate with a precision of 50%. Still, the results of the three replicate measurements per site or soil type are adequate to show clearly that the infiltration capacities at all study sites were low.

The atypical shape of the infiltration curves in this study may be a feature of the low infiltration rates measured. The first measurements were taken at 1, 5 and 15 minute intervals after the start of the trials. Due to the low infiltration rates, the water levels in the rings moved very slowly and this may have affected the accuracy of the first few readings.

The considerable difference between the drop of water levels in the holes and the infiltration rates measured in the ring systems, points to the occurrence of topsoil compaction and/or sealing (McColl et al., 1985) at the site at the Cowlands and on soil types A2 and A3 at the Beef Unit. The drop in water level in the holes in the ground is not really comparable with infiltration rates measured with ring infiltrometers because the walls of the holes are not impermeable. Still, the fact that the differences between rates measured in the holes and with the infiltrometers were greatest at the sites with infiltration rates smaller or equal to 1 mm/h suggests that a comparison of the two types of measurements is of value.

On soil type A3, the similarity of the percolation rates at 5 cm and the infiltration rates in the ring system in combination with the much higher percolation rates at 10 cm furthermore suggests that this soil type was affected by compaction to a greater depth than soil A2. The measurements at soil type C3 point to some degree of compaction but also indicate that this soil type may have been affected less than the other soils at the Beef Unit. Compaction probably did not affect the sites in the Warren. At the Warren 2, the infiltration rates measured in the ring system exceeded the percolation rates estimated with the holes in the ground. This was not the case at the Warren 1, but the difference between the rates estimated with the two methods was small. As the holes at the Warren 1 were near the ring system which gave a 2 day infiltration capacity of zero, they were located in an area which was likely to be characterised by particularly low infiltration values. Thus, even if compaction did impede infiltration at this particular location, it is unlikely to have affected other areas at the Warren 1.

The Cowlands and the sites at the Beef Unit were all grazed during the spring and summer of 1998. The fields at the Warren, on the other hand, were cut that particular summer. The presence of grazing animals is known to lead to compaction and/or sealing of the topsoil (Drewry and Paton, 2000; Drewry et al., 2000; McColl et al., 1985) and it is very likely that this happened at the Cowlands and the Beef Unit in summer 1998.

4.4.3 Dye Studies

Dyed water had flowed down the soil profile along preferential pathways at both sites, which suggests a rapid movement of solution below the rooting depth in a small part of the soil profiles (Bouma and Dekker, 1978; Jensen et al., 2000). The flow pattern and the depth to which bypass flow occurred were, however, vastly different at the two sites.

The dye distribution at Dye 1 recalls the flow patterns described by Garrido et al. (2001). They observed a zone of lateral spreading of percolating solution followed by preferential flow further down the soil profile. In the study reported here, the lateral spreading was biased in a downhill direction and preferential flow started at the interface of the sandy loam topsoil with the loamy sand layer below it. As suggested by Magid et al. (1992) and Starr et al. (1978), the texture change may have been the reason for the wetting front to split. The coloured tongues in the loamy sand layer are likely to be areas of greater permeability. Whether the presence of roots made them more permeable or whether roots chose them because they were areas of weaker consistence is unclear. The lighter colour (in soil profiles that were not dyed) around the roots may have been caused by a removal of iron and manganese by products of the breakdown of organic matter (chelates). This would indicate that at least some of the roots were dead (Sticher, 1988).

The areas free of dye just below the layer of grass at Dye 2 suggest that infiltration below the top 2 cm did not happen in some areas. Stamm et al. (1998) described a similar pattern. In the present study, patches of impeded infiltration may have been due to compaction caused by grazing animals. The occurrence of bypass flow through large pores to considerable depth and of lateral seepage (indicated by coloured area around pores) from large pores into the surrounding soil matrix was again similar to the findings of Stamm et al. (1998). The fact that a large vertical pore was observed to lead directly down to a subsurface drain may have been a coincidence, or the installation of the artificial field drains may have encouraged macropore development. The profile above the subsurface drain looked the same as that of the surrounding soil, but the backfill over the drains may have been looser than the rest of the soil. Thus, it might have been easier for an earthworm or a plant root to penetrate the backfill than the soil around it.

The dye in this study was applied by flood irrigation. As the soil may respond differently to ponded rather than sprinkled application of solution (Flury et al. 1994; Ghodrati and Jury, 1990), the flow paths active during the dye studies may not be representative of water movement during a rainfall event. Unless a sprinkler apparatus reproduces the characteristics of natural rainfall, however, it is unclear how much more representative of water movement during natural rainfall

results from sprinkled applications are. The dye studies reported on here were mainly to illustrate whether preferential flow is likely to occur at our study sites. Even if the flow pathways used by the dye differ from the ones active during some or most natural rainstorms, the dye studies were still able to demonstrate that the soil is not homogeneous and that, at some locations, water flow down the soil profile occurs along preferred pathways rather than evenly through the soil matrix.

4.4.4 Water Table Levels

The tightly spaced grid of water table tubes at the Warren 1 and the Cowlands yielded valuable information on general trends (average values) and on short-term changes of the water table levels at the sites.

The data show clearly that, on the whole, the sites were wetter in winter 97/98 than in winter 96/97, and that the water table was nearer the soil surface at the Warren 1 than at the Cowlands. As the soil texture and structure are similar at the two sites (see Section 3.4.1), the difference in average water table depth may suggest that it normally takes less precipitation to initiate saturation excess overland flow at the Warren 1 than at the Cowlands. The fact that a spring rises in the Warren 1 confirms the SWAMP finding of an upward water pressure at that site.

The small-scale variations of the average water table levels at the Cowlands and the Warren 1 provide evidence of the existence of variable source areas of overland flow production. This is corroborated by the fact that the water table levels measured at different locations within a site varied in the extent to which they responded to weather conditions. For example, the amount of rain necessary to bring the water table level to the soil surface varied considerably within the area of each of the overland flow sites. These local variations in water table level fluctuations point to the presence of variable source areas with dynamic responses to the prevalent weather conditions within the boundaries of all three sites. One example is the elevated water table and the quick response to rainfall of the area around the spring at the Warren 1. Areas of saturation, which change according to weather conditions, have often been described as important sources of stormflow production (Dunne and Black, 1970a; 1970b; McColl et al. 1985). The saturated areas have been observed to give rise to both return flow and overland flow due to rain falling onto the waterlogged, and thus nearly impermeable, soil surface (Cooke and Dons, 1988; Pionke et al., 1986).

The water table in the soil fluctuates according to the inputs and outputs of water to the system. Inputs mainly consist of rainfall and water draining from other areas, and the outputs of water removed by evapotranspiration and water draining to other areas. The SMD appears if the

evapotranspiration of a period exceeds rainfall. It indicates the number of mm of rainfall that are necessary to balance total evapotranspiration and total rain of a period. The negative SMD therefore does not take account of soil drainage or the effect of the air filled pore space on the water table rise caused by 1 mm of rain.

The value of the mm negative SMD often compares well with the figure for the depth of the water table in cm measured in the wettest areas of the overland flow sites (Figures 4.23-4.25). Thus, in wet parts of the fields, the soil water level below the surface tends to be 10 times greater than the negative SMD. The similarity between the shapes of the negative SMD and the water table level curves suggests that the balance between evapotranspiration and rainfall mainly governs the soil water levels. To test this theory the effect of soil drainage is assumed to be negligible. Then each mm of rain would have to lead to a water table level rise of 10 mm in order for the measured soil water levels to be achieved. SWAMP personnel measured the air filled pore space (AFPS) at the Warren 1 and the Cowlands (Ryan, 1998). Their figures suggest that, in the top 20 cm of soil (water table level at 20 cm below surface), 1 mm of rain leads to a water table rise of 16 mm at the Warren 1 and of 29 mm at the Cowlands. At greater depth, however, these figures change to 12 mm and 11 mm for the Warren 1 and the Cowlands, respectively.

These values are close to the water table level rise per mm of rainfall required to confirm the theory that changes in the water table due to soil drainage (e.g. deep percolation) are negligible. It can, therefore, be said that within the fields monitored for overland flow, there are wet, very poorly drained areas. The water table levels in these areas are mainly governed by meteorological variables. In these wet patches, the water table can be expected to reach the surface earlier during rainfall events than in the rest of the fields.

Another interesting feature shown up by the AFPS measurements is that, in the top 20 cm of soil (water table level at 20 cm below surface) 1 mm of rain triggers a more substantial soil water level rise than when the water table is at greater depth. This is true for the sites at the Warren 1 and the Cowlands. (Note: topsoil compaction by grazing animals tends to be restricted to the top 10 cm of soil (Drewry et al., 2000), whereas AFPS was determined for 20 cm intervals (Ryan, 1998)). It may at least partly explain why the negative SMD and the water table level curves were in better agreement during predominantly dry rather than very wet periods, as the soil water level would generally have been close to the surface at wet times.

CHAPTER 5: WATER QUALITY PARAMETERS

5.1 Introduction

5.1.1 Phosphorus

The standard methods for the examination of water and wastewater (Anon, 1995) describe three types of test procedures commonly carried out on freshwater samples: direct colorimetry, acid hydrolysis followed by colorimetry and digestion followed by colorimetry (Figure 5.1). All three sets of analyses can be carried out on filtered and on unfiltered samples. The recommended filter size to separate dissolved from particulate forms of P is 0.45 μm. This is an arbitrary figure and no claim is made that it provides a true division between dissolved and particulate forms of P (Anon, 1995). A varying proportion of P is known to be associated with minute particles (colloids) (Mayer and Jarrell, 1995), some of which are smaller than 0.45 μm (Haygarth et al., 1997). If filtration through a 0.45 μm filter is used to separate dissolved and particulate P, P bound to colloids <0.45 μm is lumped in with the dissolved P. This means that the amount of truly dissolved P is likely to be overestimated and that P fractions called 'dissolved' also contain P associated with particles <0.45 μm. However, as 0.45 μm filtration is commonly used and provides a replicable way of achieving a gross separation into dissolved and particulate forms of P (Anon, 1995), this approach was followed in the study in hand.

Colorimetrically determined P in samples which did not undergo acid-hydrolysis or digestion is called reactive P. The name of this P fraction is dissolved reactive P (DRP) in filtered and total reactive P (TRP) in unfiltered samples (Anon, 1995) (Figure 5.1). The most commonly used colorimetric test for P determination is based on the method described by Murphy and Riley (1962). During the course of the analysis, the phosphate ions contained in the water sample react with added reagents to form molybdenum blue colour. TRP or DRP are therefore called molybdate reactive P (MRP) in some studies (McGarrigle et al., 2002; Torpey and Morgan, 1999).

Reactive P is assumed to be a good measure of the amount of orthophosphate present in a sample (Anon, 1995; Flanagan, 1992). Baldwin (1998) and Stevens (1980) point out that during analysis, condensed (oxidised organic compounds and inorganic polyphosphates (Ron Vaz et al., 1993)) and organic forms of P can also be transformed to orthophosphate. Even though the amount of orthophosphate in a freshwater sample may therefore be overestimated (Levine and Schindler, 1989; Stainton, 1980), reactive P (especially DRP) can still serve as a measure of the biologically readily available P concentration (Bradford and Peters, 1987; Ekholm, 1998; Herve and Kauppi, 1986).

Acid hydrolysis followed by colorimetry measures the combined amount of reactive and acid hydrolysable P (Figure 5.1). The amount of total acid hydrolysable P is determined by subtracting TRP from the combined amount measured on unfiltered samples. Subtracting DRP from the combined amount of P measured on filtered samples assesses the quantity of dissolved acid hydrolysable P. The amount of acid hydrolysable P is an approximation of the condensed P content of a water sample (Anon, 1995). Even though this fraction can be important in soil water samples (Ron Vaz et al., 1993) it was not specifically targeted in this study. Acid hydrolysable P was, therefore, not measured.

To assess the total amount of P contained in a sample, a digestion procedure is used to turn all forms of P into orthophosphate, which is then measured colorimetrically (Figure 5.1). The unfiltered sample is used to determine total P (TP) and the filtered sample to measure total dissolved P (TDP). Several methods of digestion are commonly used and their performance is largely influenced by the type of sample to be analysed (Anon, 1995; Logan et al., 1979; O'Connor and Syers, 1975). The measurement of total P is important because it indicates how much P can potentially become available to aquatic life immediately and over time (Moore and Reddy, 1994).

In combination with other P measurement, TP and TDP allow the calculation of other P fractions, of which unreactive P and particulate P are most commonly used:

- Unreactive P: Total unreactive P = TP – TRP
  Dissolved unreactive P = TDP – DRP
- Particulate P: (Total) particulate P = TP – TDP
  Reactive particulate P = TRP – DRP
  Unreactive particulate P = Total particulate P – reactive particulate P

Particulate P can be reactive or unreactive. Like in the case of dissolved reactive P, particulate reactive P is assumed to be immediately available to algae and macrophytes. The term unreactive P refers to all the forms of P which do not react during the direct colorimetric test (see above). These include unreactive particulate P and dissolved organic and condensed forms of P. These P fractions are less readily available than reactive P (Ekholm, 1998; Stevens and Stewart, 1982b). The concentration of those forms of P is nonetheless important, because they can become available through transformation processes in water bodies (Ball and Hooper, 1963; Lean, 1973).

Determining the concentrations of all the P forms in water samples was not feasible in this project. Given the methods and analytical instruments used in the water laboratory at Johnstown Castle, the measurement of dissolved reactive P (DRP), total dissolved P (TDP) and, on a smaller number of samples, total P (TP) was considered the most effective use of the resources available. From these

P fractions, the amounts of dissolved unreactive P (TDP – DRP) and total particulate P (TP – TDP) could be calculated. In the analysis of the relative importance of the different P fractions at sites used in this study, preference was given to describing the relationship between TDP and DRP and the relationship between TP and TDP over calculating dissolved unreactive P and total particulate P as described above. This approach puts the information about the deducted P fractions automatically in the context of the magnitude of the P levels determined for the measured P forms. This is important because it will reveal whether the concentration of a particular type of P is related to the level of another P form. Working with relationships between measured parameters also yields a description of the general trends of the behaviour of the P forms in relation to each other.

To summarise, the P fractions discussed in this thesis and the names used (bold) for them are listed below:

- **Total P (TP)**: All forms of P.
- **Total dissolved P (TDP)**: All dissolved forms of P and all colloidal P associated with colloids <0.45 μm.
- **Dissolved reactive P (DRP)**: Dissolved P and colloidal P (colloids <0.45 μm) that reacted with the reagents to form molybdenum blue during direct (no pre-treatment of sample other than filtration) colorimetric analysis. DRP is mainly made up of orthophosphate (dissolved and colloidal (colloids <0.45 μm)), but condensed and organic forms of P (dissolved and colloidal (colloids <0.45 μm)) may also contribute (Stevens, 1980).
- **Dissolved unreactive P**: Dissolved P and colloidal P (colloids <0.45 μm) that did not react with the reagents to form molybdenum blue during direct (no pre-treatment of sample other than filtration) colorimetric analysis. This P fraction mainly contains **dissolved organic and condensed P** and organic and condensed forms of P associated with colloids <0.45 μm.
- (Total) **particulate P (PP)**: All forms of P associated with solids.

In this chapter, the water analysis and general relationships between P fractions are described. Specific aspects of the significance of the P fractions in relation to the particular sites from which the samples were collected will follow in Chapters 7-9.

5.1.2 Additional Parameters Measured

Conductivity, pH, suspended solids (not on all samples), total oxidised nitrogen (TON), total ammonia (TA) and potassium (K) were measured in the water samples because they might help to interpret the P data. Apart from pH, these additional parameters are, therefore, considered in

relation to P in Chapters 7-9. Turbidity was measured on a number of samples to explore the possibility of using this parameter to estimate TP concentrations (Grayson et al., 1996).

5.2 Methods

5.2.1 Water Analysis at Johnstown Castle

All water samples were analysed in the water laboratory at Johnstown Castle, which measures reactive P using a continuous flow analysis system and the automated ascorbic acid reduction method (Anon, 1995). This system has been in place since 1985. It is used to analyse commercial and research samples. The laboratory takes part in the intercalibration scheme set up and run by the Environmental Protection Agency (EPA). Thus an approximate assessment of the accuracy of the P analysis is possible.

A new continuous flow analyser to measure TP on filtered and unfiltered samples was purchased in January 1997. This system breaks down higher phosphates by oxidative hydrolysis by potassium persulphate in sulphuric acid under Ultra-Violet radiation. The orthophosphate concentration is then determined by the automated ascorbic acid reduction method (Anon, 1995). Total P analysis is not included in the EPA intercalibration scheme. To assess the effectiveness of the TP digestion unit, sets of filtered and unfiltered samples were digested manually using the persulphate microwave digestion method described by Johnes and Heathwaite (1992). During the analysis of samples taken during the last 3 months of monitoring (January to March 1998), samples with known pyrophosphate concentrations were used on a continuous basis to check on the performance of the machine. A specialist in automated analysis carries out preventative maintenance on both systems every 6 months on contract.

Total ammonia (TA) and total oxidised nitrogen (TON) concentrations were determined with the same continuous flow analysis system used for DRP analysis. The analyses were therefore also carried out on filtered (0.45 μm) samples. The total ammonia method is based on the reaction of ammonia with saliclyate and dichloroisocyanurate in alkaline solution. The automated hydrazine reduction method was used for total oxidised nitrogen determination (Anon, 1995). Potassium (K) levels were measured by flame atomic absorption spectrometry, pH by the electrometric method and turbidity by the nephelometric method (Anon, 1995). Conductivity and suspended solids (total suspended solids) were determined as described by Anon (1995).

5.2.2 Selection of P Fractions to be Analysed

To determine the dissolved and suspended (total reactive P minus dissolved reactive P) amounts of reactive P, filtered and unfiltered sub-samples need to be analysed. As this doubles the number of samples to be analysed, considering both fractions was beyond the resources available in this project.

Preference was given to the determination DRP because analysis of total reactive phosphorus (TRP) was thought to be less reliable. To measure TRP on the continuous flow analysis system, 2 ml of well mixed samples are poured into cups, which are arranged on a carousel. The automatic sampler of the analyser then sub-samples those cups. By the time the sub-samples for analysis are taken, some suspended solids may have settled at the bottom of the cups. The samples are, therefore, no longer representative of the well-mixed original sample.

The analyser for total P is also a continuous flow analysis system. Analysis of TDP was therefore assumed to be more reliable than analysis of TP. However, to obtain information on the relationship between TP and TDP was considered important. A number of unfiltered samples were, therefore, also analysed with the TP machine.

5.2.3 General Laboratory Procedures

During storm flow producing rainfall events, water samples were collected from the automatic samplers at the study sites every morning and analysed for DRP, TON and TA within 24 hours (longer during weekends) of sampling. When the laboratories were closed or no technician to operate the analyser was available, DRP/TON/TA analysis was not carried out. This affected some of the samples taken in July/August 1997 and in December/January 1997/98.

Great care was taken to avoid contamination of the samples. All sampling bottles were soaked in 10% HCl for several hours after use, and afterwards washed out with distilled water several times. The effectiveness of the cleaning procedure was assessed by randomly selecting washed bottles, which were filled with distilled water and left over night. The water was then analysed and no measurable traces of P or N were found in any such samples. This test was carried out 6 times over the sampling period.

Samples for DRP, TON and TA analysis were filtered through 0.45 μm syringe filters. The first few ml of filtrate were discarded. About 20 ml of sample was then filtered and stored in 25 ml disposable plastic tubes. The syringes were acid washed (as described for the bottles) after use. To assess the possibility of P or N contamination due to the filters or tubes, they were tested. The

tubes were filled with distilled water and left over night. This water was then filtered in the usual manner and the filtrate analysed for DRP, TON, TA and TDP. All test samples were free of N and P compounds.

Samples for TDP and TP analysis were either analysed immediately or, depending on the anticipated length of the storage period, frozen or stored in a cold room (4°C). Freezing and cold storage are acceptable preservation methods for TP and TDP analysis(Kothlash and Chessman, 1998). Sub-samples for TDP analysis were filtered before storage.

Conductivity and pH were measured the day the samples were brought into the laboratory. Depending on work pressure, suspended solids and turbidity were either determined immediately or else within a week of sampling. In the latter case, the samples were stored at 4° C as suggested by the 'Standard Methods for the Examination of Water and Wastewater' (Anon, 1995).

5.2.4 Manual Digestion and its Comparison to Automatic Digestion

To assess the accuracy of the digestion step of the TP and TDP analysis, 114 unfiltered and 60 filtered samples were digested by the microwave digestion technique described in Johnes and Heathwaite (1992). To check whether the above technique yielded satisfactory results for this study, 6 of each 0.05 and 1.00 mg P/l pyrophosphate samples were also digested manually. The orthophosphate in the digested samples was then determined on the TP continuous flow analyser by bypassing the digestion unit. Filtered samples, which did not exceed the range of the instrument, were selected. The unfiltered samples, on the other hand, included dilutions because the dilution process could affect the amount of solids in samples. Unfiltered samples with various amounts of suspended solids were chosen for manual digestion.

5.2.5 Limits and Accuracy of P Analysis

Dissolved Reactive P

The calibration curve for DRP analysis is drawn up on the basis of five standards with P concentrations of 0.060, 0.120, 0.180, 0.240 and 0.300 mg P/l. The top standard defines the upper limit of the range of the instrument. All samples above 0.300 mg/l were therefore diluted.

The limit of detection of the instrument was calculated following the procedure suggested by the suppliers (Anon, 1991). A series of low standard replicates were analysed. The standard deviation

of those replicates was estimated and then multiplied by 4.65 (Anon, 1991). These calculations gave a limit of detection of 0.005 mg P/l for the DRP analysis.

The results of the EPA intercalibration scheme were used to determine the accuracy (precision and bias) of the DRP analysis at Johnstown Castle. The Standard Methods (Anon, 1995) define the combined bias of a method and its use by a specific laboratory as the difference between the laboratory's average recovery rate and the true value. To estimate the precision of an analysis, the Standard Methods (Anon, 1995) suggest calculating the average difference or range by summing the differences of duplicate samples and dividing them by the number of observations. In the EPA intercalibration scheme, samples of unknown concentrations are sent out to participating laboratories. Those samples are to be analysed in duplicate and the true P concentration of the samples is disclosed after the results of the individual laboratories have been submitted. Data for 20 rounds of that scheme were available. On two occasions, the P concentrations determined by Johnstown Castle differed greatly from the true value. Those incidences are not representative of the normal performance of the laboratory and were, therefore, omitted. The remaining 18 sets of results were used to calculate the bias as suggested in the 'Standard Methods for the Examination of Water and Wastewater' (Anon, 1995).

Total P and TDP

The calibration curve of the TP/TDP analysis was drawn up on the basis of 5 standards (0.20, 0.40, 0.60 0.80 and 1.00 mg P/l). The suppliers (M. B. Scientific Services Ltd.) specify a limit of detection of 0.05 mg P/l. The range of the instrument is therefore 0.05 to 1.00 mg P/l. Samples with P concentrations exceeding the top standard needed to be diluted.

As the EPA intercalibration scheme does not include TP and TDP, the accuracy of the analysis was assessed by analysing samples with known concentrations of pyrophosphate. Samples containing 0.50 and/or 1.00 mg P/l were added to sets of unknowns from samples taken from January 1998 onwards. The certified orthophosphate sample of 1.01 mg P/l (Commission of the European Communities, certified reference material 399) was also analysed.

The bias was assessed by assuming that the made up pyrophosphate samples are of known concentration and calculating the difference between the recovery of the machine and the true value. The precision was estimated by calculating the standard deviations of the results of the pyrophosphate samples. To assess the loss of accuracy associated with the process of dilution, the precision of the analysis of 22 diluted TDP samples with concentrations ranging from 1.32 to 2.55 mg P/l was estimated.

5.2.6 Relationships between P Fractions

The relative concentrations of DRP, TDP and TP were studied separately for each site. To compare DRP with TDP, linear least square regression analyses were carried out. Datasets were prepared in which the subsets of samples which had been analysed for both parameters were included, the values of DRP below the limit of detection were set to 0, and the samples below the TDP limit of detection were omitted. The guide value to indicate a meaningful difference between P fractions was estimated at 0.05 mg P/l (see Section 5.4.1). If the values of two P fractions of a sample were closer than that, no difference between the fractions was assumed. However, regressions based on samples with a meaningful difference between two fractions (partial datasets) only describe the relationships between the fractions for a part of the samples. Thus, regressions including samples in which the difference between two P fractions was smaller than 0.05 mg/l (full datasets) were also calculated. Due to the small number of samples taken at the Dairy Farm sites, only regressions based on the full datasets were drawn up for these sites.

The confidence intervals ($p<0.05$) of the regression slopes and coefficients were calculated by multiplying the relevant standard error with the appropriate t-value and then adding and subtracting the product from the constant/coefficient of the regression equation (Walford, 1995). To make sure that the data fulfil the assumptions of the significance tests of the regression models (Walford, 1995), the residuals were plotted against the predicted values and Normal plots of the residuals were drawn up. If the residuals were not approximately randomly distributed around 0 or if the Normal plot of the residuals did not resemble a straight line, the assumptions were considered to be violated. This was noted and the data were transformed or the variables split.

The same procedure was followed when investigating the relationship between TDP and TP, except that all samples below the limit of detection were omitted. Dissolved RP was set to be the independent variable for the TDP/DRP regressions. The DRP data were considered to be more reliable (lower limit of detection, higher resolution). Therefore the dependence of TDP on DRP was examined. Total P was set in relation to TDP and not DRP because TP and TDP were analysed on the same instrument and are therefore more comparable to each other than to DRP. Total P was expressed in dependence on TDP because most TP values were already the result of a calculation (see Section 5.4.1) and, therefore, bound to be less accurate than TDP data.

Dissolved RP was the P fraction measured on the greatest number of samples and especially useful because of the low detection limit of the analysis. It was therefore desirable to have at least an estimate of DRP for all events. Thus, for events with missing DRP data (see Section 5.2.3), the

DRP levels were estimated using the TDP concentrations. Dissolved RP of samples before and after the missing ones were regressed against TDP of those samples. Hence a relationship specific to that time was determined and the missing values were calculated.

5.3 Results

5.3.1 Manual Digestion and its Comparison to Automatic Digestion

The analysis of the pyrophosphate samples, which were digested manually to check the use of the method described by Johnes and Heathwaite (1992), gave satisfactory results. The means, maxima and minima of the 0.50 mg P/l pyrophosphate samples were 0.53, 0.54 and 0.51 mg P/l. The same parameters amounted to 1.00, 1.02 and 0.99 mg P/l for the 1.00 mg P/l pyrophosphate samples.

The slope, but not the constant, of the regression of manual versus automatic digestion of unfiltered samples was statistically significant ($P<0.0001$). The R square of the relationship was 94.2%. The equation was calculated as

TP automatic = 0.004 + 0.777 (+/-0.036)*TP manual

The slope of the regression of manually and automatically digested filtered samples was also statistically significant ($p<0.001$) and had an R square of 98.6%. The equation was

TDP automatic = 0.989 * TDP manual,

and the confidence interval ($p<0.05$) of the value of the slope 0.959 to 1.019.

5.3.2 Accuracy of P Analysis

The 18 sets of DRP results of the EPA intercalibration scheme covered a range of 0.07 to 0.82 mg P/l. The mean bias of these results amounted to 0.002 mg P/l (range: -0.080 to 0.080 mg P/l). The percentages of the differences between the mean of the laboratory duplicates and the true values ranged from 0 to 19.5 with an average of 5.9%. A scatterplot of the true DRP values against the differences between the mean of the Johnstown Castle recovery rate and the true value (Figure 5.2) indicates a slight trend of differences to be greater when the P concentration of a sample exceeds the range of the instrument (0.300 mg P/l).

For the duplicate analysis of the EPA samples and a 1.01 mg P/l reference sample (Commission of the European Communities, certified reference material 399), the average range amounted to 0.007 mg P/l which corresponds to a standard deviation of 0.005. To obtain an indication of the precision of the instrument across the operating range, the suppliers (M. B. Scientific Services Ltd.,

continuous flow analysis manual) advise running a series of replicates of the standards in random order and calculating the coefficient of variation for each set of standards. The coefficients for the 0.060, 0.120, 0.180, 0.240 and 0.300 mg P/l standards amounted to 13.1%, 6.5%, 4.7%, 2.5% and 1.2%, respectively. Thus, when expressed as a percentage of the mean concentration, the precision of the instrument increases from the bottom to the top end of its range. This trend is less clear in absolute terms. However, the standard deviations associated with the top two standards were lower than those of the results of the three lower standards (standard deviations of 0.007, 0.007, 0.009, 0.006 and 0.004 mg P/l for the 0.060, 0.120, 0.180, 0.240 and 0.300 mg P/l standards respectively).

The automatic TP/TDP analyser recovered 0.98 mg P/l from the 1.01 mg P/l certified reference sample (Commission of the European Communities, certified reference material 399). The mean recoveries of the 0.50 and 1.00 mg P/l pyrophosphate samples were 0.50 (26 analyses) and 0.99 (24 analyses) mg P/l. The mean of the difference between the true value and the machine recovery rate was -0.003 mg P/l (range: -0.05 to 0.03 mg P/l) and 0.01 mg P/l (range: -0.04 to 0.04 mg P/l) for the 0.50 and 1.00 mg P/l samples, respectively. The percentages of the difference between the true value and the recovery rate ranged from 0 to 10% with a mean of 2.2% for the 0.50 mg P/l sample and from 0 to 4% with a mean of 1.9% for the 1.00 mg P/l sample. The mean range of precision was 0.02 mg P/l for both samples. The coefficient of variance amounted to 3.4% for the 0.50 mg P/l and 2 % for the 1.00 mg P/l sample.

The mean range of precision of the 22 diluted TDP samples used to assess the loss of accuracy with dilution was 0.06 P mg/l. The minimum and maximum differences between replicates were 0 and 0.22 mg P/l.

5.3.3 Relationships between P Fractions

For the sites at the Warren, the Cowlands and the Beef Unit, the numbers of samples which were analysed for each fraction and had concentrations greater than the TDP/TP detection limit, and the number of samples used for comparison are shown in Table 5.1.

Only a small number of samples from the two sites at the Dairy Farm were analysed for TP and TDP, and most of them were taken in April and May 1997. Of the 31 available DRP/TDP pairs and the 25 available TDP/TP pairs at the upstream site, only 5 and 4 pairs, respectively, had differences smaller than 0.05 mg P/l between the two values. At the downstream site, the difference of 3 of the 38 DRP/TDP pairs and of 7 of the 36 TDP/TP pairs was smaller than 0.05 mg P/l.

Table 5.1: Numbers of samples analysed for the various fractions, numbers of samples above the limit of detection and numbers of samples with differences greater than or equal to 0.05 mg P/l between two fractions.

Site	Warren 1	Cowlands	Warren 2	Beef Unit
No. Samples	787	786	254	266
No. DRP	717	712	226	238
No. TDP	721	621	251	266
No. TDP <0.05	175	0	34	61
No. DRP/TDP pairs	497	449	189	177
No. Diff. TDP/DRP >= 0.05	191	355	68	81
No. TP	529	520	184	177
No. TP <0.05	29	0	0	9
No. TDP/TP pairs	524	496	158	127
No. Diff. TP/TDP >= 0.05	258	454	123	66

Regressions Based on Full and Partial Datasets

The normal probability plot of the residuals for regression of the TDP and TP concentrations at the Cowlands suggested that the residuals were not normally distributed around the regression line. A base 10 logarithmic transformation of the data was, therefore, carried out and the base 10 logarithm (log) of the TP levels regressed against the log TDP concentrations (Table 5.3). The normal probability plots of the residuals of these regressions was satisfactory. Because of the use of log transformed data for the regression calculation, the equation for the relationship between TDP and TP is: $\log TP = \log a + b * \log TDP$

(a is a constant and b is the value of the slope).

Table 5.2: R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the full and partial TDP/DRP datasets of the sites at the Warren, the Cowlands and the Beef Unit (TDP dependent, DRP independent variable).

Site	Warren 1	Cowlands	Warren 2	Beef Unit
All pairs				
%R sq.	85.5	91.0	84.7	95.6
Slope	1.1143	1.1459	0.9901	1.1018
P slope	0.0001	0.0001	0.0001	0.0001
Confidence interv. slope				
($p<0.05$)	1.0739 to 1.1547	1.1157 to 1.1706	0.9297 to 1.0506	1.0665 to 1.1371
Constant	0.0420	0.0819	0.0385	0.0339
P constant	0.0001	0.0001	0.0001	0.0001
Confidence interv.				
constant ($p<0.05$)	-0.0024 to 0.0073	0.0483 to 0.1155	0.0331 to 0.0440	0.0253 to 0.0425
Pairs with diff. > 0.05 mg P/l				
%R sq.	89.4	90.7	95.4	98.2
Slope	1.2139	1.1415	0.9676	1.1277
P slope	0.0001	0.0001	0.0001	0.0001
Confidence interv. slope				
($p<0.05$)	1.1543 to 1.2736	1.1033 to 1.1797	0.9158 to 1.0194	1.0929 to 1.1625
Constant	0.0671	0.1712	0.065	0.0628
P constant	0.0001	0.0001	0.0001	0.0001
Confidence interv.				
constant ($p<0.05$)	0.0597 to 0.0754	0.1230 to 0.2193	0.0605 to 0.0695	0.0523 to 0.0732

Table 5.3: R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the full and partial TP/TDP datasets of the sites at the Warren, the Cowlands and the Beef Unit (TP dependent, TDP independent variable).

Site	Warren 1	Cowlands	Warren 2	Beef Unit
All pairs				
%R sq.	98.3	96.6	70.2	98.5
Slope	1.3174	0.9274	1.6351	1.433
P slope	0.0001	<0.0001	0.0001	0.0001
Confidence interv.		0.9122 to 0.9427		
slope ($p<0.05$)	1.3011 to 1.3336		1.5673 to 1.8022	1.4022 to 1.4637
Constant	0.0278	0.1229	0.036	0.0034
P constant	0.0001	<0.0001	0.0015	not stat. significant
Confidence interv.		0.1171 to 0.1286		
constant ($p<0.05$)	0.0226 to 0.0329		0.0140 to 0.0581	
Pairs with diff. > 0.05 mg P/l				
%R sq.	98.8	97.5	69.7	98.6
Slope	1.2939	0.9201	1.52014	1.3921
P slope	0.0001	<0.0001	0.0001	0.0001
Confidence interv.	1.2766 to 1.3112	0.9067 to 0.9335	1.3407 to 1.6995	1.3501 to 1.4341
slope ($p<0.05$)				
Constant	0.053	0.1335	0.0659	0.0334
P constant	0.0001	<0.0001	0.0001	0.0006
Confidence interv.		0.1284 to 0.1385		
constant ($p<0.05$)	0.0460 to 0.0599		0.0404 to 0.0913	0.0150 to 0.0518

A comparison of the equations based on full and partial datasets (Tables 5.2 and 5.3) reveals overlapping confidence intervals for the slopes of all regressions. Thus, the rates of TDP (TP) increase with DRP (TDP) levels were similar for the full and partial datsets. The higher values of the constants associated with the subsets of data merely reflect that those regression analyses were carried out on data selected for a difference between two fractions.

Dissolved Reactive P and Total Dissolved P

Quite a high proportion of TDP concentrations in samples from the Warren 1, the Warren 2 and the Beef Unit were below the limit of detection. Furthermore, TDP was at least 0.05 mg P/l higher than DRP in just 38%, 36% and 45 % of the respective samples at those sites. At the Cowlands, on the other hand, no TDP contents were below the limit of detection, and 79% of TDP values were at least 0.05 mg P/l higher than the corresponding DRP concentrations.

Strong, statistically significant, positive, linear relationships between DRP and TDP existed at all but the Dairy sites (Tables 5.2 and 5.5). The TDP concentrations at the Cowlands were 0.0819 mg P/l plus 1.15 times the DRP levels greater than the DRP values. At the Warren 1 and the Beef Unit, the TDP levels amounted to 1.11 times the DRP concentrations (the constant does not need to be considered at this site because its confidence interval includes 0) and to 0.0339 mg P/l plus 1.10 times the DRP contents respectively. The smallest difference between the two P fractions occurred in the Warren 2. Total DP was merely 0.033 to 0.044 mg P/l higher than DRP.

The plots of TDP against the DRP concentrations (Figures 5.3 and 5.5) indicated the existence of distinct clusters above the main body of points at the Warren 1 and the Cowlands. The plots of the residuals against the DRP concentrations (Figures 5.4 and 5.6) confirmed these trends. It turned out that the 25 samples, which make up the separate trend at the Warren 1, were taken during the first five days of event 14 (20th to 24th August 97) and the first day of event 15 (19th September 97). The 11 samples forming the cluster in the Cowlands dataset were taken during the first two days of event 14.2 (23rd/24th August 97).

The datasets of the Warren 1 and the Cowlands were split as described above, and separate regressions were carried out for the two trends at each site (Table 5.4). Splitting the datasets resulted in improved normal probability distributions of the residuals. The R^2 values of the regressions based on the split datasets of the Warren 1 were both higher than the R^2 value of the complete dataset. The main, but not the secondary trend at the Cowlands also resulted in an R^2 greater than that of the equation of the complete dataset. The regression model based on the secondary trend at the Warren 1 will clearly calculate higher TDP concentrations than the equations determined for the complete dataset and the main trend. Excluding the secondary trend from the regression results in an equation quite different to that based on the complete dataset of the Warren 1. The confidence interval of the constant no longer includes 0 but the confidence interval of the slope does. Due to the high standard error of the regression model of the secondary trend at the Cowlands, the confidence intervals of the slope and the constant are extremely wide and overlap with the confidence intervals of the equations based on the complete dataset and the main trend. The model of the main trend results in a similar constant but smaller slope than the equation based on the complete dataset.

Table 5.4: R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the main and secondary trends in the full DRP/TDP datasets of the Warren 1 and the Cowlands (TDP dependent, DRP independent variable).

Sites	**Warren 1**		**Cowlands**	
Sampling period	Main trend	Secondary trend	Main trend	Secondary trend
%R sq.	92.4	91.3	96.4	80.7
Slope	1.0233	1.3358	1.0888	1.5254
P slope	<0.0001	<0.0001	<0.0001	<0.0001
Confidence interv. slope (p<0.05)	0.9967 to 1.0499	1.1622 to 1.5093	1.0710 to 1.1067	0.9985 to 2.0522
Constant	0.042	0.1393	0.09174	1.0001
P constant	<0.0001	<0.0001	<0.0001	0.0451
Confidence interv. constant (p<0.05)	0.0389 to 0.0450	0.1047 to 0.1740	0.0722 to 0.1113	0.0281 to 0.9721

The regression calculated for the DRP/TDP data of the upstream site at the Dairy Farm is characterised by comparatively low R^2 value, a high standard error and, therefore, a wide confidence interval. Unity is encompassed in the confidence intervals of the slope and the constant lies between 0.04 and 0.27 with a probability of 95%. The R^2 value of the DRP/TDP regression model at the downstream site is greater than 90% but 1 is again encompassed in the confidence interval of the slope. The constant of this equation is more reliable. It is between 0.07 and 0.11 with a probability of 95%.

Table 5.5: R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the full DRP/TDP datasets of the upstream and downstream sites at the Dairy Farm (TDP dependent, DRP independent variable).

Sites	**Upstream**	**Downstream**
%R sq.	75.3	91.4
Slope	0.9753	1.0035
P slope	<0.0001	<0.0001
Confidence interv. slope (p<0.05)	0.7677 to 1.1830	0.9016 to 1.1054
Constant	0.1565	0.0909
P constant	0.008	<0.0001
Confidence interv. constant (p<0.05)	0.0438 to 0.2692	0.0724 to 0.1094

Total Dissolved P and Total P

The linear relationships between log TDP and log TP at the Cowlands and between TDP and TP at the sites in the Warren and the Beef Unit are strong, statistically significant and positive (Table

5.5). The TP concentrations at the Warren 1 and the Cowlands are generally about 30% (TDP = 100%) higher than the TDP concentrations. The constant at the Warren 1 indicates a higher percentage at low TDP levels and the exponent of 0.9274 at the Cowlands suggests a percentage lower than 30% at very high TDP concentrations. The difference between TP and TDP was greater at the Beef Unit. TP in subsurface drainage water at that site was about 43% higher than TDP (TDP = 100%). The scatterplots of the TDP/TP or logTDP/logTP data pairs display consistent and clear trends for the Warren 1 (Figure 5.7), the Beef Unit (Figure 5.8) and the Cowlands (Figure 5.9).

The equation describing the TDP/TP relationship for the Warren 2 differs greatly from the equations for the other sites. The TP concentrations at the Warren 2 were overall about 0.036 + 63.5% of the TDP levels higher than the TDP concentrations. The scatterplot of the TDP/TP values (Figure 5.10) does not illustrate different trends or clusters, just a wide spread of values around a general trend and two samples with disproportionately high TP levels. One of those samples is the first one taken at that site and the other one has no distinguishing characteristics.

Table 5.6: R square values, slopes, constants and confidence intervals of slopes and constants of the regression equations of the full TDP/TP datasets of the upstream and downstream sites at the Dairy Farm (TP dependent, TDP independent variable).

Sites	Upstream	Downstream
%R sq.	75.8	no clear relationship
Slope	1.0998	
P slope	<0.0001	
Confidence interv. slope ($p<0.05$)	0.8388 to 1.3608	
Constant	0.1457	
P constant	not stat. significant	

In the stream at the Dairy, there was no clear relationship between TDP and TP at the downstream site and the relationship at the upstream site was not very strong. The equation shows (Table 5.6) that confidence interval of the slope includes 1 and that the constant is not statistically significant.

5.3.4 Turbidity and pH

Both turbidity and TP data were available for 85 samples. The samples were taken from the Warren 1, the Cowlands, and the Dairy Farm stream. The scatterplot of turbidity against TP (Figure 5.11) shows that there was no relationship between the two parameters. Plotting the data for each site separately did not reveal a relationship either (Figures 5.12-5.15).

The maximum and minimum pH values in samples taken between November 1996 and January 1997 from the Warren 1, the Cowlands and the stream at the Dairy are summarised in Table 5.7. The maximum pH values in samples of the four sites are nearly the same. The minimum levels are also similar. Only the difference between the minimum values of the upstream and downstream sites at the Dairy may be noteworthy.

Table 5.7: Minimum and maximum pH values at the Warren 1, the Cowlands and the Dairy Farm sites.

Site	Minimum	Maximum
Warren 1	6.6	7.9
Cowlands	7.0	7.8
Dairy, upstream	6.7	8.0
Dairy, downstream	7.5	7.9

5.4 Discussion

5.4.1 Quality of P Data

Reactive P analysis should be carried out as soon after sampling as possible (Haygarth et al. 1995; Henriksen, 1969) because there are no satisfactory methods of preserving samples for DRP analysis (Haygarth et al. 1995; Johnson et al., 1975). As the study in hand generally adhered to the time intervals between sampling and reactive P analysis suggested by Haygarth et al. (1995), the DRP concentrations at the time of analysis are assumed to be close to those at the time of sampling. The same can be said of TP and TDP levels because both refrigeration and freezing have been described as acceptable ways of preserving samples for these tests (Kothlash and Chessman, 1998). Fitzgerald and Faust (1967) documented an increase of TP levels in samples due to freezing but this finding was not confirmed by the later study of Kothlash and Chessman (1998).

The DRP determination was of higher precision than the TDP analysis. The positive mean laboratory bias (as defined by Anon, 1995) of the DRP analysis (0.002 mg P/l) was satisfactory but the range of differences between the average laboratory recovery rates and the true values was very wide (-0.080 to 0.080 mg P/l). The mean laboratory bias (-0.003 mg P/l and 0.01 mg P/l for the 0.50 mg P/l and the 1.00 mg P/l control samples, respectively) and the range of differences between the average laboratory recovery rates and the true values (-0.05 to 0.03 mg P/l and -0.04 to 0.04 mg P/l for the 0.50 mg P/l and the 1.00 mg P/l control samples, respectively) of the TDP method were quite high considering the effect on water quality attributed to even small amounts of P

(Vollenweider, 1971). The relative impact of the determined bias is much greater in samples of low than high P levels and the concentrations measured in this study were usually high. Low levels of TDP could not even be determined due the high detection limit of the analysis.

Overall, inaccuracies associated with dilutions are expected to be greater for the DRP data because the maximum measurable concentration of the TDP analysis was more than 3 times higher than that of the DRP analysis. Dissolved reactive P analysis therefore required samples to be diluted more frequently and by a higher factor. However, dilution was clearly shown to affect the precision and thus the accuracy of the TDP data whereas there was only a slight trend of greater differences between true and determined DRP values in diluted samples.

The results of the manual digestion of TDP samples confirmed the adequate performance of the automatic digestion unit. The fact that the confidence interval of the value of the slope ranges from 0.959 to 1.019 shows that the automatic digestion of filtered samples recovers practically the same amount of P as the manual digestion method. The results of manual digestion of unfiltered samples, on the other hand, clearly indicated that, in most cases, the automatic digestion underestimates the amount of P present in unfiltered samples. As this was not the case in filtered samples, it is safe to conclude that the presence of suspended solids is the reason for the inaccuracy of the automatic analysis of unfiltered samples. Suspended material does settle down after the samples have been poured into the cups of the automatic analyser. The sub-samples taken by the automatic sampler of the analyser are, therefore, not an accurate representation of the well-mixed original samples. On top of the errors associated with the sub-sampling procedure, the persulphate method is thought to underestimate the TP levels of some samples with high contents of suspended solids of mineral origin (Logan et al., 1979; O'Connor and Syers, 1975).

Because of the importance of the parameter TP and the high R square (94.2%) of the relationship between manually and automatically digested samples, analysis of unfiltered samples was continued but the regression equation was used to obtain a more accurate estimate of the TP concentrations. The TP results thus include a calculation based on a regression equation with R square of 94.2% and are, therefore, somewhat less accurate than the TDP results.

As DRP and TDP/TP analyses varied in accuracy, range and limit of detection, it was necessary to estimate the smallest difference between the parameters which was likely to reflect a real difference between the fractions to compare the datasets. Considering the wide ranges of the laboratory biases of the methods and the TP/TDP detection limit of 0.05 mg P/l, this concentration was chosen as a guide value to indicate a meaningful difference. This is a high value but it does reflect the levels of accuracy achieved in connection with the different P measurements.

For 0.8 % of the samples, the DRP concentrations were more than 0.05 mg P/l (guide value for meaningful difference between samples) higher than the TDP concentrations. All of those samples had been diluted for DRP analysis. The P concentrations of some of these samples also exceeded the limit of the TDP analysis. However, because of the top standard of the TDP analysis (1.0 mg P/l) contains more than 3 times as much P as the top standard used for DRP analysis (0.3 mg P/l) greater dilution was necessary for DRP analysis. Overall, the TDP results are therefore likely to be less affected by the dilution process than the DRP results. The DRP values of the above mentioned 0.8 % samples were therefore discarded and the TDP concentrations used instead.

5.4.2 Relationships between the P Fractions

The regression equations carried out on the full and partial datasets show that a meaningful difference between the fractions does not fundamentally alter the relationships between DRP and TDP and between TDP and TP. Hence good descriptions of the overall relationships are given by the regression equations based on the full datasets.

Overall, the P concentrations were higher at the Cowlands and the Dairy Farm sites than at the monitoring points at Warren and the Beef Unit. The TP was divided into about 23% particulate and 77% dissolved P at the Cowlands and the Warren 1. The percentage of particulate P (PP) was higher in water from artificial subsurface drains (Beef Unit). It amounted to 30% of the TP. Thus, at equal TDP levels, samples from the subsurface drainage site generally contain about 7% more particulate P than overland flow samples from the Warren 1 or the Cowlands. Considering that the artificial subsurface drainage discharge was only monitored for a fraction of the overland flow monitoring period, 7% is a small difference and it may not be meaningful. However, a comparable result was achieved by Haygarth et al. (1998), who measured 12% less PP in overland (PP 31% of TP) than artificial subsurface flow (PP 43% of TP). The amount of PP measured in the subsurface drains also compares well to the 46-21% of PP (TP 100%) determined in leachate from monolith lysimeters of different soil types (Turner and Haygarth, 2000). Both studies quoted above were investigating subsurface movement of P under agricultural grassland in southwest England.

At the three above-mentioned sites, a clear and consistent majority of the TDP was reactive (i.e. DRP), which is in line with the findings of Dils and Heathwaite (1996), Haygarth et al. (1998) and Stamm et al. (1998). The dissolved organic and condensed P fraction (unreactive portion of TDP) was of more consequence at the Cowlands than at the other sites. This may be partly due to the fact that the limit of detection of the TDP analysis is more suited to the P concentrations of samples from the Cowlands than the P levels of samples from the other sites. On average, the dissolved

organic and condensed P amounted to 0.082 mg P/l + 14.6% of DRP at the Cowlands, 11.4 % of DRP at the Warren 1, 0.034 mg P/l + 10.2 % of DRP at the Beef Unit. The secondary trend in the DRP/TDP relationships at the Warren 1 and the Cowlands suggests that the amounts of dissolved organic and condensed P at the time these samples were taken was higher than usually expected at comparable DRP levels. The samples making up the secondary trends were taken during the grazing season and at low overland flow rates (see Section 7.4.2). During the course of the events in question, the unusually high differences between TDP and DRP disappeared. Thus, periods of low flow at the beginning of events during the grazing season coincided with elevated levels of dissolved organic and condensed P in overland flow. As organic P is one of the P fractions that can be leached from fresh cattle faeces (Jensen et al., 2000), manure deposits in the fields may have been the source of this type of P in overland flow at these times. This interpretation ties in with the observation that organic, and especially dissolved organic (i.e. dissolved organic and condensed P) (Sharpley and Syers, 1976), P levels in overland flow from heavily grazed land can be very high (Heathwaite, 1993). Sharpley and Syers (1976) reported that the dissolved organic and condensed P fraction in overland flow was enhanced for an extended period after grazing. The elevated dissolved organic and condensed P levels in overland flow from the Cowlands rather than the Warren 1 (see above) may, therefore, reflect the greater stocking rates during the summer months at the former site. Such enhanced grazing pressure may impact on the physical characteristics of the topsoil (Mullen et al., 1974), and will result in increased amounts of excreta being deposited in an area (Heathwaite and Johnes, 1996). The data collected in this study does not yield information on which one (if any) of the aforementioned effects may have led to the elevated dissolved organic and condensed P levels in overland flow from the Cowlands.

The regression equations between TP and TDP indicate that the PP levels in overland flow at the Warren 2 were quite variable and generally considerably higher than those in samples with similar TDP levels taken from the other overland flow sites (Warren 1 and Cowlands). Suspended solid concentrations (see Section 7.3.3) in overland flow at the Warren 2 were certainly higher than the solids found in samples from the other sites. The source of the suspended matter was the mound of low P subsoil at the upstream boundary of the site (see section 7.2.1). Once suspended in the water, the soil particles may have interacted with P in solution and bound some of it (Green et al., 1978; House et al., 1995; McCallister and Logan, 1978). This may have been an important contributory factor to the high amounts of particulate P found in samples from the Warren 2. The relationship between reactive and non-reactive dissolved P was also quite different at this than at the other overland flow sites. No clear evidence of an increase of the dissolved organic and condensed P levels with rising DRP concentrations was found (confidence interval of slope included 1) and the dissolved organic and condensed P concentrations generally amounted to 0.039 mg P/l at the Warren 2. The more or less constant dissolved organic and condensed P levels could

result from the interactions of dissolved P with the low P solids at this site. The modifying influence of suspended material on TDP concentrations has been demonstrated (Maguire et al., 1998; Sharpley and Smith, 1990), and Froehlich (1988) and Yli-Halla and Hartikainan (1996) reported a buffering effect of solids on DRP concentrations in water. Such a mechanism did not seem to affect the DRP data in this study but it may have led to the more or less stable dissolved organic and condensed P concentrations in overland flow from the Warren 2. The fact that the Warren 2 was only monitored during one winter may also explain a part of the difference of the variability of the dissolved organic and condensed P concentrations between the Warren 2 and the other overland flow sites. Because of the shorter monitoring period, the conditions encountered at the Warren 2 encompassed less variability than those that affected the other sites.

The only strong and clear trend regarding the relationships between the P fractions at the Dairy Farm sites is that the TDP levels at the downstream site were generally between 0.07 and 0.11 mg P/l greater than the DRP concentrations. The lack of other clear relationships may suggest that the samples were influenced by a variety of different P sources, pathways and flow conditions. Each set of circumstances may have given rise to a particular set of relationships between the P fractions, and a mix of these may be what is reflected in samples from the stream running through the Dairy.

5.4.3 Turbidity and pH

Measurements of both of these parameters were discontinued after evaluating the value of the information gained from them in this study. The good correlations between turbidity and TP, which were described by Grayson et al. (1996), were not found in this study and the variability of pH levels between different samples was typically comparable to the difference between measurements made on the same sample at different times. Real differences of pH values between samples could, therefore, not be distinguished from differences due to analytical error.

CHAPTER 6: RAINFALL AND ITS P CONTENT

6.1 Introduction

Rain usually contributes little immediately available P to the area it falls on because DRP concentrations in rainwater are mostly low. Total P inputs tend to be greater (Gibson et al., 1995; Sharpley and Syers, 1979). Their potential impact on water quality generally depends on catchment characteristics and is particularly influenced by type and intensity of land use.

Rainwater starts off as pure condensed water but can then pick up P from small particles in the atmosphere (Keup, 1968) and from sea-spray (Jordan, 1997). Sharpley and Syers (1979), for example estimated 0.009 mg P/l and 0.037 mg P/l mean annual DRP and TP respectively in rain falling on a New Zealand pasture catchment, and Jordan (1997) gave 0.01 mg P/l DRP and 0.025 mg P/l TP as typical concentrations in Irish rain. However, maximum levels of 0.04 mg P/l DRP (Cooke, 1988), 0.052 mg P/l TDP and 0.126 mg P/l TP (Sharpley et al., 1986) have been measured in rainwater.

6.2 Methods

The weather data used in this study were generally obtained from the meteorological station at Johnstown Castle. However, the amount of rainfall is known to vary over small areas. To assess this variation, a standard manually operated 127 mm diameter Met Eireann rain gauge was established at the Cowlands in summer 1996. The Cowlands are at a distance of 1.2 km from the Johnstown Castle meteorological station. The manually operated rain gauge at the meteorological station was also a standard 127 mm diameter Met Eireann rain gauge. Both manually operated rain gauges were set up and rainfall recorded following the guidelines laid down by Met Eireann.

Hourly rainfall amounts were available from the automatic rain gauge at the meteorological station at Johnstown Castle. However, preliminary investigations showed that the cumulative quantities of rainfall measured with the automatic gauge were about 20% lower than those obtained from the manual standard Met Eireann instrument at the meteorological station at Johnstown Castle. The automatic data collection or transmission also failed quite frequently at the time this project was carried out, and the time for which the occurrence of rainfall was recorded was often incorrect. All the above restricted the usefulness of the automatic rainfall data considerably. Thus, the manual daily rainfall readings were the main rainfall data used in this study.

Rainwater samples were collected during overland flow events and analysed as described in Chapter 5. The rain gauge was washed frequently with de-ionised water.

6.3 Results

6.3.1 Amount of Rain

There was very good agreement between the total amount of rainfall collected at the Johnstown Castle meteorological station standard manually operated rain gauge and at the site in the Cowlands (Figure 6.1). Between 9th November 1996 and 31st March 1998, 1616.7 mm (100%) and 1643.4 mm (101.7% of the rain at the Johnstown Castle meteorological station) of rain fell at the meteorological station and the Cowlands, respectively.

Figures 6.2 and 6.3 set the monthly rainfall during the monitoring period in context with the monthly rainfall measured at the Johnstown Castle meteorological station since 1950. Figure 6.2 shows the monthly rainfall from January 1950 to March 1998. The months during which monitoring took place are represented by large, coloured symbols. The average monthly figures form January 1950 to December 1995 are displayed alongside the monthly rainfall values for the monitoring period in Figure 6.3.

August and June 1997 had record (since 1950) amounts of rainfall. In May and November 1997 and January 1998 rainfall was also substantially above average. December 1996, January, March and April 1997 and February 1998 were comparatively dry months. The average rainfall of the years 1950 to 1995 was 1020 mm, the range 733 to 1366 mm. The yearly amount of rainfall for the monitoring period at Johnstown Castle meteorological station was estimated to be 1232 mm (1,246.0 mm at the rain gauge in the Cowlands). This annual amount was only exceeded 3 times since 1950 (1958, 1960 and 1966).

6.3.2 Rainfall Intensity

Due to the questionable quality of the hourly rainfall data from the automatic rain gauge, these data were only used to get a general impression of the variation of the rainfall intensities over the study period. Figure 6.4 shows the amount of rain (mm) falling per hour as measured by the automatic rain gauge. The maximum rainfall intensity measured occurred 4th August 1997. It was only sustained for one hour. Values achieved shortly before and after the maximum were high but in the region of the levels also achieved during other events monitored.

6.3.3 Phosphorus in Rainwater

Of the 80 rainwater samples analysed for DRP, 63 were below the limit of detection (0.005 mg P/l). The DRP results are displayed in Figure 6.5. As the limit of detection was very low, values below it were plotted as zero. The maximum DRP concentration of 0.030 mg P/l was measured in the rain sample taken 6th January 1998. The average DRP concentration of the 17 samples above or at the limit of detection was 0.014 mg P/l.

Of the 49 samples for which the TDP concentration was determined, only 5 were below the limit of detection (0.05 mg P/l). The limit of detection for TDP analysis was quite high at 0.05 mg P/l. Equating values below the limit of detection with zero could not be justified and such values were, therefore, omitted from the figure displaying the TDP results (Figure 6.6). The mean of the other 44 samples was 0.13 mg P/l. The maximum concentration 0.35 mg P/l was measured in the sample collected 19th May 1997.

Fifteen of the 54 samples analysed for TP were below the limit of detection (0.05 mg P/l) (Figure 6.7). As in the case of TDP, samples with TP below the limit of detection were omitted from Figure 6.7 rather than displayed as zero. The other 39 samples had a mean and maximum concentration of 0.16 and 0.55 mg P/l respectively. The highest TP value was measured in the sample taken 19th May 1997.

No seasonal or other patterns of the P concentrations are apparent in Figures 6.5 to 6.7.

6.4 Discussion

6.4.1 Amount and Intensity of Rain

The small overall difference of 1.7 % and the pattern of the cumulative rainfall at two rainfall measurement sites (Figure 6.1) suggest that the distribution of rainfall over the Johnstown Castle estate was uniform during the monitoring period. Rainfall at the meteorological station is measured every day, including weekends. The rainfall records from the Cowlands, on the other hand, contain a few summary readings after missed days. The good agreement between the measurements at the two gauges makes it possible to use the more complete dataset from the meteorological station whenever necessary. Both gauges may, however, underestimate the real quantity of rainfall by about 8% due to wind action (Rodda, 1967).

Overall, the amount of precipitation during this study was significantly above average. Record (since 1950) high rainfall values were measured in two months of summer 1997 and the monthly rainfall was considerably above average in a further three of the months monitored.
The maximum hourly rainfall with a return period of 5 years is estimated at 16 mm for Wexford (Rohan, 1986). Figure 6.4 illustrates that, even when considering that the automatic gauge underestimates rainfall, the rainfall intensities during the monitoring period did not reach the 16 mm/hour. The rainfall intensities achieved during many events were similar to each other. Elevated rainfall intensities were, furthermore, never sustained for long.

6.4.2 Phosphorus in Rainwater

The DRP inputs through rain are mostly below detection and therefore negligible. The maximum DRP concentration of 0.03 mg P/l lies within the range of 0 to 0.04 mg P/l given by Cooke (1988). Measurable and sometimes surprisingly high amounts of TDP and TP were contained in rainwater. The maximum concentrations of both parameters clearly exceed those measured by Cooke (1988) and Sharpley et al. (1986). The mean of the TP concentrations which exceeded the limit of detection was close to Sharpley et al.' (1986) maximum TP level of 0.126 mg P/l.

It is unlikely that the high TDP and TP concentrations measured in rain at Johnstown Castle are attributable to contamination because the gauge is designed to minimise splashing and it was cleaned often. The DRP levels furthermore remained low. The TDP/TP analyses were not geared towards measurement of low P concentrations. The limit of detection of these analyses was high and the accuracy relatively low (see Section 5.4.1). The accuracy of the TP results is further affected by the fact that the TP data are the outcome of a calculation based on the raw data (see Section 5.4.1). Still, the TDP/TP concentrations are high, even when the quality of the TDP/TP data is being considered.

Collectors which were only uncovered during rainfall were used by some other studies to collect rainwater samples (Cooke, 1988; Sharpley et al., 1986). Our rain gauge was always open. Our results therefore describe a combination of wet and dry atmospheric deposition, which may go towards explaining the high values for TDP/TP. It is also possible that dust from the land around the rain gauge gained access to the gauge during dry periods. As the gauge was located in a grassland field, dust would only have been an issue after extended dry periods. Elevated TDP/TP levels, on the other hand, were not restricted to rainfall after dry periods. Dust could furthermore be expected to affect DRP levels as well as TDP/TP concentrations, but the DRP values are generally low.

Figures 6.5 to 6.7 indicate that the main P fraction in rain at Johnstown Castle is usually dissolved unreactive P, which encompasses mainly dissolved and colloidal (colloids <0.45 μm) organic and condensed P (see Section 5.1.1). To explain our high TDP/TP values, a source that contributes organic and condensed P to the atmosphere therefore needs to be identified. As Jordan (1997) assumes atmospheric P in Ireland to be of marine origin, the proximity of Johnstown Castle to the sea could help to explain the high levels of dissolved and colloidal (colloids <0.45 μm) organic and condensed P in wet and dry deposition.

CHAPTER 7: PHOSPHORUS IN OVERLAND FLOW

7.1 Introduction

The proportion of runoff contributed by overland flow and its significance as regards nutrient delivery to water bodies are spatially and temporally variable (Pionke et al., 1988; Yli-Halla et al., 1995) (see Section 2.5). Where overland flow does occur in considerable quantities, it has, depending on the presence of a P source and a hydrological connection to a water body, the potential to deliver significant amounts of P to water bodies within a short period of time (Turtola and Jaakkola, 1995).

The land-related sources of P include organic (Misselbrook et al., 1995) and inorganic (Nash et al., 2000) fertilisers, soil (McDowell and Sharpley, 2002) and dead and live organic matter (e.g. plants, excrements) (Jawson et al., 1982; Wendt and Corey, 1980). The relative magnitude and importance of these sources vary with changes in site characteristics, management systems and environmental conditions.

Because overland flow is an important P transport pathway (Sharpley and Syers, 1979) (Section 2.6), estimates of annual P losses in overland flow from field-sized areas are necessary to help assess the magnitude of the potential grassland related P contributions to surface water bodies. Work on the quantification of edge-of-field P losses from grassland areas has been carried out before. In a 6 year study to assess P losses due to fertiliser usage, Burke et al. (1974) measured P exports between 0.9 and 5.2 kg/ha in overland flow from small grassland plots (2.4 by 22 m). Soil P levels in that study were not measured. The amount of P fertiliser applied to the plots was high and ranged from 40 – 130 kg P/ha. The timing of fertiliser applications in relation to the occurrence of rainfall was the main factor influencing the P exports from their small grassland plots. The importance of this factor was confirmed by studies carried out on pasture areas in southwest England (Haygarth and Jarvis, 1997) and southeast Australia (Nash et al., 2000). However, Nash et al. (2000) also state that, even apart from P exports as a result of fertiliser applications followed by rainfall, P concentrations in overland flow from their high soil P pastures were unacceptably high.

In studies using artificial rainfall to produce overland flow, the P concentrations in overland flow from grassland areas were shown to be greatly influenced by the P levels of the soils (Daniel et al., 1993; Pote et al., 1996; 1999). In contrast to P fertilisation, the soil may be represent a constant source of P to enrich overland flow.

The main focus of the study in hand was therefore to quantify P losses with overland flow and describe P concentrations in overland flow from field sized areas with reference to different soil P levels (see aims 1.1, 1.3 and 1.4 Section 1.4). Hence the quantities of overland flow and the P levels therein were monitored for 3 grassland fields at Johnstown Castle (see Section 3.4 for site descriptions and management): the Warren 1, which had a soil P level of 4 mg P/l Morgan's (called low P site), the Warren 2 with a soil P level of 8 mg P/l Morgan's (called medium P site) and the Cowlands with a soil P level of 17 mg P/l Morgan's (called high P site) (see Section 4.4.1). Because grazing is the land use most commonly associated with grassland in Ireland, it was decided to manage the study areas as pastures. The soils of the overland flow sites were poorly drained gleys (see Section 3.4.1 for detailed soil descriptions). Subsurface flow was not collected or sampled at the overland flow sites. Thus the calculated quantities of P exported solely refer to losses in overland flow.

To gain information on P exports and concentrations in overland flow across environmental conditions (see aim 1.4 Section 1.4) and thus obtain a realistic estimate of annual edge-of-field P losses with overland flow, the low and the high soil P site were monitored for 16 months. The medium soil P site was set up a year later than the other two overland flow monitoring areas. Overland flow quantity and composition from the medium soil P site was therefore only measured for about 5 months.

When using a field as a monitoring unit, it is important to keep in mind that small-scale variations of soil hydrological and chemical characteristics can be substantial (Daniels et al., 2001; Vieira et al., 1981). However, these variations are discussed in Sections 4.4.1, 4.4.2 and 4.4.4, and they are only referred to when necessary in connection with other issues in this chapter.

Overland flow generally occurs as either infiltration excess overland flow, saturation excess overland flow or return flow (Cooke and Dons, 1988; Pionke et al., 1986). The amount of overland flow produced and the environmental conditions under which overland flow arises are likely to be affected by the type of overland flow prevalent at a site. For example, where infiltration excess overland flow is the rule, overland flow occurs if the rate of rainfall exceeds the infiltration capacity of the soil (environmental condition). At such a site, all rain falling at rates greater than the infiltration capacity becomes overland flow. At sites predominantly producing saturation excess overland flow on the other hand, some rain is necessary to elevate the soil moisture levels before overland flow can occur. On the basis of the soil hydrological information compiled in Sections 4.3.2 and 4.3.4 and the overland flow measurements reported on here (Section 7.3.1), the importance of the different overland flow mechanisms at the monitored sites are discussed in Chapter 7 (see aim 1.2 Section 1.4).

Work in England (Dils and Heathwaite, 1996) and other countries (Nash and Murdoch, 1997; Sharpley et al., 1976) has shown that the relationships between P concentrations in overland flow and the rates of flow are complex and variable across environmental conditions. These relationships are explored in reference to the three overland flow sites monitored in this study (see aims 1.3 and 1.4 in Section 1.4).

The forms of P prevalent in overland flow are above all influenced by the state of the land surface. Particulate P, for example, was found to be dominant over other forms in overland flow from arable (Uusitalo et al., 2001) and heavily poached land (Heathwaite and Johnes, 1996), whereas dissolved forms of P have been measured to make up the majority of P exports in overland flow from grassland areas (Nash et al., 2000). The forms of P and the general relationships between them are discussed in Section 5.4.2. However, specific aspects of the behaviour and prevalence of the different forms of P in overland flow are further elucidated in this chapter (see aim 4 Section 1.4).

7.2 Methods

7.2.1 Installation and Instrumentation of Sites

The land surfaces of the three sites were hydrologically isolated from the surrounding land with man-made trenches and berms around the boundaries of the sites. All the overland flow from the sites was collected and measured with the help of large tanks fitted with sharp-crested (thin plate) v-notch weirs and water level recorders. The tanks were partly covered and, thus, open to rainfall to some degree. However, the uncovered areas of the tanks were very small in comparison with the areas of the sites. The effect of this direct input of rainwater on the water level in the tanks was considered negligible (open tank areas amount to less than 0.05% of the respective site areas).

The Warren 1 (Figure 7.1) was first established as a site to measure and sample overland flow in 1986. The site was restored in 1994 (Tunney et al., 1997) and has been in use ever since. Open trenches run along three sides of the Warren 1. The average depths of the trenches forming the upstream, left and right (facing upstream) hand side boundaries amount to 1.5, 1.8 and 0.9 m respectively. An open drain coated with butyl rubber (40 cm wide and 45 cm deep) separates the site from downstream areas and collects the overland flow originating within the isolated field. At the lowest point of the collection drain, the overland flow enters a pipe, which leads to the weir tank. The drain covers an area of about 66 m^2 and 0.43% of the area of the site.

In autumn 1996, a discrete automatic water sampler (SIGMA 900) replaced an old composite sampling system. Both systems sample(d) water from the pipe which leads the overland flow from the collection drain to the weir tank. The old composite system led a small proportion of the water flowing through the pipe into a large drum, where the composite sample was stored. The water samples from the discrete system used in this research were are taken just before the water flows from the delivery pipe into the tank. In 1997 an automatic shaft encoder with integral data logger (OTT, Thales) to measure and record water levels was installed in the weir tank. This system replaced the existing chart recorder. Details of the water level measurement and sampling protocols are given in Section 7.2.2 and 7.2.3 respectively.

The site at the Cowlands (Figure 7.2) was set up in summer and autumn 1996. The upstream boundary of the site is formed by a ditch of about 60 cm depth. Along the other sides of the field, trenches of about 25 cm depth were backfilled with heavy subsoil. On top of this, 10 to 20 cm high earth banks were built up and re-seeded with grass. The overland flow originating within the site flows towards the lowest corner of the field where it enters a pipe (15 cm diameter) set in a concrete funnel. The water then runs through the pipe down to the weir tank.

Originally, sediment traps were installed at the Warren 1 and the Cowlands. They consisted of concrete sumps which intercepted the water flowing off the fields. The pipes leading to the weir tanks formed the outlet of the sumps. The sediment traps were considered to render the determination of the course of P concentrations during overland flow events impossible. They were, therefore, bypassed by extending the pipe at the outflow of the sumps to the concrete funnel at the Cowlands and to the lowest point of the collection drain at the Warren 1. The concrete sump at the Cowlands was open to the rain and needed to be emptied regularly to stop it from overflowing into the site. The sump at the Warren 1 was covered. However, the concrete structure at this site was very old and started to leak in summer 1997. As the pipe from the collection drain had been inserted into the pipe at the outflow of the sump, the connection was not waterproof. However, the sump at the Warren 1 was also emptied regularly and the water level in it was, therefore, kept below the outlet pipe.

The site at the Warren 2 (Figure 7.3) was prepared during summer and autumn 1997. The area resembles the shape of a halved truncated cone. Trenches of about 2 and 1 m depths run along the right and left hand sides respectively (facing upstream) of it. A farm roadway defines the upstream (wider end) boundary of the field. Following the contours of the field, the roadway runs through a depression. The lowest point of the depression is nearly half way between the left and right hand boundaries of the field. At this point, water had often been observed to flow from the road down into the site. A pit about 1.1 m deep was therefore opened just below the roadway to find an

existing subsurface drain running down the field along the dip. The drain was found to be blocked and was therefore excavated and replaced with a drain of larger diameter. At the location of the pit, a proper concrete block manhole was built to catch all water coming from the road and lead it into the new drain. At both sides of the manhole, all along the upstream boundary of the site, trenches of about 1 m depth were excavated and backfilled with heavy subsoil to about 10 cm below the surface. The subsoil was rich in clay and was obtained from the excavations at the building site of the Department of Agriculture, Food and Rural Development headquarters (Figure 1.1). Downstream of this small channel, earth banks of impermeable soil were constructed to ensure that no surface water from upstream areas could enter the site. The downstream boundary of the site was, like in the Cowlands, formed by an earth bank built on a 25 cm deep trench backfilled with impermeable soil. At the lowest point of the field, the water again flowed into a concrete funnel, and through a 15 cm (diameter) pipe down to the tank. The areas covered by the concrete funnels were very small. In relation to the total area of the site the funnel covered about 0.03% of the Cowlands and 0.02% of the Warren 2.

The construction of the Warren 2 was often disrupted by the wet weather in summer 1997. Therefore, a big mound of subsoil, which had been used to backfill the trenches, had to be left in the site because the soil was too wet for the digger to drive in when the construction was completed. The mound was located in the middle of the upstream boundary of the site. Subsoil is generally extremely low in P and the amount of Morgan's P measured in samples taken from the mound were <1 mg P/l. The mound did, therefore, not contaminate the site with P. However, it may have provided a source of suspended particulate matter (see Section 7.3.3).

Discrete automatic samplers with integral water level recorders (SIGMA 900 Max) were installed at the weir tanks in the Warren 2 and the Cowlands. The depth probes were pressure transducers with a range of 0 to 1.8 m and an accuracy of 0.2% (best straight line for combined non-linearity, hysteresis and repeatability).

Overland flow at all three sites was sampled from the pipes, just before they discharged into the tanks. The concrete funnels at the Cowlands and the Warren 2, the collection drain at the Warren 1 and the tanks were cleaned as required. The depth probes and samplers were re-calibrated and maintained as suggested by the manufacturers.

The tanks at the Warren 1 and the Cowlands were of glass re-enforced polyester. Length, width and height are 2.06, 1.00 and 0.76 m respectively. The tank at the Warren 2 was an old concrete block structure. Its length, width and height were 3.64, 1.84 and 1.1 m respectively. When monitoring at the Warren 2 started, it was discovered that the concrete weir tank was leaking. The

leak could not be pinpointed and the weather conditions were too wet to allow re-plastering of the tank. The calculations on the data of that site took account of the loss of water from the tank (see Section 7.2.4).

The weir tanks at the three overland flow sites were fitted with triangular thin-plate (sharp crested v-notch) weirs. The angles of the weirs and the heights of the vertices above the bottom of the weirs were 90° and 69 cm for the Warren 2, 60° and 46 cm for the Warren 1 and 30° and 45 cm for the Cowlands. The weirs were calibrated to obtain an accurate relationship between the water level in the tank and the flow through the weir. The discharge (Q) was measured at several water levels (h) by recording the time it took to fill a graduated barrel. The base 10 logarithm of the water level was then plotted against the base 10 logarithm of the discharge, and the regression equation was calculated. Based on this equation, values for a and b in the discharge relationship $Q = a*h^b$ could be determined. The constants and slopes of the regression equations were all statistically significant ($p<0.0001$) and the R square values ranged from 97.8% for the Cowlands to 99.6% for the Warren 2.

7.2.2 Water Level Recording

During most of the monitoring period, loggers were set to record an average water level reading every 5 minutes. The logging interval at the Warren 2 was 15 minutes from 17th November to 1st December 1997. The automatic logger at the Warren 1 was installed in September 1997. Thus, the logging interval of 5 minutes only applies since then at this site.

At the start of the monitoring programme in the Cowlands (November 1996), the logger was set to record an average water level reading every minute. Five-minute averages were then calculated and water level data were plotted at the two intervals. A comparison of the graphs (Figures 7.4 and 7.5) confirmed that increasing the logging interval from 1 to 5 minutes did not lead to a loss of information.

7.2.3 Sampling Programme

With a view to ensuring the comparability of the sites, time related sampling programmes were operated at all overland flow sites. Flow related sampling is more efficient but could not be carried out with the instrumentation at the Warren 1.

The sampling programmes were initiated by a water level rise in the tanks. At the Cowlands, initially a water level of 5 mm (above the lowest point of the weir) was programmed to trigger the

time related sampling programme. On one occasion, such a rise was caused by rain directly landing in the tank and, as a consequence, the sampling programme had started before any overland flow had occurred. From then on, the sampler was set to initiate the programme at a water level of 7 or 8 mm. As the water level recorder was not integrated into the sampler at the Warren 1, the time related sampling programmes at that site were triggered by a float level actuator, which was connected to the sampler. The level actuator was not as precise as the depth probes. The level at which it triggered the time related sampling programme varied slightly but was generally around 14 mm above the lowest point of the weir. At first, the level actuator was positioned to initiate sampling at about 5 mm. This often led to premature sampling and the actuator was gradually moved up until it only triggered the time related sampling programmes when overland flow actually occurred.

Apart from the loss of precision associated with the actuator, the fact that more flow was necessary to allow the collection of a sample at the Warren 1 than the Cowlands also contributed to the occurrence that the reliable trigger point was higher at the former site. The pipe leading into the tank at the Warren 1 was of much greater diameter than the pipe at the Cowlands. This pipe was built into a concrete brick wall and could therefore not be changed easily. The long overland flow collection drain at the Warren 1 may also have influenced the water level in the tank during heavy rain. Rainwater falling into the collection drain was of no consequence during an overland flow event but may have led to a slight and early water level rise in the tank at the beginning of events. No constant trigger level could be defined for the Warren 2 because of the leak in the tank at that site. The water level to initiate sampling was therefore adjusted downward as needed during every visit to the site.

Sampling at all overland flow sites was most frequent at the beginning of events. The time interval between samples usually increased from 30 minutes to 3 hours during an event. A regular sampling interval of 3 to 4 hours was employed if several events followed each other very closely. During holiday periods, the sampling interval was set to 5 hours.

When monitoring at the Warren 1 and the Cowlands started (November 1996) the sampling interval at the beginning of events was 15 minutes. Crosses in Figure 7.6 indicate the DRP levels of samples taken at that interval and circles display the DRP concentrations of samples taken at 30 minute to 8 hour intervals. Figure 7.6 shows that there are always at least two consecutive samples of similar P concentration at the 15 minute sampling interval. One instead of two data points would therefore be sufficient. Thus the minimum sampling interval was increased to 30 minutes.

Samples of spring water at the Warren 1 and 2 were collected during overland flow events.

7.2.4 Data Treatment and Calculations

Water Levels, Flow and P Export

The water level and quality data were combined in Microsoft Excel® workbooks. Each workbook held the data for one distinct event. Many events consisted of several flow peaks. In the case of overland flow, the absence of any flow for more than 12 hours was the factor which separated one event from the next.

The flow at the overland flow sites was calculated using the water level data from the loggers and the discharge formulae determined by gauging the weirs. To obtain digital water level information from the Warren 1 for the period during which the data were collected by a chart recorder, the charts were digitised in Autocad® and saved as drawing interchange files. Next, coverages of those files were built in ARC/INFO. In order to increase the resolution of the digitised files, the grain tolerance was lowered and the command SPLINE was used to create extra vertices. The command UNGENERATE then converted the new coverage of higher resolution into an x/y spreadsheet.

The multiplication of the mean P concentration of adjacent samples with the flow during the interval between the samples was found to represent an accurate way of estimating P loadings (Magette and Ifft, 1989). This procedure was, therefore, adopted. Whenever, in the course of an overland flow event, a flow peak following a period of extremely low flow coincided with a considerable change of P concentration, the concentrations of samples defining the interval were not averaged. Flow up to the water level rise was then multiplied with the P content of the sample at the beginning of the interval, and the flow from the water level rise onward with the concentration at the end of the interval. The flow-weighted average P concentrations were calculated by dividing the total P export per event by the total flow during the same period of time.

Based on the information presented in Sections 5.2.5 and 5.4.1, export figures calculated with DRP data were considered to be of much higher accuracy than exports estimated with TDP or even TP concentrations. For example, no TDP values were available for the 14% of samples analysed for TDP which were below the detection limit of the analysis, and the TP concentrations were the outcome of a regression calculation. Daily export figures were therefore only estimated for DRP, and TDP/TP exports for the whole monitoring periods were calculated using the equations described in Section 5.3.3.

Flow at the Warren 2

The flow calculations at the Warren 2 needed to be adjusted for the water loss due to the leak in the tank. In a first step, the empty volume below the weir at the beginning of an event was multiplied by the P concentrations of the samples taken at or near to the time the tank was filling up. When time was plotted against the levels below the weir for all instances in which the water level dropped significantly, it became obvious that the rate of loss varied between events. Thus a rate was estimated for each event and was added to the discharge. This rate of loss only approximates the real loss, which depends on the head of water in the tank. The plots of time against the water levels below the weir clearly illustrate this dependence (Figure 7.7 is an example). However, they also show that there was an almost linear relationship between the time and the drop in water level for the first 10 cm below the weir. Hence an average rate could be calculated by multiplying the length and width of the tank by 10 cm and dividing the product by the length of time necessary for that drop in level to occur. The loss of water per time was also calculated for every logged level measurement (5 or 15 minute intervals) between 0 (lowest point of weir) and –10 cm. Those rates of loss were plotted against time to ensure that they were randomly distributed (Figure 7.8 is an example). This was the case for all but one event (end of event 18.3). On November 29th, the water level decrease per time interval was lower from 0 to –4 cm than from –4 to –10 cm. A quantity of overland flow, which was smaller than the water loss from the tank, must have been trickling into the tank at that time. The rate of loss was determined on the basis of the data from –4 to –10 cm. Then the trickle of overland flow was estimated by calculating the loss rate for each logged water level above –4 cm, deducting the rate of loss below –4 cm and multiplying the result by the time interval between 0 and –4 cm.

Relationships Between Flow and P concentrations, and Between P Concentrations and Other Water Quality Parameters

An attempt was made to use least square regression analysis to look at the relationships between flow and P concentrations. However, as the residuals of this analysis were not normally distributed and no suitable transformation was apparent, scatterplots were used to gain information on the relationships between flow and P concentrations.

The same approach was adopted to investigate the relationships between P concentrations and other water quality parameters.

7.3 Results

7.3.1 Occurrence and Quantity of Overland Flow

Overland Flow Events

To make a comparison of the sites possible, the events at the Warren 1 were numbered from 1 to 22 (see Section 7.2.4 for definition of an event). Events at the Cowlands that occurred during an event at the Warren 1 were given the same number as the event at the Warren 1. Multiple events at the Cowlands during one event at the Warren 1 are indicated with the number of the event at the Warren 1 plus decimal places. This system was extended to the Warren 2. The numbering system is presented in Table 7.1.

Special occurrences during these events are tabulated in Table 7.2. Note that DRP results of some of the events were derived from the TDP measurements (see Chapter 5), that the tank at the Warren 1 was tampered with at the beginning of December 1996 and that some water level data at the Warren 1 were missing because the pre-event 15 chart recorder failed. The drum of the chart recorder failed to turn at the end of event 7 and during parts of events 5 and 8 (see Table 7.2). The end of event 7 could be filled in by hand as it was known when the water level in the tank reached zero. Even though the drum did not turn, the heights for the missing peaks of events 5 and 8 (see Table 7.2) could be made out on the charts. Figures 7.102 to 7.116 show that the timing of the flow peak was often similar at the Warren 1 and the Cowlands. Graphs from the Cowlands were, therefore, used in combination with the peak heights recorded on the charts from the Warren 1 to draw up an approximation of the hydrographs of events 5 and 8 for overland flow at the Warren 1.

Table 7.1: Numbers allocated to the overland flow events at the Warren 1 and the corresponding events at the other sites.

Date start	Date end	Warren 1	Cowlands	Warren 2
24-Nov-96	05-Dec-96	1	1	
17-Dec-96	22-Dec-96	2	2	
10-Jan-97	19-Jan-97	3		
23-Jan-97	23-Jan-97	4		
01-Feb-97	26-Feb-97	5	5.1, 5.2	
24-Apr-97	29-Apr-97	6		
04-May-97	15-May-97	7	7	
18-May-97	26-May-97	8	8	
05-Jun-97	16-Jun-97	9	9.1, 9.2	
19-Jun-97	30-Jun-97	10	10.1, 10.2	
01-Jul-97	07-Jul-97	11		
29-Jul-97	31-Jul-97	12	12	
03-Aug-97	10-Aug-97	13	13	
20-Aug-97	07-Sep-97	14	14.1, 14.2	
19-Sep-97	23-Sep-97	15	15	
08-Oct-97	13-Oct-97	16	16	
14-Oct-97	20-Oct-97	17	17	
30-Oct-97	16-Dec-97	18	18.1, 18.2, 18.3, 18.4	18.2, 18.3, 18.4
17-Dec-97	02-Feb-98	19	19.1, 19.2, 19.3	19.1, 19.2, 19.3.1, 19.3.2
06-Feb-98	16-Feb-98	20		
02-Mar-98	14-Mar-98	21	21	21
24-Mar-98	31-Mar-98	22	22	22.1, 22.2

Table 7.2: Special occurrences during events.

No. of event	Site	Comment
1	Warren 1	The valve of the tank at the Warren 1 was found open at the end of the event (vandalism) and the amount of flow measured for this event is therefore an underestimate.
5	Warren 1	Failure of chart recorder (see text). Based on the maximum peak height and data from the Cowlands, the end of the event was re-drawn.
7	Warren 1	Failure of chart recorder (see text). There was a very small bit of flow data missing and filled in by hand at the end of the event.
8	Warren 1	Failure of chart recorder (see text). Based on the maximum peak and the shape of the curve at the Cowlands, the beginning of the event was re-drawn.
12	Warren 1, Cowlands	DRP results calculated.
13	Warren 1, Cowlands	DRP results calculated.
18	Warren 1	Two samples with excessively high P concentration before the event started properly were probably due to dirt accumulation in the drain collecting overland flow.
19	Warren 1	DRP results in the middle of the event calculated.
19.2	Warren 2, Cowlands	DRP results calculated.
19.3	Cowlands	DRP results calculated.
19.3.1	Warren 2	DRP results calculated.
22	Warren 1	Event not quite finished at the end of the monitoring period.

Comparison of Overland Flow at the Three Sites

During the monitoring period of 493 days (24th November, 1996 to 31st March, 1998), 1,643 mm of rain was measured at the rain gauge in the Cowlands. For the same period, the Warren 1 produced 1,007 mm and the Cowlands 591 mm of overland flow. When converting these figures into yearly amounts, the averages of months that were monitored in two successive years (December, January, February and March) were used for the calculation. Annual figures of 1,246 mm of rain, 774 mm of overland flow from the Warren 1 and 443 mm from the Cowlands were calculated

The Warren 2 was monitored for 144 days. The rainfall amounted to 575 mm during this time. Concurrently there was 511 mm of overland flow that ran off the Warren 1, 436 mm off the Warren 2 and 328 mm off the Cowlands.

The amount of overland flow from the Warren 1 exceeded the overland flow from the Cowlands during all events. Figure 7.9 illustrates that, with the exception of December 1996, monthly overland flow values for the Warren 1 were higher than those for the Cowlands (see Section 7.4.1 for clarification on December overland flow figures). Flow from the Warren 2 was greater than overland flow from the Cowlands for all but the last event in November 1997. Flow per month from the Warren 2 showed no consistent relationship with overland flow from the Warren 1 (Figure 7.10). Figure 7.11 illustrates that there is a positive correlation (Pearson Product-Moment Correlation) between the daily flow at the Warren 1 and at the Cowlands (R^2 of 75.0 %, $p<0.0001$). On the first 2 days of event 13, flow from the Cowlands was lower than usual when compared with flow at the Warren 1. The daily flow values of the Warren 2 showed no clear relationship with those of either the Warren 1 or the Cowlands.

In January 1998, flow from the Warren 1 and 2 exceeded rainfall. To investigate this issue further, the differences between the cumulative daily flows and the cumulative daily rainfall values were studied. As long as rainfall exceeds or equals overland flow, the difference between the cumulative values increases or remains constant. A decrease of the difference indicates excessive overland flow in excess of precipitation. Figure 7.12 shows a clear drop in the curve of differences for the Warren 1 between the end of December 1997 and the middle of January 1998. This trend is much more pronounced in the curve for the Warren 2 (Figure 7.13). At both sites there are also small decreases, which are, however, cancelled out by immediate rises of the curve.

The hydrological similarities and differences between the overland flow sites also become apparent when studying corresponding events (Figures 7.14 to 7.71). One of the most obvious facets is that several rainfall events triggered overland flow in the Warren 1 but not in the Cowlands (see Table 7.1) or, in the case of event 20, the Warren 2. Furthermore, the Warren 1 generally started producing overland flow hours earlier than the site at the Cowlands and continued long after the site at the Cowlands was dry (see Figures 7.23, 7.44 and 7.45 for example). The Warren 2 usually started before the Cowlands. Figures 7.60 and 7.69 show this on the example of event 21. The shapes of the hydrographs of the three sites look similar but the relative heights of the peaks vary greatly (Figures 7.14 to 7.71). This is well illustrated by Figures 7.102 to 7.112, which present hydrographs from the Warren 1 and the Cowlands on the same figure, and by Figures 7.113 to 7.116, which show the hydrographs of all three overland flow sites on the same figure.

The maximum flow during an event often occurred at an earlier time in the Warren 1 than the Cowlands (see Figure 7.103 for example). The greatest flow at the Warren 2 was recorded at the same peak as the maximum flow at the Cowlands during all events but one (event 19.3.1/19.3), during which it occurred at a later peak at the Warren 2 than at the Cowlands.

Plots of the cumulative percentages (in reference to the total overland flow per event and site) of overland flow at the Warren 1 and the Cowlands during the course of events allow the comparison of the hydrological response of the sites over time (Figures 7.73 to 7.86). To highlight the relative changes of the curves, the difference between the cumulative percentage curves was also graphed (cumulative percentage at the Warren 1 minus cumulative percentage at the Cowlands). Days of very low flow at the beginning or end of events at the Warren 1 were omitted from the calculations in order to make the data of the two sites more comparable. This affected events 5, 18 and 19. The last part of event 18 was furthermore split to correspond with event 18.4 at the Cowlands. The low flow days at the Warren 1 which occurred between events 18.3 and 18.4 at the Cowland were not considered. No plots were drawn up for events 7, 8 and 12 because the amounts of overland flow at the Cowlands during these events were extremely small.

The cumulative percentage curves for the Warren 1 and the Cowlands are quite similar for events 14, 18 and 21 (Figures 7.78, 7.82 and 7.85) and very similar for events 2 and 19 (Figures 7.73 and 7.84), but in general the figures for events 2, 9, 13-17, 18.1-3, 18.4, 19, 21 and 22 (Figures 7.73, 7.75, 7.77-7.86) establish a clear trend of stronger overland flow response at the Warren 1 than the Cowlands earlier on in rainfall events. The same essentially applies to event 1. However, during the first day of event 1, the Warren 1 and the Cowlands produced an equal percentage of their respective total overland flow volumes for the event (note open valve at Warren 1 towards end of event – see Table 7.2). The graphs of the difference between the cumulative percentage curves of all those events rise at first and peak during the first half of the events. Subsequently the curves of the difference show a general downward trend, which can be broken by small increases, until the cumulative percentage curves of the Cowlands catch up with (events 1 and 17) or cross (events 2, 9, 13 - 16, 18.1-3, 18.4, 19, 21 and 22) the curves of the Warren 1.

The flow pattern during event 5 (Figure 7.74) is similar to the pattern of the events described above but the peak difference between the cumulative percentage curves occurred during the second half of the event (note that the end of event 5 is re-drawn because of a failure of the chart recorder – see Table 7.2). During event 10 (Figure 7.76), the percentage flow curve of the Warren 1 starts off very slightly higher than that of the Cowlands but then it lies below the curve of the Cowlands until the difference between the curves reaches 0 at the end of the event.

The differences between the cumulative percentage curves of the Warren 1 and the Warren 2 (cumulative percentage of Warren 1 minus cumulative percentage of Warren 2) are small for events 18.4, 21 and 22 (Figures 7.88, 7.90 and 7.91). For the same events, the difference between the cumulative percentages of the Cowlands and the Warren 2 (cumulative percentage of Cowlands minus cumulative percentage of Warren 2) indicates that a greater proportion of overland flow was produced earlier on in the events at the Warren 2 than at the Cowlands. The cumulative percentage curves of overland flow during events 18.2-3 and 19 (Figures 7.87 and 7.89) at the Warren 1 and the Cowlands are quite similar but are very different to those at the Warren 2. The Warren 2 produced a much higher percentage of its overland flow of event 18.2-3 early on in the event. The difference between the Warren 2 and the other sites started to decrease on the day of the maximum rainfall of the event. During event 19 (i.e. events at the Warren 2 which correspond to event 19 at the Warren 1), the Warren 2 produced a comparatively small proportion of its overland flow during the first half of the event but a very large percentage in one day of the second half.

To further investigate the differences in the timing of flow from the sites, area adjusted flow curves of multi-peak events were drawn up (Figures 7.102 – 7.116). To produce these, flow values from the Cowlands and the Warren 2 were scaled by the ratio of the area of the Warren 1 to their area. Note that scaling was done for illustrative purposes only and that scaled hydrographs were not used for loading calculations. The figures of events 14 and 19 show similar area adjusted flow at the Warren 1 and the Cowlands. The general shapes of the hydrographs were also alike for events 9, 10, 15, 16 and 17, but the peaks at the Cowlands were smaller than those at the Warren 1. In the case of events 5, 13, 18, 21 and 22 mainly the first peaks were noticeably lower at the Cowlands and area adjusted flows were comparable at some later peaks. During events 7 and 8 very little overland flow was produced at the Cowlands. The curves for event 1 were atypical and at least partly influenced by the open valve at the Warren 1. In general, the area adjusted flow from the Warren 2 was similar to flow from the Warren 1. However, some excessively high flow peaks occurred during event 19 at the Warren 2.

Seasonal Patterns

A maximum (in reference to the monitoring period) monthly rainfall of 288.4 mm rain fell in August 1997 and a minimum of 16.3 mm in March 1997. The overland flow maxima at the Warren 1 and the Cowlands coincided with the peak rainfall in August 1997. The rainfall and overland flow values measured for the same months in successive years differed. January rainfall, for example, amounted to 32.6 mm in 1997 and 177.2 mm in 1998. In January 1997, there was no overland flow from either of the sites, whereas 124.8 mm ran off the Cowlands and 188.1 mm off the Warren 1 in January 1998 (Figure 7.9).

Monthly and yearly differences were not only found in the absolute amount of overland flow but also in its percentage of the rainfall. The highest percentages occurred in January 1998 at all sites. Overland flow amounted to 70.4, 106.1 and 134.4 % of rainfall at the Cowlands, the Warren 1 and 2 respectively. Two months later, in March 1998, those figures had changed to 31.8, 64.8 and 64.1% (Figure 7.92). Plots of the percentages of monthly rainfall which became overland flow at the Warren 1 and the Cowlands reveal that the percentages tended to increase with rainfall at both sites (Figures 7.93 and 7.94). The correlation (Pearson Product-Moment Correlation) between the two parameters was stronger at the Warren 1 (R^2 of 66.6%, $p<0.0001$) than the Cowlands (R^2 of 53.0%, $p<0.0014$). To include more climatic variables into the comparison, the potential evapotranspiration (PE, evapotranspiration at unlimited availability of water) was subtracted from the rainfall (net rainfall). The percentages of overland flow of the rainfall were then related to estimated net rainfall (Figures 7.95 and 7.96). The R^2 of the correlations between the two variables were 73.1% ($p<0.0001$) for the Warren 1 and 68.9% ($p<0.0001$) for the Cowlands. The amount of net rainfall was often exceeded by the amount of overland flow at the Warren 1 but not at the Cowlands (Figures 7.97 and 7.98). In July 1997 overland flow occurred at the Warren 1 despite the fact that monthly potential evapotranspiration was greater than monthly rainfall.

Overland flow and Water Table Levels

The water level in tubes with high ground water levels (B2 at the Cowlands, B4 and C2 at the Warren 1 and tube 2 at the Warren 2) and the negative soil moisture deficit calculated according to the model of Brereton and Hope-Cawdery (1988) were compared with the occurrence of overland flow and rainfall (Figures 7.99-7.103).

The water level in either tube B4 or tube C2 normally reached the surface during overland flow events at the Warren 1. Just in connection with the event which started at the end of October 1997 (event 18), the groundwater levels reached the surface with a few days delay. Only during events in May and June 1997 (events 7-10.2), the water levels recorded in tube B2 at the Cowlands were not at ground level when measured while overland flow occurred. However, Figures 4.13-4.15 show that, during those events, the water levels in other tubes in that field (A2, B1, B3, E2 and E3) came close to or reached the surface. Measurements taken during events at the Warren 2 always showed the water levels in tube 2 to be at or near the soil surface.

As could be expected from the similarity between the negative SMD and water table levels (see Section 4.4.4), the negative SMD nearly always became zero when water table levels reached the ground surface.

7.3.2 Phosphorus Concentrations in Overland Flow

Differences between the Sites

The minimum, maximum and flow-weighted averages of the DRP concentrations of the overland flow events are displayed in Figure 7.117 for the Warren 1, Figure 7.118 for the Cowlands and Figure 7.119 for the Warren 2. Note that some of the concentrations during events 12, 13 and 19 were calculated from the TDP levels (see Table 7.2 and Section 5.2.3).

Table 7.3 summarises some of the information displayed in Figures 7.117 to 7.119. For each site it shows the ranges of the maximum DRP levels and of the flow-weighted average DRP concentrations measured. For the Warren 1 and the Cowlands the ranges are given for all events with two or more samples, over the 16 months monitoring period. For all three sites Table 7.3 lists the ranges of above mentioned parameters for all events with two or more samples, over the monitoring period at the Warren 2. The high maximum DRP concentrations in samples from the Warren 1, which were taken at the beginning of event 18, were probably due to dirt that had accumulated in the drain at that site. These results were therefore not likely to be a true representation of the maximum DRP concentrations in overland flow at the Warren 1. They were therefore not considered when working out the maximum DRP concentration for event 18 (Figure 7.117). Table 7.3 shows the highest of these excessive values in brackets but lists the maximum DRP level otherwise achieved as the upper range of the maximum DRP concentrations from the Warren 1. However, the dirt in the drain was only a presumed reason for the high DRP levels at the beginning of event 18. To ensure that the P concentrations and P exports in overland flow from the Warren 1 were not underestimated, the high DRP data of event 18 were not excluded when calculating the flow-weighted average DRP concentration and the P export (Section 7.3.4) for event 18.

The Figures 7.117 to 7.119 demonstrate clearly that the Warren 1 normally delivered the lowest minimum DRP concentrations. The lowest DRP minima measured at that site were below detection (<0.005 mg P/l). Such low values occurred during events 1, 10, 18 and 22. The minima measured during corresponding events at the Cowlands amounted to 0.130, 0.650, 0.315 and 0.095 mg P/l. Events comparable to 18 and 22 were also monitored at the Warren 2, and DRP minima of 0.012 and 0.084 mg P/l were recorded.

Figures 7.117 to 7.119 and Table 7.3 illustrate furthermore that the maxima and flow-weighted averages of DRP concentrations of comparable events were generally highest in overland flow

from the Cowlands and lowest in overland flow from the Warren 1. The flow-weighted average DRP concentration at the Cowlands was higher than 0.3 mg P/l during all but three events. The flow-weighted average DRP concentrations at the Warren 1, on the other hand, only exceeded 0.3 mg P/l for events 12, 15 and 20. Event 20 consisted of just one sample.
Speculative figures for yearly average flow-weighted DRP concentrations at the Warren 1 and the Cowlands can be obtained by dividing the yearly amount of overland flow (calculated in Section 7.3.1) at each site by the yearly DRP export (calculated in Section 7.3.4) from each site. The outcomes of these divisions are yearly average flow-weighted DRP concentrations of 0.090 mg P/l and 1.076 mg P/l for the Warren 1 and the Cowlands respectively.

The pattern of increasing DRP minima, maxima and flow-weighted average concentrations from the Warren 1 to the Warren 2 and the Cowlands, which was only broken during the last recorded event (event 22: 24th to 31st March 1998), was also apparent in the TDP and TP data (Figures 7.16-7.35 and 7.37-7.71). During event 22, the highest maximum DRP and TP concentrations were found in samples from the Warren 1 and the lowest maximum DRP, TDP and TP concentrations in samples from the Cowlands. Furthermore, the flow-weighted average DRP concentrations were higher in overland flow from the Warren 2 than from the Cowlands for that event.

Table 7.3: The range of flow-weighted average and maximum DRP concentrations at the Warren 1, the Cowlands and the Warren 2.

	Warren 1	Cowlands	Warren 2
Range of flow-weighted average DRP concentrations 24th Nov. 96 to 31st Mar. 98 (mg P/l)	0.013 to 1.050	0.122 to 5.102	
Range of maximum DRP concentrations 24th Nov. 96 to 31st Mar. 98 (mg P/l)	0.048 to 1.385 (2.960*)	0.173 to 6.852	
Range of flow-weighted average DRP concentrations 8th Nov. 97 to 31st Mar. 98 (mg P/l)	0.013 to 0.049	0.122 to 0.697	0.050 to 0.208
Range of maximum DRP concentrations 8th Nov. 97 to 31st Mar. 98 (mg P/l)	0.048 to 0.471	0.173 to 0.721	0.078 to 0.324

*Highest of the excessive values presumably due to dirty drain

P Concentrations throughout the monitoring periods

Figures 7.117-7.119 and the graphs of the overland flow events (Figures 7.17–7.71) show that in overland flow from each site, an enormous range of P concentrations was measured during the monitoring periods. For example, the highest flow-weighted average DRP concentration measured at the Warren 1 occurred during event 12. This flow-weighted average concentration was more than 90 times greater than the lowest flow-weighted average DRP concentration determined at that site. In overland flow from the Cowlands the maximum flow-weighted average DRP level was over 40 times higher than the minimum value. For the shorter period during which the Warren 2 was also monitored, the maximum flow-weighted average DRP concentrations were in excess of 3, 5 and 4 times greater than the minimum flow-weighted average DRP levels at the Warren 1, the Warren 2 and the Cowlands, respectively.

The P concentrations of samples taken during all events monitored are graphed in Figure 7.120 for the Warren 1, Figure 7.121 for the Cowlands and Figure 7.122 for the Warren 2. The start of each event is indicated in these figures. The length of the periods separating events is indicated by the gap between the date of the last P concentration of one event and the marker for the start day of the next event. Figures 7.120 and 7.121 suggest the possibility of some seasonal trends in the DRP concentrations at the Warren 1 and the Cowlands. The DRP levels at the Cowlands tended to be higher for the period May 1997 to middle of November 1997 than for the rest of the monitoring period. The concentrations furthermore, generally increased from May to the end of August and then dropped again. The minimum DRP concentrations at the Cowlands (shown in Figure 7.118) also offer some evidence of seasonality. They consistently exceeded 0.5 mg P/l between mid June 1997 and early November 1997, and were always lower than 0.5 mg P/l for the rest of the monitoring dates. The possibility of a seasonal trend in P concentrations of overland flow is less clear at the Warren 1, and not confirmed by a pattern in the minimum P concentrations (Figure 7.117). Still, DRP concentrations were more likely to be high in November to late December 1996, April to early November 1997 and late March 1998 than for other sampling dates.

Generally the trends of TDP and TP concentrations at the two sites were very similar to those described for the DRP levels. However, the difference between DRP and the other parameters was greater than usual on 23rd and on 24th August 1997 at the Cowlands (Figure 7.121) and, less noticeably, on 20th to 24th August and on 19th September 1997 at the Warren 1 (Figure 7.120).

The monitoring period at the Warren 2 was a year shorter than the one at the Warren 1 and the Cowlands. Figure 7.122 shows that, at the beginning of November 1997 and the end of March 1998, the P concentrations in overland flow from the Warren 2 tended to be higher than during the rest of the monitoring period. The difference between DRP and TDP levels was generally greater

during November 1997 than during December 1997-March 1998. The TP levels were often considerably higher than the DRP and TDP concentrations.

P Concentrations in Overland Flow During the Course of Events

Figures 7.17 to 7.35, 7.36 to 7.61 and 7.62 to 7.71 display the hydro- and chemographs for the overland flow events at the Warren 1, the Cowlands and the Warren 2 respectively. These figures and Figures 7.117-7.119, which summarise the data, document that at each site, the P levels in overland flow during the events varied considerably.

To compare the variability of the measured DRP levels between events and sites, the ratios of the maximum and minimum DRP concentrations per event were worked out for all events at each site (Figures 7.123-7.125). This ratio between the minimum and the maximum DRP value was usually between 1 and 3 at the Cowlands (Figure 7.123). During events 1, 9.2, 13, 14.1 and 21, however, the ratio exceeded 3 considerably. The maximum rates of flow achieved during the first three of these events were also greater than those of other events between November 1996 and the middle of August 1997. The maximum flow rates of events 14.1 and 21, however, were not exceptional in comparison with the rates realized in neighbouring events. Moreover, high maximum flow rates during events 18.3 and 19.3 did not coincide with ratios between maximum and minimum DRP concentrations which were in excess of 3. The ratios of maximum to minimum DRP concentrations achieved at the Warren 1 and 2 were much greater and more variable than those calculated for the Cowlands (Figures 7.124 and 7.125). There was no obvious pattern in the relationship between the maximum flow per event and the ratios of maximum to minimum DRP levels at the Warren 1 or 2.

During most events, at all sites, there was a resemblance of the flow and the P concentration curves, but also a lack of a clear, strong, direct relationship between flow and concentrations. The highest P concentrations at the Warren 1 often coincided with the first flow peak of an event, or the first peak at least gave rise to proportionately higher P concentrations than later peaks (Figures 7.18, 7.20-7.23, 7.26-7.32). The elevated P levels at the beginning of events at the Warren 1 also show up in Figure 7.120, whereas Figures 7.121 and 7.122 suggest similar but less distinct tendencies for the Cowlands and the Warren 2. Figures of the events at the Cowlands and Warren 2 illustrate that the P-to-rate of flow ratio at these sites was usually higher at the beginning than at the end of events (Figures 7.36, 7.38, 7.39, 7.42, 7.47, 7.49, 7.51, 7.56, 7.57, 7.61 and 7.62 - 7.67, 7.70) but the effect was not as distinct as that at the Warren 1.

Relationships between Flow and P Concentrations

To find out whether there was a clear correlation between the rates of overland flow and the P contents of it, the TP, TDP and DRP levels measured in samples from a site were plotted against the rate of flow at the time of sampling. A separate graph was drawn up for each of the three overland flow sites. Two samples taken at the Warren 2 during very high flow 8th and 13th January 1998 were omitted from the relevant figure so that the scale of the graph could be chosen to show the remaining data with an acceptable degree of resolution. The omitted data are displayed in Figures 7.67 and 7.68, which show the events during which the samples in question were taken (events 19.3.1 and 19.3.2)

The scatterplots of the flow and P data for each site revealed no strong relationships (Figures 7.126–7.128). Scatterplots of P concentrations against flow were then drawn up for every single event. Figure 7.129 is an example. No clear patterns became apparent in plots from the Warren 1 and the Cowlands. The only clearly recognisable trend was that the minimum concentration of an event tended to occur at very low flow. The above assessment applied to most data from the Warren 2. However, Figure 7.129 illustrates that there was a slight but recognisable general trend for the TP levels to increase with rising rates of flow during event 18.2. Note though that the maximum TP concentration was measured at a very low rate of flow. The DRP and TDP values in Figure 7.129 follow the common pattern of the minimum concentrations to coincide with low values for the rate of flow.

Springs

As groundwater from springs is thought to have contributed to overland flow at the Warren 1 and 2 during prolonged and heavy rainfall events (see Section 7.4.1), the possibility of P inputs to those sites via groundwater was investigated. Both springs were caught in subsurface drains and a mixture of subsurface drainage and spring water could, therefore, be sampled. The subsurface drain outlet pipe at the Warren 2 was difficult to sample due to site constraints. Grab samples were, therefore, taken on only two occasions. Furthermore, sampling was only possible at very high flows. Samples taken under such conditions contain a high proportion of subsurface drainage water and can give little information about the P contents of the spring water. However, the P concentrations measured in the samples from the outlet pipe at the Warren 2 were low despite the considerable subsurface drainage water contribution.

At the Warren 1, 63 of the 81 spring/subsurface water samples analysed for DRP, 33 out of 48 and 26 out of 45 samples analysed for TDP and TP, respectively, were below the limit of detection. Whenever P was present, it was mainly at low levels (Appendix 2).

7.3.3 Other Water Quality Parameters in Overland Flow and Their Relationship to P

In addition to P, overland flow samples were also analysed for total oxidised nitrogen (TON), total ammonia (TA), potassium (K) and conductivity. Suspended solids (ss) were measured on a subset of samples (Section 5.1.2). Furthermore, the usefulness of pH and turbidity measurements was explored and these results were presented and discussed in Sections 5.3.4 and 5.4.3. The TON and TA information for the Warren 1, the Cowlands and the Warren 2 is compiled in Figures 7.130-7.132, the K data for the three sites in Figures 7.133-7.135, the conductivity values in Figures 7.136-7.138 and the levels of suspended solids in Figures 7.139-7.141. Note that whenever DRP analyses could not be carried out (Section 5.2.3) TON and TA were not measured either. Values for those parameters are therefore missing 29th July to 7th August 1997 and 23rd December 1997 to 1st January 1998.

As was the case with P concentrations, the levels of the other water quality parameters often varied considerably during events. The TON levels were normally low (below 4 mg N/l) at all sites but higher concentrations occurred during several events (Figures 7.130–7.132). Some of the concentrations of events 7 and 8 (9/10th May, 18/19th May) at the Cowlands were very high and the maximum TON level measured during these events amounted to 49.3 mg N/l. Two smaller peaks with maximum values of 8.3 and 9.9 mg N/l occurred on 5/6th June and 20th August during events 9.1 and 14.1 respectively. The maximum TON concentrations in overland flow from the sites at the Warren did not exceed 10 mg N/l, and the TON concentrations at the Warren 2 were below the limit of detection for all events but 22.1 and 22.2. On 29th March (event 22.2) the maximum value of 4.8 mg N/l was measured. The TON data from the Warren 1 contains several peaks (Figure 7.130). The main ones occurred during events 1, 5, 6, 9, 15, 18 and 20.

The TA concentrations at the sites at the Warren were commonly below 1 mg N/l and the TA levels at the Cowlands below 5 mg N/l. Higher concentrations occurred during several events though. Exceptionally high TA levels were measured during events 7, 8, 14.1 and 21 at the Cowlands, events 15, 18 and 20 at the Warren 1 and events 22.1 and 22.2 at the Warren 2.

The K concentrations at the Cowlands tended to reach higher levels than those at the Warren 1. Concentrations in excess of 20 mg K/l at the Warren 1 and 30 mg K/l at the Cowlands were measured more commonly in August to October and May to October respectively than during the rest of the monitoring period. The main K peaks occurred during events 12, 15 and 18 at the Warren 1 and during event 14.1 at the Cowlands. The K levels at the Warren 2 were of the same

order of magnitude as those at the Warren 1. They decreased from event 18.3 to event 21 but reached higher levels again during event 22.1.

The conductivity values at the Cowlands and the Warren 2 usually ranged between 200 and 400 µS/cm but maximum values of 760 µS/cm on 20th August 1997 and 628 µS/cm on 25th March 1998 respectively were measured at the two sites. Conductivity in samples from the Warren 1 (Figure 7.136) was normally between 100 and 300 µS/cm and reached a maximum value of 1199 µS/cm on 29th July 1997 (event 12).

The suspended solids amounted to less than 50 mg/l in most samples from the Cowlands and the Warren 1 but considerably higher values occurred at both sites (Figures 7.139 and 7.140). The maximum value measured at the Warren 1 was about double that found at the Cowlands. The suspended solids levels at the Warren 2 were generally higher than those measured at the other sites (Figure 7.141).

Generally the correlations between P and other water quality variables were very weak. The clearest trends are described below. Figures 7.142 to 7.145 show that there were positive relationships between DRP and K and DRP and ss at the Warren 1 and the Cowlands. At the Warren 2, the TA levels were found to have increased with DRP levels (Figure 7.146). Note that this relationship is only documented for the last two events because the TA levels of all other events at this site were below the limit of detection.

7.3.4 Phosphorus Export in Overland Flow

The DRP and TDP exports in overland flow that occurred during the two monitoring periods at the three sites are summarised in Table 7.4. The TDP exports were calculated using the equations described in Section 5.3.3 and discussed in Section 5.4.2.

The DRP and TDP exports measured during the 493 days of monitoring at the Warren 1 and the Cowlands were much lower at the former than the latter site. For the 144 days during which all three sites were monitored, DRP and TDP exports in overland flow were greatest at the high soil P site (Cowlands), intermediate at the medium soil P site (Warren 2) and lowest at the low soil P site (Warren 1).

The annual DRP losses in overland flow from the Warren 1 and the Cowlands were calculated as follows: Annual DRP loss = (DRP loss Dec 96 + DRP loss Dec 97)/2 + (DRP loss Jan 97 + DRP loss Jan 98)/2 + (DRP loss Feb 97 + DRP loss Feb 98)/2 + (DRP loss March 97 + DRP loss March

98)/2 + DRP loss April 97 + DRP loss May 97 + DRP loss June 97 + DRP loss July 97 + DRP loss Aug 97 + DRP loss Sept 97 + DRP loss Oct 97 + DRP loss Nov 97. The annual DRP losses amounted to 698 g/ha at the Warren 1 and and 4,764 g/ha at the Cowlands.

Table 7.4: Amounts of TDP and DRP exported in overland flow from the Warren 1 and the Cowlands during the monitoring periods of 493 and 144 days, and from the Warren 2 during the monitoring period of 144 days.

Period of measurement	Warren 1		Cowlands		Warren 2	
	DRP	TDP	DRP	TDP	DRP	TDP
	(g/ha)					
24th Nov. 96 to 31st Mar. 98	778	867	5,299	6,556		
8th Nov. 97 to 31 Mar. 98	111	124	1,162	1,713	300	465

According to the regression equations of Section 5.3.3, the TP losses at the Warren 1 and the Cowlands are in the order of 23% (TP=100%) higher than the TDP exports. Thus about 23% of the TP exports occurred in the form of particulate P (PP) at the Warren 1 and the Cowlands (see Section 5.4.2). This means that over the monitoring period of 493 days about 260 g/ha and 1,967 g/ha PP was lost in overland flow from the Warren 1 and the Cowlands respectively.

As already suggested in Section 5.4.2, the majority of the dissolved P losses was reactive at all overland flow sites, but the organic and condensed P fraction made up a greater proportion of the dissolved P losses at the Warren 1 than at the Cowlands. Calculated by subtracting DRP from TDP exports (see Section 5.1.1) the dissolved organic and condensed P lost amounted to 89 g/ha at the Warren 1 and to 1,257 g/ha at the Cowlands over the monitoring period 24th November 1996 to 31st March 1998. Thus dissolved organic and condensed P made up just over 10% of the total dissolved P export at the Warren 1 and about 19% of the total dissolved P losses at the Cowlands.

At the Warren 2, the relationship between TP and TDP was quite weak (see Section 5.3.3), suggesting that the TP exports may exceed TDP losses by about 38% (TP=100%). An approximate figure of 280 g/ha could therefore be taken as a rough estimate of the PP exports in overland flow from the Warren 2 during the 144 days of monitoring at that site.

The monthly DRP exports in overland flow from the three sites are shown in Figures 7.147 and 7.148. The maximum monthly DRP export in August 1997 at the Cowlands dwarfs exports during all other months and losses from the Warren 1 (Figure 7.147). August 1997 was also the month of maximum flow at the Cowlands but the value is similar to the amount of overland flow achieved in November 1997 and January 1998 (Figure 7.9). Furthermore, considerably more water ran off the

Warren 1 than the Cowlands in August 1997 but, reflecting the impact of the relative magnitude of the DRP concentrations, the DRP exports from the Cowlands were still much greater than those from the Warren 1.

The effect of high DRP concentrations on export figures also becomes apparent in Figures 7.149 and 7.150, which show a comparison of the cumulative daily flow and the cumulative daily DRP export curves for the Warren 1 and the Cowlands respectively. The response of the DRP export curves of the Warren 1 and the Cowlands was much greater to the rise of cumulative flow at beginning of August 1997 than to a similar increase of flow at the end of December 1997/beginning of January 1998. At both sites, 41% of the total DRP exports of the 16 months monitoring period occurred between 3rd August and 10th August 1997.

Like the DRP concentrations, the DRP exports calculated for the Warren 2 were intermediate between those estimated for the Warren 1 and the Cowlands. This comparison can be seen in Figure 7.148.

7.4 Discussion

7.4.1 Occurrence and Quantity of Overland Flow

Overview of the Differences Between Sites

The monthly variation in rainfall was reflected in the monthly amounts of overland flow (Figure 7.9). The high variability of the yearly amounts of rainfall (Chapter 6) and the differences in overland flow measured during the same months of consecutive years suggest a considerable variation of the amounts of overland flow for different years. Thus, yearly values based on 16 months of monitoring may not be very meaningful as absolute figures, but they are very useful for comparative purposes.

The yearly amounts of overland flow from the Warren 1 were nearly double those measured at the Cowlands. This considerable difference in the ability of the sites to produce overland flow is further highlighted by the fact that overland flow from the Warren 1 exceeded flow from the Cowlands during all events and all but one month (Figure 7.9). As the flow at the Warren 1 in December 1996 is an underestimate because of the open valve in the tank at the Warren 1 towards the end of event 1 (Table 7.2), it is reasonable to assume that the monthly overland flow figure for the Warren 1 was always greater than the one for the Cowlands. Furthermore, overland flow occurred more frequently at the Warren 1 than the Cowlands, and the events at the former site were

generally of longer duration. Overall, the flow from the Warren 2 was intermediate but neither the monthly nor the daily values showed a consistent relationship with those of the other two sites (Figure 7.10).

On a yearly basis, 62% of the rainfall became overland flow at the Warren 1, whereas the flow from the Cowlands amounted to 36% of rainfall. The figure for the Cowlands compares well to the 35% of quickflow, which was largely made up by overland flow, measured in a New Zealand pasture catchment (McColl et al., 1985). The % overland flow measured at the Warren 1 was very high yet similar figures were worked out for wet grassland areas in North Wyke in Devon, UK (Misselbrook et al., 1995). At that site overland flow from October to February and from February to March made up 62% and 84% of rainfall.

Mechanisms of Overland Flow Production

The trends of the daily flow values were similar at the Warren 1 and the Cowlands (Figure 7.11). This indicates that overall, the response of the two sites to changing weather conditions was comparable. The distribution of overland flow during the course of the events, on the other hand, highlights the hydrological differences between the sites (Figures 7.72-7.91). In comparison with the Warren 1, the beginning of events was generally less important for the overall flow production at the Cowlands, and the height of early peaks was often stunted. Events characterised by unexpectedly low early peaks or low total flow values at the Cowlands and events that produced overland flow at the Warren 1 but not the Cowlands were either preceded by low water table levels at that site or by high SMD figures (used where no water table measurements were available) (Figures 7.99 and 7.100). The above suggests that the water table levels were the main factor controlling the occurrence of overland flow at the Cowlands and the Warren 1. The importance of soil moisture status for the conversion of rain into overland flow has been recognised (Armstrong and Garwood, 1991; Misselbrook et al., 1995), and the aforementioned interpretation of data from this study is further supported by the fact that the SMD normally approximated zero and the water table levels usually reached the soil surface in some areas of the Cowlands, the Warren 1 and the Warren 2 when overland flow occurred. Consistent with the importance of the water table levels for overland flow production is the observation that the mean water table levels were higher at the Warren 1 than the site at the Cowlands (Section 4.4.4), which also produced consistently less overland flow.

Saturation excess overland flow can thus be assumed to represent the main mechanism of overland flow production at the study sites. Still, the low infiltration capacities measured at all overland flow sites (Section 4.4.2) suggest that infiltration excess overland flow was also likely to occur.

The prevalence of saturation excess over infiltration excess overland flow in agricultural grassland of humid temperate climate zones was also observed by Cooke and Dons (1988), Armstrong and Garwood (1991) and McColl et al. (1985).

Return flow is furthermore strongly suspected to have contributed to the overland flow measured at the Warren 2, and possibly also the Warren 1, during extended, very wet periods. In comparison with flows recorded at the Warren 1 and the Cowlands, the Warren 2 gave rise to exceptionally high flow peaks during events between 1st and 13th January 1998 (events 19.3.1 and 19.3.2) (Figure 7.114). These exceptional peaks came about at the time when the highest percentages of overland flow, relative to rainfall, were achieved at all sites. During this period of very wet weather, the water levels at the Warren 2 were at or near the soil surface and there was no SMD (Figure 7.101). This, in combination with the fact that the daily overland flow values at that time exceeded the amounts of daily rainfall, suggests that return flow occurred at the Warren 2. During very wet weather, the subsurface drain leading the water from the spring to the open drain at the right-hand (upstream facing) side of the site must have been overcharged and spring water, which is likely to have been made up of groundwater from outside the study area, reached the surface and contributed to the overland flow. At the Warren 1, overland flow slightly exceeded rainfall during event 19. Thus, small amounts of return flow from the spring may also have happened at that site. Alternatively, the amounts of excess overland flow at the Warren 1 were small enough to be explained by the possibility that standard Met Eireann rain gauges can underestimate rainfall by up to 8% (Rodda, 1967).

When considering overland flow production in the light of the detailed water table level information described in Sections 4.4.4 and 7.3.1, it becomes clear that not only were saturation excess overland flow and return flow the most important types at our sites but their occurrence was, furthermore, highly variable between sites (see above) and within sites. The intra site variation of the production of saturation excess overland flow is suggested by the variations of water table levels within each site (Sections 4.4.4 and 7.3.1). As the saturated areas shrank and expanded according to environmental conditions, the overland flow contributing areas within each site must have varied greatly between events (McColl et al., 1985; Pionke et al., 1988).

Hydrology of the Sites Throughout the Monitoring Period

The maximum rates of flow during very wet periods were comparable at the Warren 1 and the Cowlands but, as discussed in the previous section, more rain was often necessary to bring the water table to the soil surface and initiate overland flow at the latter site. This observation may explain the fact that the relationship between monthly rainfall and percentage overland flow was

stronger at the Warren 1 than the Cowlands, which means that the amount of rainfall accounted for a greater proportion of the monthly variability of the overland flow to rainfall ratio at the Warren 1 than at the Cowlands. There is an improved relationship when net monthly rainfall (rain minus potential evapotranspiration) rather than rainfall is plotted against percentage overland flow (relative to monthly rainfall) (Figures 7.93-7.96). This is due to the fact that the net rainfall data allows for the variable amount of rainwater which is returned to the atmosphere and is, therefore, not available for overland flow. The rainfall adjustment was most important during the warm summer months when evapotranspiration figures were elevated.

An interesting point is that, at the Cowlands, there was a greater increase in the strength of the correlation (+15.9%) when net rainfall rather than gross rainfall was related to the percentage overland flow than at the Warren 1 (+6.5%) (see Section 7.3.1). It seems that the evapotranspiration measurement originating from the lysimeter at the weather station at Johnstown Castle was a better estimate of the evapotranspiration at the Cowlands than the Warren 1. The look of the vegetation at the sites confirmed this assumption. The sward at the lysimeter is kept at a height of about 5 cm and contains only grasses. It is more similar to the regularly grazed high productivity grassland at the Cowlands than the rush infested rough grassland at the Warren 1, and the more comparable the vegetated surfaces are, the closer the evapotranspiration from them is likely to be. The fact that the amount of monthly overland flow at the Warren 1 was often greater than the net rainfall value (Figure 7.97) may also suggest that the evapontranspiration estimate based on lysimeter measurements was an overestimate for the area of rough pasture. The occurrence of return flow offers another explanation for excess monthly overland flow. Return flow at the Warren 1 is only thought to occur after prolonged wet periods (see above). Thus, return flow may have contributed to most instances of monthly overland flow exceeding monthly net rainfall, but return flow is very unlikely to have given rise to the excess overland flow in May 1997.

Even though the relationship between monthly rainfall and percentage overland flow at the Cowlands improved greatly after being adjusted for evapotranspiration, it was still weaker than the relationship at the Warren 1. This implies that a source of variability other than evapotranspiration had a greater effect on the response of the land to rainfall at the Cowlands than the Warren 1. As the overland flow/rainfall relationship was higher at the Warren 1 than the Cowlands, the other source of variability must be a water loss, like evapotranspiration. The greater importance of the export of water via subsurface drainage from the Cowlands than from the Warren 1 is a plausible explanation for the differences in the monthly rainfall to percentage overland flow relationships at the two sites. Thus, the lower water table at the Cowlands was probably due to differences in evapotranspiration and drainage from the sites.

Management and Overland Flow

The above discussion shows that the variable amounts of overland flow produced at the Warren 1 and the Cowlands were mainly due to differences in water table levels. These are partly governed by site characteristics but, in comparison with the rough grassland at the Warren 1, the high productivity sward at the Cowlands was likely to lead to higher evaporative losses and, therefore, lower water table levels.

It can therefore be argued that, in this study, the more intensive management may have led to a decrease in overland flow production. Increased grazing pressure can augment the occurrence of overland flow (Heathwaite et al., 1989). As grazing animals can cause compaction and/or sealing of the topsoil and thus a lowering of infiltration rates (McColl et al., 1985), they would mainly impact the infiltration excess type of overland flow. Such an effect was not perceptible at the grazing pressures and under the environmental conditions prevalent at our sites during the overland flow monitoring period. The infiltration measurements discussed in Section 4.4.2 suggest though that compaction may have affected the topsoil infiltration rates at the Cowlands during the summer after the end of the monitoring of overland flow (summer 1998).

7.4.2 P Concentration in Overland Flow

Land as a Diffuse Source of P

In comparison with the DRP concentrations in rainwater, which are presented in Chapter 6, overland flow from even the site characterised by the lowest concentrations (Warren 1) was clearly enriched with DRP. The difference of TDP/TP concentrations between rain and overland flow was less pronounced than in the case of DRP. Still, on all but two occasions (first days of events 8 and 19), the TDP and TP concentrations in overland flow from the Warren 1 were typically greater than those in rainwater. All P fractions were invariably higher in overland flow from the Warren 2 and the Cowlands than in rainwater.

There are some indications that, much like rainwater that had been turned into overland flow, groundwater surfacing as return flow at the site(s) in the Warren may also have acquired P due to its interactions with the surface of the field(s). Despite the negligible amounts of P measured in spring water at the Warren, the P concentrations in overland flow during times which may have been dominated by return flow were comparable with the P concentrations in samples taken adjacent to those periods (Figures 7.67 and 7.68).

The above shows that the results of this study offer strong evidence for the occurrence of P transfer from land to overland flow. Compared with the P levels usually found in e.g. lakes (McGarrigle et al., 2002), the concentrations measured at all sites were high at times. The flow-weighted average DRP concentrations at the low soil P site (Warren 1) ranged from 0.013 mg P/l to 1.050 mg P/l (Table 7.3). Thus, even the DRP levels at the low soil P site were commonly above the median TRP value of 0.015 mg P/l, which is thought to indicate unpolluted conditions in rivers (Government Supplies Agency, 1998). However, P concentrations in overland flow are normally not equal to P levels in rivers and streams. For one thing, overland flow only occurs intermittently and thus does not represent a continuous P input to the water bodies. Moreover, even during storm flow conditions, river water usually consists of a mix of subsurface water, which is often low in P (Pionke et al., 1988), and overland flow (Pionke et al., 1986; 1988). Overland flow will therefore be diluted and the P level in the water body will be lower than the values measured in overland flow.

Dilution in streams may, however, not always have a sufficiently lowering effect on P concentrations in overland flow as high as those measured at the Cowlands. The maximum DRP concentrations in overland flow at the high soil P site (Figure 7.118) were comparable with the lower range of the annual average TRP concentrations measured in the discharge from a sewage treatment plant without P removal (McGarrigle et al., 1993). Furthermore, the flow-weighted average DRP levels during summer and early autumn events at the Cowlands always exceeded 1 mg P/l. This approximately converts to a TP concentration of 1.6 mg P/l – a figure which is comparable with the standards set for discharges from urban waste water treatment plants to sensitive waters (CEC, 1991). Hence TP concentrations during summer and early autumn events at the high soil P site often exceeded the requirements set down for effluent of wastewater treatment plants. DRP concentrations in excess of 1 mg P/l were also measured for intensively farmed grassland areas in other countries (Dils and Heathwaite, 1996; Nash et al., 2000).

The mean yearly DRP concentration (calculated by dividing yearly export by yearly flow) of 0.090 mg P/l at the Warren 1 was equal to the median DRP in overland flow from unfertilised grassland (Pionke et al., 1988). Further, the DRP levels measured in overland flow from unfertilised native grassland, were at the lower end of the range of average flow-weighted DRP concentrations at the Warren 1 (Figure 7.117) (Sharpley and Smith, 1990; 1992).

Management Influences on P Levels in Overland Flow

Because of the interrelatedness of land-related agricultural sources of P in overland flow, the fact that, for all but the last recorded event, the DRP, TDP and TP concentrations unmistakeably

increased from the Warren 1 to the Warren 2 to the Cowlands (Figures 7.117-7.119) is not unambiguously attributable to one factor alone. The most obvious difference between the overland flow sites was the soil P level, and it rose in the same order as the P concentrations in overland flow. However, the higher the soil P levels, the greater the P concentrations in herbage are reported to be, and the P contents in grass in turn can have a bearing on P excreted by grazing animals (Haynes and Williams, 1992). It can be said though that the differences in P concentrations of overland flow from the three sites were highly likely to be due to soil P status and/or to factors related to the soil P levels (e.g. P in dead and live organic matter).

Pote et al. (1996) describe linear relationships for soil P levels (various tests) and DRP measured in overland flow produced from artificial rainfall. Due to the similarity between Morgan's P and P extracted by water, approximate water extractable soil P values on a weight basis can be estimated from the 2 cm samples taken at the Warren 1 and the Cowlands (bulk density assumed to be about 0.8 kg/l (Daly, 1999)). When used in Pote's equation describing the relationship between soil P extracted by water and DRP in overland flow, the mean DRP concentrations for the Warren 1 and the Cowlands come out as 0.191 and 0.458 mg P/l respectively. For both sites, the calculated concentration is within the range of flow-weighted average DRP concentrations achieved during single events. However, this is probably more a reflection of the wide scatter of concentrations achieved at a site than of the applicability of Pote's formula. The calculated values are quite different from the mean yearly concentrations of 0.090 mg P/l at the Warren 1 and 1.076 mg P/l at the Cowlands (Section 7.3.2). More importantly, the regression model underestimates the ratio of DRP Cowlands : DRP Warren 1 considerably. During comparable events this ratio was normally at least double the value of 2.4, which is the ratio of DRP Cowlands : DRP Warren 1 predicted using Pote's equation (Figures 7.117 and 7.118), and overall it amounted to nearly 12. This lack of agreement is not surprising considering that the relationship between soil P and DRP in overland flow was shown to vary according to soil properties and hydrology (Daniel et al., 1993; Sharpley et al., 1977) and soil type (McDowell and Sharpley, 2001; 2002; Pote et al., 1999; Sharpley, 1995), and also that the regression model was based on rainfall simulation experiments and applied to data from natural events (Cox and Hendricks, 2000).

There is of course also a connection between fertiliser applications and the P levels of a site. The land use and the organic and inorganic fertiliser applications at the overland flow sites are summarised in Table 3.2. The high soil P site (Cowlands) received much more N and P than the low soil P site (Warren 1), to which no P was applied. P amounts comparable to those used at the Cowlands were added to the medium soil P site (Warren 2) in slurry (Table 3.2) but N usage was again higher at the Cowlands. High P concentrations in overland flow due to fertiliser applications have been measured in several studies (Austin et al., 1996; Baker and Laflen, 1982; Cooke, 1988;

Nash et al., 2000) (see Sections 2.5.1 and 2.5.3). The effect is usually greatest during events shortly after the fertilisation (Burke et al., 1974; McColl, 1979), but it was reported to still be noticeable several months later (Powell and Taylor, 1979; Sharpley and Syers, 1976). There was really only one occasion where a short-term increase of the P concentrations in overland flow due to P fertiliser applications could have been observed. This was during the overland flow event following P fertilisation at the Cowlands (fertilisation 20th March 1997). Overland flow of event 7 was, however, not characterised by exceptionally high P levels (Figure 7.118). On the contrary, at the Cowlands there was a general trend for the P concentrations in overland flow to increase gradually from May 1997 to the end of August 1997 (Figure 7.121). It is likely that the short-term effect of P fertilisation was not detectable because event 7 started as much as 44 days after the fertiliser application. The results of this study suggest that the long-term effect of P fertilisation occurred via the soil. That is to say that the fertiliser P was incorporated into the soil P pool and its availability was then governed by the circumstances which generally affect P release from soil. As the P levels at the Cowlands were high, it is likely that fertiliser P mainly enhanced the labile soil P pool (Holford and Mattingly, 1976; Leinweber et al., 1999; Ogaard, 1996) in the short term, and thus ensured P to be readily available to plants and overland flow.

An increase in TA and TON in overland flow very shortly after Calcium Ammonium Nitrate (CAN) application was measured during events 7 and 8 at the Cowlands. Overland flow events occurring a few days after urea applications at the Cowlands (event 21) and the Warren 2 (event 22.1) were distinguished by excessively high TA levels at these two sites (Figures 7.130 and 7.132). These responses to N fertilisation are much in line with findings of other studies (Baker and Laflen, 1982). It is furthermore possible though that the urea application at the Cowlands effected a lowering of P concentrations in the overland flow of event 22 (Figure 7.61), which occurred 24th March 1998 to 30th March 1998. This event started 19 days after urea fertilisation. It was characterised by low P levels in overland flow from the Cowlands both in absolute (lowest maximum P concentrations for the monitoring period at that site) terms and when compared to the P concentrations measured at the sites at the Warren (Figures 7.117 and 7.118). The urea application at the Cowlands may have led to a growth response, which depleted the available soil P pool. This theory is backed by the fact that the potassium concentrations in samples from the Cowlands for this event were also depressed in relative and absolute terms (Figures 7.133 and 7.134). In his study of overland flow from sheep pasture, McColl (1979) also considers plant uptake responsible for low nutrient levels in overland flow in springtime.

The high TA concentrations of event 22.1 at the Warren 2 concur with the highest minimum, maximum and flow-weighted average DRP concentrations measured at that site (Figure 7.132). The maximum DRP levels for event 22 at the Warren 1 were also quite high but the minimum and

flow-weighted average DRP concentrations were not (Figure 7.119). The elevated P concentrations in overland flow events which took place in late March 1998 may, thus, have been more pronounced for the Warren 2 than the Warren 1. Moreover, there was a clear linear relationship between rising TA and DRP levels at the Warren 2 during event 22.1 (Figure 7.146). However, correlation does not establish causation and both parameters could have risen in response to another factor. Hence, if there was an increase in P concentrations in overland flow due to urea fertilisation at the Warren 2, the effect was not very clear. Of interest is, however, the fact that exceptionally high P (i.e. TDP and TP, DRP results were missing) levels were achieved during the overland flow event following 2 days after a CAN and K application to the Warren 1 in July 1997 (event 12) (Figure 7.25). As K fertilisation has been shown to lead to high K concentrations in overland flow (Burke et al., 1974; McColl et al., 1975) and conductivity was greatly influenced by TA and TON concentrations (not measured for that event) at our sites, it is not surprising that the K and conductivity levels were also elevated (Figures 7.133 and 7.136). Note that the fact that event 12 occurred 13 days after the bullocks were removed from the Warren 1 (Table 3.2) may also have had implications on the nutrient concentrations in overland flow.

At the Cowlands, neither the urea applications in March 1997 and 1998, nor the dressing of CAN in May 1997 or the K fertilisation in March 1997 led to perceptibly enhanced P levels in overland flow. The dry periods following the K and urea 1997 applications may have inhibited possible effects on P levels in overland flow, but the CAN and the urea 1998 applications were followed by overland flow events within a few days. The possibility of P release due to fertilisation has been mentioned in the literature. Cationic uptake of plant nutrients was reported to lead to OH^- release by the plant and thus a local acidification of soil (Bekele et al., 1983). This may in turn lead to greater amounts of P being released by the soil, and thus made available for transport, at times of enhanced K^+ and $NH4^+$ uptake. N is normally assimilated as $NO3^-$ but $NH4^+$ uptake is possible under anaerobic or very acidic conditions (Bekele et al., 1983). This circumstance might explain why P release in response to N fertilisation would have happened at the sites at the Warren but not the Cowlands. Thus, the theory fits the findings: if enhanced P levels in overland flow due to N and/or K applications did occur, they happened only if fertiliser was applied immediately before or during an overland flow event and, in the case of N, only on very wet land. In their work on run-off water quality of recently reclaimed land, Roberts et al. (1989) detected elevated P concentrations in response to a nitrogenous fertiliser application. Also, Liu et al. (1997) measured higher levels of P in overland flow from plots fertilised than from plots not fertilised with N (NH_4NO_3). Still, overall the data from overland flow sites used in this study do not offer enough evidence to either support or dismiss the theory.

The high P concentrations at the Warren 1 at the beginning of event 15 (Figure 7.28) were likely to have been a result of the presence of grazing animals shortly before rainfall. The Warren 1 was grazed for two periods in summer 1997 (Table 3.2). Events 12 and 15 were the first overland flow events post grazing. Event 15 started the day the bullocks left the site. Not only P but also TA, K and, to a lesser degree, the TON levels were raised (Figures 7.131 and 7.133). This may be evidence of the impact of grazing animals on overland flow of event 15 because high TA and P concentrations in water have been identified as a consequence of the presence of grazing animals and their faeces (Dou et al., 2000; Heathwaite and Johnes, 1996; Jensen et al., 2000), and elevated K concentrations in overland flow after grazing have been observed (McColl, 1979). As a positive effect of grazing pressure on organic P contents in overland flow has been documented (Sharpley and Syers, 1976; Heathwaite et al., 1990a), the unusually high proportions of dissolved unreactive P, which is mainly made up of dissolved organic and condensed P (see Section 5.1.1), in overland flow samples taken at the beginning of event 15 (Figure 7.28) may also have been brought about by the faecal material on the soil surface (see Section 5.4.2).

Samples collected at the beginning of event 14 at the Warren 1 also contained high proportions of unreactive dissolved P (Figure 7.27). The TA and K levels of some of these samples were slightly elevated but to a much smaller degree than at the beginning of event 15 (Figures 7.131 and 7.133). Between the removal of the grazing animals from the Warren 1 and the beginning of event 14 there were 13 days of no flow and two overland flow events. CAN and K fertilisation was carried out before event 12. Furthermore, DRP, TA and TON were not measured for events 12 and 13. Thus none of the parameters which were thought to indicate the influence of grazing animals on overland flow during event 15 can be used in the case of events 12 and 13. It is, however, possible that animal manure, which had time to dry out and consolidate (Mohr, 1943) prior to event 12, still influenced overland flow during the first few days of low flow of event 14.

At the Cowlands records of entry and removal of the animals to the site were not available. Their presence was, however, physically observed during event 13 (Figure 7.134). Again, the DRP, TA and TON measurements are missing for this event, but the K contents were only elevated in few of the samples taken during event 13. The TA and K concentrations were obviously enhanced during event 14.1 and the first two days of event 14.2 (Figures 7.130 and 7.134). Furthermore the ratio of maximum and minimum DRP levels was unusually high during events 13 (calculated DRP) and 14.1 (Figure 7.123). This may indicate the existence of an extra source of variability, i.e. an additional source of P, which affected P in overland flow. Also, extraordinarily high proportions of unreactive P were detected for samples taken during the two days of low flow at the beginning of event 14.2 (Figure 7.49). Thus, at the Cowlands as well as the Warren 1, some of the elevated P concentrations during late spring, summer and early autumn were probably due to the presence of

grazing animals at the sites (see also Section 5.4.2). Laboratory studies have shown that a large proportion of the P in cattle manure is of high potential availability to water (Dou et al., 2000) and field studies have found an association between high P concentrations in overland flow and the presence of grazing animals on land (Heathwaite, 1993; Nash et al., 2000). Elevated concentrations in overland flow have, like in our case, mainly been detected while or shortly after the animals were present within a monitored area (Jawson et al., 1982; Sharpley and Syers, 1976). The grazing pressure observed was often greater than at our overland flow sites (Heathwaite, 1993), and winter grazing was investigated in some studies (Sharpley and Syers, 1976).

Seasonal Influences on P Levels in Overland Flow

The high ratios of the maximum and minimum flow-weighted average DRP concentrations for the monitoring period at the Warren 1 and the Cowlands underline the wide range of P values that occur in overland flow. The ratios were much lower for all sites during the 5 months (November to March) of monitoring at the Warren 2 (Figures 7.123-7.125). The greatest variability of P levels in overland flow thus happened during the summer half year – a time which is characterised by an increased likelihood of the occurrence of high P levels in overland flow. Management practices associated with the summer/autumn half year explain some of these observations (see above).

A clue which suggests an increase in P levels of overland flow due to seasonal environmental conditions (as opposed to seasonal management practices) is for example the tendency of elevated P values in overland flow in springtime at the Warren 1 (events 6-10) (Figure 7.117), because these events took place prior to grazing or fertiliser additions. At the Cowlands seasonal environmental and management effects were at no time clearly separable. However, the general increase in P concentrations from May to the end of August 1997, and the subsequent decline towards mid November can certainly not be attributed to one single management practice.

McColl and Gibson (1979) attributed low nutrient concentrations in overland flow during the winter rather than summer months to the diluting effect of large volumes of overland flow. This theory may hold true for the overland flow over the winter period as a whole. However, as indicated by the high P concentrations achieved during the record summer rainfall event monitored (event 13), it is not applicable to sites in this study on a single event basis. The flow values for the Warren 1 and the Cowlands (Figures 7.26 and 7.47) indicate that the areas producing overland flow during event 13 were likely to have been as extensive as those of some of the winter storms. The high rates of flow achieved during 5th August 1997 were comparable to those measured in winter events (e.g. event 19). Event 13 resulted from the maximum rainfall intensities during the study period (Figure 6.4). The high intensities occurred 3rd and 4th August 1997. A similar extent of

overland flow producing areas during a winter and a summer event is thus indicated by the comparable rates of flow and rainfall intensities for some peaks of events 13 (Figures 7.26 and 7.47) and 19 (Figures 7.32, 7.57-7.59). The fact that the concentrations of event 13 were in line with other summer values dismisses the suggestion that seasonal variations of P in overland flow reflect the differences in hydrologically active areas (Duda and Finan, 1983).

Differences in DRP concentrations of overland flow have also been explained to be a consequence of variations in labile P, temperature, ionic strength and solution-to-soil ratio (Liu et al. 1997; Yli-Halla and Hartikainan 1996), which were not determined in this study. As an increase in labile soil P in summer due to fertilisation and/or grazing animals was likely at our sites, it could, in combination with the higher summer temperatures, have contributed to the trend of higher DRP levels in overland flow during summer. There was very little evidence of a seasonal pattern in conductivity levels (Figures 7.136 and 7.137), which are related to ionic strengths (Flanagan, 1992). The lack of a strong relationship between conductivity and DRP concentrations furthermore implies that the effect of ionic strength was not detectable in these data anyway. Despite suspended solid measurements, the soil-to-solution ratio could not be determined in the study in hand because the ratio is influenced by the amount of stationary soil the water comes in contact with as well as the concentrations of suspended material in overland flow (Yli-Halla et al., 1995).

The elevated levels of P in overland flow during the summer are also thought to be caused by the accumulation of nutrients at the soil surface during dry periods (Dils and Heathwaite, 1996; McColl and Gibson, 1979). This effect must have been counter acted by management or other environmental factors at the Warren 1 and the Cowlands, because the high P exports during event 13 were not followed by low P concentrations during event 14 (Figures 7.27 and 7.48).

P Concentrations During the Course of Events

Many studies have commented on the lack of a linear correlation between the rate of flow and dissolved P (Haygarth and Jarvis, 1997; Sharpley et al., 1976). However, the absence of clear relationship between the rate of flow and TP at sites in this study (Figures 7.126-7.128) seems unusual (compared for example with Haygarth and Jarvis (1997) and Sharpley et al. (1976)). This indicates that factors other than the rate of flow had an overpowering influence on P concentrations in overland flow from our sites.

Even though there are no clear, strong relationships between the rates of flow and the P concentrations in overland flow, the similarities between the hydro- and chemographs for most events (Figures 7.14-7.16, 7.18-7.23, 7.25-7.32, 7.34-7.45 and 7.47-7.70) suggest an influence of

flow on P levels in overland flow. Generally the P concentrations rose and fell in sequence with, but not in proportion to, the rates of flow. Similar patterns were found for TP but not dissolved P by Sharpley et al., (1976) but nearly opposite trends were reported by Nash and Murdoch (1997). It is commonly accepted that P mobilisation from land to overland flow occurs due to P transfers from stationary soil (Yli-Halla and Hartikainan, 1996) and dead and live organic material (Baker and Laflen, 1982), from soil solution (Ingram and Woolhiser, 1980), and due to P release from suspended soil particles (Yli-Halla and Hartikainan, 1996). The dependence of these processes on flow energy (Sharpley, 1985a) can explain the similarity in shape of chemo- and hydrographs.

Nash and Murdoch (1997), on the other hand, attributed their deceasing P concentrations with rising rates of flow to the dilution of mobilised P with increasing amounts of water. Thus the process dominating P levels in overland flow at their site with its specific characteristics (e.g. soil type, management practices) was different than that at sites used in this study. It may have been of consequence that their rates of P fertiliser application were much higher than the ones in this study and that their soil P level was closer to that of the high than that of the low P site in this study (Humphreys et al., 1998) because the agreement of the trends in hydro- and chemographs was more pronounced at the low (Warren 1) than the high P site (Cowlands). Partly this occurred because the ratio between the minimum and the maximum P concentrations of an overland flow event was generally greater at the former site (Figures 7.123 and 7.124). The ratio as such was independent of the rate of flow at the Warren 1 and the tenuous suggestion that it may have been driven up by high rates of flow during some events at the Cowlands can probably be dismissed. What factors other than the rate of flow can influence the variability of P concentrations in overland flow during an overland flow event? The often, in comparison with flow peaks, excessively high P levels near the beginning of events suggest the importance of environmental conditions prior to the occurrence of overland flow. Available P not assimilated by plants may accumulate during dry periods. Figures 7.120 to 7.122 show that in this study, the number of dry days between events generally did not have a perceptible influence on P levels in overland flow. The above mentioned accumulation of available P may, thus, have occurred at our sites, but not in proportion to the duration of the period without overland flow. Pote et al. (1996) attributed high P values in overland flow samples taken during early stages of events to the contribution of P from soil solution, and Turner and Haygarth (2001) to a release of biomass P when soils are re-wet. In the latter case the trend may then be more pronounced at the Warren 1 than at the other sites because, at the low P site, the normally low plant and overland flow available P levels could be driven up temporarily by the microbial P release on re-wetting of the soil.

Influences on P in Overland Flow: Summary

Factors including rainfall intensity (Haygarth and Jarvis, 1997, Sharpley et al., 1981c) slope and land cover (Ahuja et al., 1982) are known to affect the P release from soil to water but these parameters were not investigated in the study in hand. However, it is expected that at any one time, these factors were comparable at the three overland flow sites described here. On the basis of the above discussion it can be said though that P concentrations in overland flow at our sites were predominantly influenced by the soil P levels (or related factors) of the sites, management factors, time of year, the time since the start of the event and, to some degree, by the rate of flow. The combination of these parameters led to the enormous variability observed in P concentrations of overland flow. The minimum P levels were generally less variable than the maximum or flow-weighted average concentrations, and this was true on an event and a yearly basis.

Apart from the correlation between TA and DRP at the Warren 2, no strong relationships between P and any of the other parameters monitored in overland flow (TON, TA, K, ss, conductivity) were detected during this study. This indicates that none of the other water quality measures were affected by the same site, management and/or environmental characteristics to an equal degree as the P levels. It is probably this lack of strong relationships which makes some of the other water quality parameters useful aids for interpreting the P data.

7.4.3 P Export

Phosphorus loadings were calculated by multiplying the total flow of a time interval by the mean P concentration measured during that period (see Section 7.2.4). The accuracy of the export figures thus depends on the quality of the flow and concentration datasets. In combination with the strong head-discharge relationships, the 5 minute logging interval and the high accuracy of the depth measurements for most of the overland flow monitoring (Section 7.2.1) were bound to ensure good quality of flow data. The accuracy of the P data is discussed in Chapter 5 and, overall, deemed satisfactory. However, the time-related discrete sampling programme left gaps in the chemographs, and this would have had a negative impact on the accuracy of the P exports calculated. Vollenweider and Kerekes (1980) estimated that an error of +/- 25% was generally associated with nutrient loading figures, and Stamm et al. (1998) worked out errors of +/- 21-35% for P loads in discharge from artificial subsurface drains. However, Vollenweider and Kerekes (1980) error estimate allowed for infrequent sampling, and Stamm et al.'s (1998) error percentage was based on annual loads which were calculated using a combination of measured and estimated P concentrations. Due to the detailed sampling programme and year round monitoring carried out in this study, the uncertainties associated with export figures of this study are likely to be closer to the +/- 15% determined by Sharpley et al. (1976).

Table 7.5: Summaries of methods and results of studies on edge-of-field measurements of overland flow and P losses from grassland areas.

Reference	Summary of relevant data collection and comments	Land use	Year	Soil P level	Annual P fertilisation (kg P/ha)	Annual amount of overland flow (mm)	Annual P export (g/ha)	Annual TDP export (g/ha)	Annual TP export (g/ha)
Burke et al., 1974	The amount of overland flow and the P concentrations in overland flow from one plot with artificial subsurface drainage (drained) and one plot without artificial subsurface drainage (undrained) were monitored for 7 years. The authors do not specify which fraction of P was measured.	Grassland	1966	Unknown	130 as chemical fertiliser	272 from drained and 637 from undrained plots	3000 from drained and 5200 from undrained plots		
			1967	Unknown	70 as chemical fertiliser	17 from drained and 353 from undrained plots	200 from drained and 3700 from undrained plots		
			1968	Unknown	40 as chemical fertiliser	45 from drained and 462 from undrained plots	200 from drained and 1900 from undrained plots		
			1969	Unknown	80 as chemical fertiliser	14 from drained and 266 from undrained plots	100 from drained and 1800 from undrained plots		
			1970	Unknown	80 as chemical fertiliser	61 from drained and 329 from undrained plots	400 from drained and 2500 from undrained plots		
			1971	Unknown	64 as chemical fertiliser	40 from drained and 154 from undrained plots	200 from drained and 900 from undrained plots		

Table 7.5: Continued.

Reference	Summary of relevant data collection and comments	Land use	Year	Soil P level	Annual P fertilisation (kg P/ha)	Annual amount of overland flow (mm)	Annual DRP export (g/ha)	Annual TDP export (g/ha)	Annual TP export (g/ha)
Sharpley and Syers, 1979	The amount of overland flow and the P concentrations in overland flow from plots with differing P fertilisation were monitored for 3 years.	Cut grassland	1975	Unknown	None on unfertilised plot and 50 on fertilised plot	133	330 from unfertilised and 1660 from fertilised plot	480 from fertilised and 1910 from unfertilised plot	850 from fertilised and 3670 from unfertilised plot
			1976	Unknown	None on unfertilised plot and 50 on fertilised plot	285	500 from unfertilised and 2800 from fertilised plot	610 from fertilised and 2890 from unfertilised plot	1280 from fertilised and 5630 from unfertilised plot
			1977	Unknown	None on unfertilised plot and 50 on fertilised plot	154	280 from unfertilised and 1710 from fertilised plot	310 from fertilised and 1780 from unfertilised plot	870 from fertilised and 3770 from unfertilised plot
Jawson et al., 1982	The amount of overland flow and the P concentrations in overland flow were monitored for 2 years.	Cut grassland	1978	Unknown	None	45	10	50	100
			1979	Unknown	None	103	20	30	70

Table 7.5: Continued.

Reference	Summary of relevant data collection and comments	Land use	Year	Soil P level	Annual P fertilisation (kg P/ha)	Annual amount of overland flow (mm)	Annual DRP export (g/ha)	Annual TDP export (g/ha)	Annual TP export (g/ha)
Turtola and Jaakkola, 1995	The amount of overland flow and the P concentrations in overland flow were monitored for 3 years.	Cut grassland	1980	3.6 mg/l (range 2.7 to 4.8 mg/l) of acid ammonium acetate soluble P in top 20 cm	63 as chemical fertiliser	139	140	Unknown	270
			1981	As 1980	63 as chemical fertiliser	250	970		1540
			1982	As 1980	63 as chemical fertiliser	225	1533		2010
Haygarth et al., 1998	A mix of overland flow and interflow to 30 cm from drained and undrained plots was gauged and sampled for some of the events occuring during a year. For each treatment (drained, undrained) data of 7 plots were used. The authors comment that P exports are estimates based on restricted data.	Pasture	1994	Drained plots: 6.6 +/- 0.1 mg/kg Olsen, undrained plots: 8.4 +/- 3.4 mg/kg Olsen in top 7.5 cm	None, or 16 kg/ha as chemical fertiliser and 16 kg/ha as cattle slurry, or 25 kg/ha as chemical fertiliser	Unknown	Drained plots: 228, Undrained plots: 1890	Drained plots: 262, undrained plots: 2174	Drained plots: 380, undrained plots: 3150

Table 7.5: Continued.

Reference	Summary of relevant data collection and comments	Land use	Year	Soil P level	Annual P fertilisation (kg P/ha)	Annual amount of overland flow (mm)	Annual DRP export (g/ha)	Annual TDP export (g/ha)	Annual TP export (g/ha)
Nash et al., 2000	The amount of overland flow and the P concentrations in overland flow were monitored for 3 years.	Pasture	1994	17 mg/kg Olsen P in top 10 cm	80	37	1700	1800	1900
			1995	Between 17 and 40 mg/kg Olsen P in top 10 cm	110	38	5300	5500	5700
			1996	40 mg/kg Olsen P in top 10 cm	110	85	9200	9400	9700

The result of the interactions between the trends of the flow and P concentration data is a new dataset with its own particular variability and trends. Still, factors leading to variability in the flow and/or P concentration data will also affect P loadings. Thus P exports must be influenced by a variety of factors related to site characteristics, weather, climate and management, and they must be highly variable among events, months and years. These assumptions are confirmed by data presented here and by findings of many other studies (e.g. Correll et al. 1999; Hawkins and Scholefield, 1996; Klausner et al., 1976; McColl, 1979; Nash et al., 2000).

For the aforementioned reasons, a comparison of our export rates to those achieved in other areas is difficult to make. Still, the results of other studies that estimated edge-of-field P losses in overland flow are summarised in Table 7.5. Note though that the studies on which Table 7.5 is based differed from the work reported on here as regards important characteristics like soil P levels, P fertilisation, land use and soil hydrology (see Table 7.5). As expected, the range of reported yearly edge-of-field P losses from grassland is very wide (Table 7.5). Generally, the P exports measured in this study were within the range of the P exports listed in Table 7.5.

The combination of the flows and P concentrations at the 3 study sites brought about that, whenever overland flow at occurred at all sites, monthly P exports from the Cowlands were consistently higher than those from the other sites, and greater monthly amounts of P flowed off the Warren 2 than the Warren 1 (Figures 7.147 and 7.148). Conditions most favourable to P loss with overland flow were high flow events during times of elevated P availability (summer half year). Such a circumstance occurred at the beginning of August 1997. This single event was then responsible for nearly half the annual losses from the Warren 1 and the Cowlands. This importance of large events for P movement with overland flow was pointed out by McColl (1979), whereas Quinton et al. (2001) established that the role of low magnitude but high frequency events cannot be neglected.

The yearly P losses from the high and the low soil P site clearly exceeded roughly estimated loss rates assumed to lead to eutrophic conditions in Lough Neagh (Tunney et al., 1998). What proportions of edge-of-field losses will reach water bodies is highly variable (McColl, 1979) and largely unknown. The potential environmental impact of the P exports measured in this study is, therefore, impossible to assess. What is noteworthy though is that, at the high soil P site (Cowlands), the annual TP export in overland flow amounted to more than 20% of the P fertiliser application to that site. Apart from the environmental significance of this unusually high percentage (Nash et al., 2000; Sharpley and Syers, 1979), it may, depending on P fertiliser prices, also be seen by farmers as economically and agriculturally significant.

For ease of reference, the yearly and 144 day (8th November 1997 to 31st March 1998) flow-weighted average DRP levels, the amounts of overland flow and P export from the three overland sites are summarised in Table 7.6. Even though there was more overland flow from the Warren 1 than the Cowlands (1.7 times), the yearly P exports from the high P site (Cowlands) were nearly 7 times in excess of those from the low P site. The reason for this occurrence must obviously lie in the P concentrations, and the mean yearly DRP levels were just short of 12 times greater in overland flow from the Cowlands than the Warren 1. Thus the difference in DRP concentrations by far outweighed the discrepancy in flow volume, and the very same pattern applied to overland flow from the low, the medium (Warren 2) and the high soil P site for the winter monitored at the Warren 2. Note that to some degree, the P concentrations are likely to be influenced by the hydrology of sites (Pote et al., 1999) but the previous section showed that other factors were probably much more important in our areas.

Table 7.6: Yearly and 144 day (8th November 1997 to 31st March 1998) amounts of overland flow and P export from the three overland flow sites. Average flow-weighted DRP concentrations for the two periods.

Parameter	**Warren 1**	**Cowlands**	**Warren 2**
Yearly amount of overland flow (mm)*	774	443	
Yearly DRP export (g/ha)*	698	4,764	
Yearly flow-weighted average DRP concentration (mg P/l)	0.090	1.076	
Amount of overland flow 8th Nov. 97 to 31st Mar. 98 (mm)	511	328	436
DRP export 8th Nov. 97 to 31st Mar. 98 (g/ha)	111	1,162	300
Flow-weighted average DRP concentration for the period 8th Nov. 97 to 31st Mar. 98 (mg P/l)	0.028	0.354	0.069

*Average values were used for months monitored in two years (Section 7.3.1).

The Warren 1 and the Cowlands were selected to represent low and high soil P conditions. Hence, their soil P levels were nearly at opposite ends of the range recommended for agronomic purposes. The sites were much closer together as regards soil drainage. Considering that the drainage scale goes from very poor, to poor, to imperfect, to moderate, to well and excessive drainage, the very poor drainage at the Warren 1 was not that different from the poor to imperfect drainage at the Cowlands. This reflects the circumstance that overland flow is predominately produced on wet (very poorly to imperfectly drained) land (Gardiner, 1986). The environmental impact of the

amounts of overland flow, and therefore P export with overland flow, from more freely draining soils can probably be neglected (Diamond and Shanley, 1998; Diamond and Sills, 1998; Monaghan et al., 2000). However, this is a subject area of ongoing investigations. Still it is likely that, when only considering overland flow as a P loss pathway, the sites which are characterised by great P loss potential are likely to be of similar drainage class. The value of the actual P loss figure then largely depends on soil P level. Hence a greater variation of P exports is possible due to differences in soil P rather than differences in drainage class. This fact assigns a higher proportion of the possible variability in P exports to the soil P status rather than the drainage class.

Despite the fact that the TDP and especially the TP measurements were of much lower accuracy than the DRP values, estimates of the relative contributions of the various P fractions to P exports are of interest. They, of course, reflect the relationships between the concentrations of the different forms of P (Section 5.3.3). The high proportion of PP losses at the Warren 2 is not likely to be typical of grassland (see Chapter 5 for discussion) and it is not further discussed here.

In Section 5.4.2 it was shown that, in reference to TP (100%), PP made up just over 20% of the overall (full monitoring period) losses at the Warren 1 and the Cowlands. The discussion of Chapter 5 (Section 5.4.2) and the export figures presented in Section 7.3.4 further show that the dissolved P was mainly reactive at the Warren 1 and the Cowlands, and that the dissolved organic and condensed fraction was more important at the Cowlands than the Warren 1. All forms of P are considered to be potentially available to aquatic life over time (Borström et al., 1988; Fitzgerald, 1970; Sonzogni et al., 1982; Viner, 1988). However, the preponderance of reactive forms of dissolved P is of environmental significance because most of this type of P is immediately available to aquatic organisms (Ekholm, 1998) (see also Section 2.1.2 and 5.1.1). The importance of DRP has been reported in connection with overland flow from grassland sites (Nash et al., 2000; Sharpley and Syers, 1979, Turtola and Jaakkola, 1995), and, like in this study, dissolved forms of P are generally found to dominate P in overland flow from intact grass swards (Haygarth et al., 1998; Nash et al., 2000; Sharpley and Syers, 1979; Turtola and Jaakkola, 1995). Thus measures to reduce P exports from such areas efficiently need to aim at the dissolved, more than the particulate, P fractions. At the Cowlands it may, for example, make more sense to assign a higher priority to managing the site with a view to achieving lower soil P levels than to establishing buffer zones or filter strips to trap PP.

The importance of addressing the issue of excessively high soil P levels where they occur on wet land is underlined by the observation that a large proportion of the P losses measured in this study can be attributed to soil P or related factors rather than short term effects of fertiliser applications.

CHAPTER 8: P IN SUBSURFACE DRAINAGE WATER

8.1 Introduction

The main focus of the study in hand was on P losses from land to water via overland flow (see Section 1.4), because overland flow has often been found to be more important as regards P export than subsurface flow (Brookes et al., 1996; Burke et al., 1974; Haygarth et al., 1998). However, when working at the small catchment scale (Dairy Farm stream), it became obvious that the issue of P transfers from land to stream water via subsurface pathways, and in particular via artificial subsurface drainage networks, needed to be considered.

A description of the importance and the mechanisms of P transport in shallow subsurface flow is given in Section 2.5.3. Shallow subsurface flow through undisturbed soil and via man made drainage networks consists of and/or is fed by matrix flow and preferential flow (meso-and macropore flow) (Germann, 1990; Stamm et al., 1998). Water in both of these pore spaces can be enriched with P (Laubel et al., 1999; Leinweber et al., 1999). However, in all but overfertilised soils (Holford et al., 1997), P concentrations in meso- and macropore flow usually exceed P levels in matrix water (Stamm et al., 1998).

The levels of P achieved in subsurface flow are affected by factors such as soil type, land use, soil P level and P fertilisation (Calvert, 1975; Culley et al., 1983; Heckrath et al., 1995; Leinweber et al., 1999). Shallow subsurface flow via natural and artificial drainage pathways can contain amounts of P which are of environmental significance (Haygarth et al., 1998; Leinweber et al., 1999). However, when monitored at the same site, P concentration in water flowing through artificial subsurface drainage networks tend to exceed P levels in natural subsurface flow (Sharpley and Syers, 1979). This may be a consequence of the fact that all interactions between the soil matrix and the water are made impossible once the water reaches an artificial subsurface drainage network (Dils and Heathwaite, 1996).

The interest in the P contents of artificial subsurface drainage water at the Beef Unit arose because monitoring of the Dairy Farm stream had shown that the P concentrations in water coming from the Beef Unit were often high (see Section 9.4.1 and Section 3.6.1 for location of sites mentioned). At the end of the work on the Dairy Farm stream it was known that high P levels were caused by discharges from the yard and associated facilities, as well as by overland flow from the land of the Beef Unit. The artificial subsurface drainage network had been observed to contribute significant amounts of water to the Dairy Farm stream, but whether this water was at times high in P was unknown. The subsurface drainage system at the Beef Unit was, furthermore, over 15 years old

and minimum maintenance had been carried out on it (Section 3.5.1). To get a more complete picture of the sources of P in the Dairy Farm stream, it was thus decided to monitor the artificial subsurface drainage system at the Beef Unit.

Stamm et al. (1998) regard flow into tile drains as a combination of matrix and preferential flow. Soil water samples largely representative of both types of flow were therefore taken to assess the influence of preferential flow and of matrix flow on the P concentration of water in the subsurface drainage network at the Beef Unit.

8.2 Methods

8.2.1 Type and Location of Study Sites at the Beef Unit

Investigations into the loss of P via artificial subsurface drains at the Beef Unit started in summer 1997. The issue was approached from three different angles. Dye studies to gain information on the movement of water down the soil profile were undertaken (see Section 4.2.3), soil water samples were taken, and water quality and quantity of an artificial subsurface drainage network was monitored from November 1997 to March 1998.

The artificial subsurface drainage network that was monitored drains a grassland area of the Beef Unit at Johnstown Castle. The size of the area drained by the network amounts to just over 24 ha (Section 3.5.1). The water quality and quantity monitoring station was located at the discharge of the artificial subsurface drainage system (Figure 3.1; monitoring station MB in Figure 3.7). This point also forms the beginning of the Dairy Farm stream (Figure 3.7).

The dye study and soil water sampling sites were located within the section of the Beef Unit drained by the artificial subsurface drainage network monitored. These sites are indicated in Figure 8.1. This figure also shows that the soil water sampling sites were situated in a field of high and one of low soil P levels.

Flow pathways down the soil profile are greatly influenced by soil texture and soil structure (Germann, 1990), and they can, therefore, be looked upon as a soil hydrological characteristic. The dye studies, which served the purpose of making the subsurface flow pathways visible, are therefore grouped with other soil information in Chapter 4. They are described and discussed in Sections 4.2.3, 4.3.3 and 4.4.3. These dye studies illustrate the existence of preferential flow pathways down the soil profile in land drained by the artificial subsurface drainage network monitored.

8.2.2 Instrumentation and Installation of the Site

As this study aimed at gaining information on the quality of subsurface water moving as matrix flow and of subsurface water flowing through preferential flow pathways, soil water samplers which approximately sample these two types of subsurface flow were used: Teflon suction cups and zero-tension samplers.

The fact that the chemical characteristics of soil water samples vary according to whether they have been obtained with or without the application of tension is well known (Haines et al., 1982; Hendershot and Courchesne, 1991). Suction cups use tension to extract water from the soil, and they are an established method of sampling soil water (Hansen and Harries, 1975; Lord and Shepherd, 1993). They primarily collect water held in micropores and tend to miss most rapidly moving water flowing down preferred pathways like large continuous soil pores (Shaffer et al., 1979; Simmons and Baker, 1993). Suction cups are often made of ceramic, which was found to adsorb and desorb P to water samples (Bottcher et al., 1984). No such process was observed with Teflon (Bottcher et al., 1984; Zimmermann et al., 1978). If P is the element of interest, Teflon suction cups deliver satisfactory soil water samples for analysis.

Water draining by gravity is often collected with zero-tension samplers (Magid et al., 1992). These samplers generally consist of a vessel with a large opening. This opening forms the interface between the soil and the reservoir to hold the collected water. A screen to support the soil covers the opening. The voids of that screen are large enough not to interfere with the free flow of water (Haines et al., 1982; Hendershot and Courchesne, 1991; Simmons and Baker, 1993). Simmons and Baker (1993) designed a system which allows insertion and servicing of the samplers from the land surface. As these features are advantageous in a field situation, this type of sampler was used here.

Teagasc, Oakpark, following the design described by Simmons and Baker (1993), manufactured the zero-tension samplers. These instruments were made from PVC pipes of an outer diameter of 5.5 cm. For a length of 17 cm, the pipes were cut lengthwise and the top halves were removed to provide open areas through which the soil water could access the tubes. The openings were covered by a mesh, which was pressed against the soil by small inner PVC tubes mounted on springs. The bottom ends of the PVC pipes were fitted with caps, and thus formed reservoirs in which the water could accumulate. Each sampler contained a rigid plastic tube (inner diameter of 5 mm) through which the water was pumped up from the reservoir.

The Teflon suction cups (outer diameter: 2 cm, length of porous surface: 5 cm) used in the study in hand were commercially available from PRENART Equipment (Copenhagen, Denmark). They

consisted of a cylinder with a conical tip at one end and a sealed in plastic tube (diameter of 2 mm) at the other end.

The Teflon suction cups were installed in July 1997 and the zero-tension samplers during a dry period at the beginning of October 1997. The Morgan's P level of the high and low P fields were 12 and 4 mg P/l respectively (Figure 8.1). Water from the topsoil was sampled at two sites in the high P field and water from the heavily gleyed deeper horizon at two sites in both the high and the low P fields (6 soil water sampling sites). Following the recommendation of Simmons and Baker (1993), all probes were inserted into holes augured at angles of 45°. The soil removed by the auger was carefully laid aside. Plates 8.1 and 8.2 show diagrams of a Teflon suction cup (Plate 8.1) and a zero-tension sampler (Plate 8.2) installed into the soil.

The suction cups were positioned in such a way that the upper end of the porous surface was at a depth of 13 cm (18 cm at 45°) for the shallow samplers and at 57 cm (80 cm at 45°) for the deep samplers. They were installed according to the suggestions of Lord and Shepherd (1993). To ensure good contact between the porous surface and the soil, the cups were embedded into a mix of silica flour and water. The plastic tubes were led up the holes to the surface. The soil removed while augering was tightly packed around the tubes in the same sequence as it had been taken out of the holes earlier. Just below the soil surface, small amounts of bentonite powder were used to form a seal around the plastic tubes. A pressure of 30 centibars was applied with a hand pump to obtain water samples.

Simmons and Baker (1993) found that only an average of 52% of zero-tension samplers inserted to a vertical depth of 1.2 metres contained water. They set out to sample channels which had developed between peds (which are individual natural soil aggregates (Gardiner and Radford, 1980) and empty samplers probably failed to intersect such a continuous interpedal space. The relatively large proportion of empty samplers in their study may have been due to the fact that macropore systems reaching from the land surface to considerable depth do not occur throughout a soil but rather at distinct locations. Thus two samplers were installed at each of our soil water sampling sites even though our samplers were used at depths much shallower than 1.2 meters. As the sample collection area of the zero-tension samplers (17 cm) was much longer than the porous surface of the Teflon suction cups (5 cm), the depth interval sampled by the zero-tension samplers was also greater. The zero-tension samplers were, therefore, positioned to include the sampling depth interval of the suction cups. A vertical sampling depth of 8-21 cm and 51-63 cm was aimed at for the shallow and deep samplers respectively. The holes were augured to provide a very tight fit for the samplers. When the instruments were inserted, they thus did not all go down the exact depth aimed for. To retrieve and re-insert them was not an option because this would have

widened the holes. The achieved sampling depths for all probes are listed in section Table 8.2. Once the samplers were inserted, soil, originally from the holes, was crushed and filled into occasional small gaps between the soil and the samplers. As with the suction cups, a small bentonite seal was constructed just below the soil surface.

Upstream of the buildings at the Beef Unit, the water from the subsurface drainage network is led into a concrete pipe (outer diameter of 30 cm). A manhole to gain access to this pipe was constructed in autumn 1997. The top part of the pipe was removed and a probe to measure water depth (pressure transducer) and velocity (doppler principle) was inserted into the pipe. The readings from the probe were stored in a data logger integrated into an automatic sampler (SIGMA 900 Max). The sampler was positioned on a shelf in the manhole and the sample uptake tube was fastened along the walls of the hole to keep it in a steady position at the bottom of the pipe.

8.2.3 Flow Recording and Sampling Programme

The flow meter at the Beef Unit measured water depth and velocity every second. It determined flow values by calculating the cross-sectional area of flow and multiplying it by the velocity. To obtain an average velocity of the typically turbulent flow in a pipe, the doppler probe took velocity readings from a representative cross section.

The logger was set to record an average water level and velocity reading every 5 minutes. A flow related sampling programme was worked out based on the information gained by time related sampling of the first event. The flow intervals between samples were smallest at the beginning of events. They were programmed to first increase and then remain constant for the remainder of the event.

The initiation of the sampling programmes was triggered by a water level rise in the drain. Due to the lengthy recession phase of the hydrographs at the Beef Unit, there was no constant trigger level. The water level in the pipe dropped gradually after an event and eventually reached a more or less constant value after extended dry periods. Until then, the water level to initiate a sampling programme was adjusted downwards during each visit to the site.

The water samples taken from the artificial subsurface drainage network were analysed for the same parameters as the samples taken at the overland flow sites. Total dissolved P (TDP) was measured on all samples, total P (TP) on more than half the samples taken and dissolved reactive P (DRP) on all but the samples taken when the labs were closed (Christmas holidays). Additionally, samples were generally analysed for total oxidised nitrogen (TON), total ammonium (TA),

potassium (K) and conductivity. Suspended solids (ss) were determined on a selection of samples. The laboratory methods and procedures, the quality of the data and the relationships between the P fractions are described and discussed in Chapter 5.

Soil water was only sampled for some events. Here P (DRP and TDP) data for samples taken during BU1, BU3, BU5 and BU8 are reported. TP was not analysed in soil water because the origin of the particulate material in zero-tension samples was unclear. Soil water samples were also analysed for TON, TA, K and conductivity. Soil water samples were generally taken less than 24 hours after the beginning of an event or main flow peak (BU3). The zero-tension samplers were kept empty between sampling occasions by pumping them out every day until they remained dry. Thus all the water in these samplers at the time of sampling had reached them between the start of the event and the time the samples were taken.

8.2.4 Data Treatment and Calculations

Flow and water quality data were again combined in Excel® workbooks (see Section 7.2.4). The separation of the subsurface drainage data into events was arbitrary because the spring caught by the drainage network ensured that the flow never stopped. An event was considered to start just before the increase of flow and to end when the hydrograph was more or less level again after the peaks. The flow rate just before the event was always lower than the flow rate at the end.

Following the rationale laid out in Section 7.2.4, the DRP data were regarded as more reliable than the TDP and TP datasets. The annual TDP/TP export figures were therefore again calculated using the DRP values and the equations drawn up in Chapter 5. The relationships between the P fractions were very strong for the data from the artificial subsurface drainage at the Beef Unit.

The P loadings were calculated as described in Section 7.2.4. Scatterplots were used to investigate the relationships between flow and P concentrations, and between P concentrations and other water quality parameters (see Section 7.2.4).

8.3 Results

8.3.1 Flow

Subsurface Drainage Network

The flow measured at the subsurface drainage site was not converted to mm because the exact area contributing to the flow (spring and subsurface drains) was unknown. The groundwater contribution to the study area could not be assessed and subtracted from the drainage water. The flow measurements thus include water from a larger area than the artificial subsurface drainage catchment. To study the relationship between drain flow and rainfall at the study site, the daily amount of precipitation falling on the area underlain by the drains was converted to m^3. Figure 8.2 shows that the heights of the drain flow peaks increased in relation to the heights of rainfall peaks during the course of an event. According to Figure 8.2 the daily drain flow seems to have been lagging behind the daily rainfall. Note though that the time intervals for the calculations of the daily values of the two parameters were different (9 am to 9 am for rain, midnight to midnight for drain flow).

The events monitored at the Beef Unit were not included in the numbering system for the overland flow events. The dates of the events and the corresponding events at the Cowlands are listed in Table 8.1.

Table 8.1: Dates and numbers of events at the Beef Unit and corresponding events at the Cowlands.

No. of event at Beef Unit	Date start	Date end	Corresponding event at Cowlands
BU1	04-Nov-97	08-Nov-97	18.1
BU2	08-Nov-97	10-Nov-97	18.2
BU3	14-Nov-97	23-Nov-97	18.3
BU4	23-Nov-97	01-Dec-97	18.3
BU5	08-Dec-97	12-Dec-97	18.4
BU6	18-Dec-97	25-Dec-97	19.1, 19.2
BU7	29-Dec-98	23-Jan-98	19.3
BU8	26-Feb-98	12-Mar-98	21
BU9	20-Mar-98	31-Mar-98	22

Event BU6 did not finish on 25th December but the cable connection between the battery and the sampler and data logger was disrupted and the end of the event was therefore missed. Due to the Christmas holidays, the DRP values for some of events BU6 (Figure 8.8) and BU7 (Figure 8.9) are calculated (see Chapter 5).

The data graphed in Figures 8.3-8.11 illustrate that drain flow events often reached peak flow rates slightly later than corresponding events at the overland flow sites (Figures 7.31-7.35, 7.53-7.71). Due to the continuous flow at the Beef Unit, the beginning of an artificial subsurface drainage event could not be identified. However, the main increase of flow towards a peak usually started around the same time at the Beef Unit and the Cowlands.

8.3.2 Phosphorus Concentrations

Subsurface Drainage Water Samples

The P concentrations measured in subsurface drainage water during the events monitored are displayed alongside the rates of flow in Figures 8.3 to 8.11. The samples taken from the subsurface drainage network were a combination of spring and drainage water at high flow. However, spring water alone was sampled during low flow conditions. The P concentrations at low flow were invariably below the limit of detection of the analyses.

Minimum, maximum and flow weighted average DRP concentrations for the events are graphed in Figure 8.12. The maximum DRP levels ranged from 0.140 mg P/l during event BU6 to 1.650 mg P/l during event BU1 and they were thus very high at times.

The plot of the P concentrations for all events monitored and the flow rates they refer to (Figure 8.13) discloses coinciding trends for both parameters but also a great variability of the DRP/rate of flow ratio. The trend of the P peak heights to decrease from BU1 to BU7 is broken at BU8. The maximum concentrations measured during that event were nearly as high as those measured during event BU1.

The scatterplot of the P concentrations against the rates of flow (Figure 8.14) displayed very weak overall correlation between the P fractions and flow but samples taken at low flow usually had low P values. Plots of P concentrations versus flow rates for single events (Figures 8.15-8.23) revealed clear relationships between the two parameters for events BU2, BU3, BU4, BU5 and BU8 but less distinct ones for BU1, BU6 and BU9. During BU2, BU3, BU4, BU5, BU7 and BU8 there was a

linear increase of all P fractions with the rate of flow from about 15 l/s onwards up to rates of below 40-50 l/s.

Soil Water Samples

Table 8.2 lists the identification codes, types and locations of the soil water samplers and the events for which samples of particular instruments were missing. TDP results for all samplers are missing for event BU8 because of a malfunction of the TDP analyser.

Table 8.2: Identifications, locations (12 mg P/l and 4 mg P/l fields) and types of soil water samplers, and sampled events for which data are missing.

ID	Field	Site	Approx. vertical depth interval cm	Type	Missing
1ZA	High soil P	1	8-21	Zero-tension sampler	
1ZB	High soil P	1	8-21	Zero-tension sampler	
2ZA	High soil P	2	6-18	Zero-tension sampler	
2ZB	High soil P	2	6-18	Zero-tension sampler	
T1	High soil P	1	13-16	Teflon suction cup	
T2	High soil P	2	13-16	Teflon suction cup	
3ZA	High soil P	3	52-64	Zero-tension sampler	
3ZB	High soil P	3	51-63	Zero-tension sampler	
4ZA	High soil P	4	51-63	Zero-tension sampler	
4ZB	High soil P	4	51-63	Zero-tension sampler	
T3	High soil P	3	57-60	Teflon suction cup	BU5
T4	High soil P	4	57-60	Teflon suction cup	BU5, BU8
5ZA	Low soil P	5	51-63	Zero-tension sampler	
5ZB	Low soil P	5	48-60	Zero-tension sampler	BU5
6ZA	Low soil P	6	48-60	Zero-tension sampler	
6ZB	Low soil P	6	53-65	Zero-tension sampler	
T5	Low soil P	5	57-60	Teflon suction cup	BU5, BU8
T6	Low soil P	6	57-60	Teflon suction cup	BU5, BU8

Apart from the zero-tension sampler at location 5ZB during event BU5, the zero-tension samplers collected water during all events targeted for soil water sampling (BU1, BU3, BU5 and BU8). Some of the samples were small. However, as the samplers were checked regularly to make sure that they were empty at the beginning of an event, there is confidence that even small samples were made up of water running into the samplers in response to a rainfall event.

The DRP concentrations of the soil water samples, which were taken at the beginning of events BU1, BU3, BU5 and BU8, are displayed in Figure 8.24. The results of all four events are displayed in Figure 8.24. A different symbol is assigned to data for each event. The samplers are organised along the x-axis in such a way that the results from the suction cups of replicate sites are shown next to each other. To their right follow the DRP levels of zero-tension samples taken at sites corresponding to the pairs of replicate suction cup sites. The DRP concentrations in suction cup samples were mostly below the limit of detection (0.005 mg P/l, see Section 5.2.5) and clearly and consistently lower then the DRP levels in samples from zero-tension samplers. Despite the great site and event specific variability, it is obvious that the DRP levels measured in zero-tension samples from the high soil P field (sites 1 to 4) were considerably higher than those found in zero-tension samples from the low soil P field (sites 5 and 6). Only during event BU3 was the highest concentration at the low soil P field (0.253 mg P/l) even close to the lowest concentration at the high soil P field (0.269 mg P/l) (values shown as labels beside relevant symbols in Figure 8.24). The DRP concentrations at the high soil P field were much more variable than those at the low soil P field. A comparison of the results from sites 1 and 2 with those from sites 3 and 4 shows that there was no evidence to suggest that the sampling depth had an influence on P levels in soil water samples taken during this study.

The TDP and DRP concentrations in samples collected by the zero-tension samplers are displayed in Figure 8.25. The three events for which both P fractions were analysed (BU1, BU3 and BU5) are all displayed in the one graph. There was a tendency for the samples from the high soil P field to contain more P during BU1 than during the other events, and elevated P concentrations in sampler 1ZB were recognisable from BU1 to BU3 and BU5 (Figure 8.25). The TDP data generally reflected the trends found in DRP concentrations. However, the dissolved unreactive P levels (TDP minus DRP) were particularly high in samples from 1ZB, 2ZA, 3ZB and 4ZA during event BU1 (Figure 8.25). Like DRP, TDP was below the limit of detection (0.05 mg P/l, Section 5.2.5) in most samples from suction cups (Appendix 3).

8.3.3 Other Water Quality Parameters and Their Relationships to P in Artificial Subsurface Drainage Discharge

TON, TA, K and conductivity levels for samples from artificial subsurface drains and soil water samples, and ss (suspended solids) data for samples from artificial subsurface drains (Section 8.2.3) are presented below. Note that whenever DRP analyses could not be carried out (Section 5.2.3) TON and TA were not measured either. Values for those parameters are therefore missing for 23rd December 1997 to 1st January 1998.

Subsurface Drainage Water Samples

The TON, TA, K, conductivity and ss concentrations measured in samples taken at the monitoring station for flow in artificial subsurface drains at the Beef Unit are shown in Figures 8.26-8.29. The DRP levels are also displayed in these figures.

As with the overland flow data (Section 7.3.3) there was considerable variation in the levels of all water quality parameters during events. The TON concentrations in subsurface drainage water ranged from below the limit of detection to 6.0 mg N/l (Figure 8.26). TON concentrations above 4.0 mg N/l were much more common in November to January than in February and March. The TA concentrations were below 1 mg N/l for all events but BU1 and BU8 (Figure 8.26). A maximum TA concentration of 18.8 mg N/l was measured on 6th March 1998 (BU 8). The highest DRP and K values were also measured during BU1 and BU8 (Figure 8.27). K concentrations of more than 15 mg K/l occurred during those events. The K levels during all other events were below 10 mg K/l and the graph of the K concentrations looks quite similar to that of the DRP levels.

The main body of conductivity values lay between 300 and 500 µS/cm but levels as high as 527 µS/cm (26th February 1998) and as low as 203 µS/cm (13th January 1998) were measured (Figure 8.28). The suspended solids were mostly below 50 mg/l but higher levels did occur (Figure 8.29).

The K concentrations in artificial subsurface drainage water showed a tendency to increase with increasing DRP levels (Figure 8.30). There also were weak negative relationships between DRP and TON (Figure 8.31) and DRP and conductivity (Figure 8.32). Conductivity and TON tended to increase with declining flows (Figures 8.33 and 8.34).

Soil Water Samples

The TON, TA, K and conductivity levels measured in soil water samples collected by zero-tension samplers at the beginning of events BU1, BU3, BU5 and BU8 are shown in Figures 8.35, 8.37 and 8.39. Figures 8.36, 8.38 and 8.40 illustrate TON, TA, K and conductivity levels in Teflon suction cups in samples taken at the beginning of events BU1, BU3, BU5 and BU8. Each figure summarises data for all events for one parameter and sampler type. The DRP levels are also displayed in these figures.

The TA concentrations in zero-tension samplers were mainly below the limit of detection (Figure 8.35). The TON levels were generally higher during BU1 than the other events (Figure 8.35). Excessively high values were measured in water from samplers 1ZA (9.7 mg N/l), 1ZB (11.1 mg N/l) and 3ZB (12.9 mg N/l). TON and TA concentrations were low in samples from Teflon suction cups (Figure 8.34). The TON levels in cup T3 were clearly higher than those in the other cups during events BU1 and BU8. TA was also comparatively elevated at T3 during BU1.

The K (Figure 8.35) and conductivity (Figure 8.37) levels of zero-tension samples tended to decrease from BU1 to BU3, BU5 and BU8. They ranged from 1.7-30.5 mg K/l and 67-462 µS/cm respectively. The maximum K contents for each sampling date was measured at 1ZB, and conductivity was extraordinarily high in samplers 1ZB and 3ZB during event BU1. All Teflon suction cups but T2 contained less than 4 mg K/l at all sampling dates (Figure 8.36). K concentrations in T2 were consistently greater than 12 mg/l. The conductivity values in suction cup samplers ranged from 254 to 569 µS/cm (Figure 8.38). Noticeably low levels were measure at T3 during all events.

8.3.4 Phosphorus Export

From 4th November 1997 to 31st March 1998, about 10 kg of DRP, 13.7 kg of TDP and 19.5 kg of TP were lost via drains from the subsurface drainage catchment area. The cumulative flow curve for the monitoring period is quite regular but the cumulative DRP export curve reflects the elevated P concentrations in November 1997 and at the beginning of March 1998 (Figure 8.41).

Due to the fact that the exact size of the catchment of the artificial subsurface drainage network is unknown, area export rates for P via drains will not be very meaningful. As P imports into the area with groundwater contributing to the spring could be excluded (see Section 8.3.2), area export rates were still calculated to allow a rough comparison of P losses monitored at the overland flow sites and at the artificial subsurface drainage site. The DRP and TDP export rates for the monitoring period at the Beef Unit (November 1997 to March 1998) are summarised in Table 8.3. The

amounts of DRP and TDP lost per ha from the Beef Unit via the artificial subsurface drainage network were more than double the per ha losses measured in overland flow at the Warren 1 (low soil P site). The DRP and TDP exports on a per hectare basis at the Cowlands (high soil P overland flow site), on the other hand, exceeded the export rates measured in water from the artificial subsurface drains at the Beef Unit considerably.

Table 8.3: DRP and TDP export (g/ha) between November 1997 and March 1998 from the artificial subsurface drainage system at the Beef Unit and the overland flow sites at the Warren 1 and the Cowlands.

Site	DRP export (g P/ha)	TDP export (g P/ha)
Beef Unit	412*	560*
Warren 1	150	167
Cowlands	1,255	1,713

*Assumed subsurface drainage catchment area of 24 ha.

8.4 Discussion

8.4.1 Rainfall and Subsurface Drain Flow

An accurate estimate of the time lag between rain and drain flow was impossible to assess due to the continuous groundwater flow in the artificial field drains. However, as indicated by the coinciding main increases of the flow rates at the Cowlands and the Beef Unit, the time delay between rain and drain flow was in the region of hours rather than days. The suggestion of a difference of a day (Figure 8.2) between the start of rain and the drain flow response is thus likely to be an overestimate due to a variation of the time intervals for the daily calculations.

This rapid reaction of drain flow to rainfall is likely to have stemmed from areas where the soil profile was saturated. At the beginning of a rainfall event, saturation may only have occurred at a few locations of limited extent. The fast response of drain flow to rainfall may have been the result of the displacement of pre-event soil matrix water down the soil profile and towards the drains by rainwater (piston flow) (DeWalle et al., 1988; Germann, 1990), or it may have been caused by preferential flow mechanisms (Armstrong and Garwood, 1991; Grant et al., 1996; Harris et al., 1984), or by both of these processes. The elevated P concentrations measured in connection with rapidly increasing rates of flow (Figures 8.3-8.11), and the high TA levels following urea application (Section 8.4.2) imply that preferential flow pathways provided a considerable proportion of drain flow under storm flow conditions. Stronger responses of drain flow to later rather than earlier rainfall peaks of an event may have been due to the wetting of increasing areas of the subsurface drainage catchment, which could then also have contributed to drain flow.

The occurrence of preferential flow in the catchment area of the artificial subsurface drainage network at the Beef Unit was also indicated by the dye studies (Sections 4.3.3 and 4.4.3). However, the contributions of matrix flow and preferential flow to the drain flow cannot be quantified on the basis of the data presented here.

8.4.2 Nutrient Concentrations and Shallow Subsurface Flow Pathways

The spring caught by the drainage network (i.e. groundwater from outside the Beef Unit catchment area) probably dominated non-storm flow, but contributions from soil water were also likely, especially during the extended recession phases of the hydrographs. The P content of non-storm flow in the drains was always low, and the P levels in samples from Teflon suction cups, which mainly collect matrix flow, were also low. Thus contributions of soil water to non-storm drain flow are as a possibility that cannot be discounted on the basis of drain flow and matrix flow composition. As water percolates through low P subsoil, P tends to be held by the soil and the concentrations in the water drop (Cooke and Williams, 1970). The very low P levels found in all soil samples taken just below the topsoil at the Beef Unit (Section 4.4.1) confirm that the P content of matrix water in that area was very low.

The lack of an overall (over the monitoring period) strong relationship between P levels and rate of flow indicates, as in the case of overland flow, the influence of factors other than the rate of flow on P concentrations in artificial subsurface drainage. The decrease of the maximum P concentrations in relation to the rates of flow from November to December/January recalls the pattern observed in overland flow from the Cowlands, where it was attributed to a depletion and/or lack of replenishment of available P (Section 7.4.2). The high P and K levels monitored in subsurface drainage during late February/early March (BU8) can probably be linked to the slurry application to some of the fields of the Beef Unit in late February (Section 3.5.2, Figure 8.1). Strong positive response of P concentrations in subsurface drainage to manure applications have been reported (Hooda et al., 1996; Jordan and Smith, 1985; Smith et al., 1998; Stamm et al., 1998). As the soil water sampling sites lay outside the area onto which slurry was spread in February 1998 (Figure 8.1), the assumption that slurry spreading led to elevated P in subsurface drain flow is confirmed by the fact that the maximum P values achieved in subsurface drainage during BU8 clearly exceeded P concentrations in samples taken from zero-tension samplers during that event. During events BU1, BU2 and BU3, on the other hand, the maximum levels of P recorded in artificial subsurface drains corresponded quite well with some of the P results determined in zero-tension samples from the high P site. The P content of these samples did span quite a wide range though.

The maximum (per event) P concentrations in subsurface drainage water were comparable with the levels found in overland flow (from other sites), and there was great similarity in the timing of the main increases of overland flow and subsurface drain flow. During events BU1 and BU8, the P levels (all fractions) in drain flow exceeded the maximum concentrations measured in overland flow of corresponding events at the Warren 1, and they were closer to maximum values of the Cowlands than the Warren 2 during events BU2, BU3, BU4 and BU5. High soil P levels did occur

in some areas of the Beef Unit and overland flow was observed. It is, therefore, likely that overland flow at the Beef Unit was enriched with P due to the interactions of rainwater with soil (Daniel et al., 1993), plant material (Wendt and Corey, 1980) and slurry (Misselbrook et al., 1995), and that this overland flow reached subsurface drains via preferred flow pathways. The observation that the P levels in zero-tension samples from the high soil P field were greater than those from the low soil P field is consistent with this explanation. As ammonia tends to be held by soil particles (Sharpley et al., 1987), the above theory is further supported by the occurrence of high TA concentrations in subsurface drainage water two days after urea application. Urea was applied to the catchment of the artificial subsurface drains monitored on 4th March 1998. Fertilisation occurred on the falling limb of the first twin peak of event BU8 (Figure 8.10). The subsequent rainfall on 5th and 6th March 1998 gave rise to drain flow characterised by high TA concentrations (Figure 8.26). Elevated TA levels in subsurface flow and in discharge from artificial subsurface drains after the application of ammonia containing fertiliser were measured by Heathwaite (1993) and Gentry et al. (2000) respectively. However, the environmental conditions during the study of Gentry et al. (2000) were quite different to those in this study. They applied the fertiliser onto snow-covered ground. TA was then thought to have reached the artificial subsurface drains via preferential flow pathways after a series of melting events.

Uusitalo et al. (2001) found similar P levels in subsurface drainage and overland flow, whereas many studies measured greater amounts of P in overland than subsurface drain flow (Bengston et al., 1988; Brookes et al., 1996; Burke et al., 1974; Sharpley and Syers, 1979). By showing that PP in subsurface flow originated from the topsoil, macropores have been identified as an important link between the surface and the subsurface drains in some soils (Bottcher et al., 1981; Laubel et al., 1999; Uusitalo et al., 2001). The findings of the study in hand suggest that, at the site described here, preferential flow pathways also provided an effective way of transferring P from the land surface to the subsurface drainage network during storm events. The potential role of macropores as conduits for water from the soil surface to the artificial subsurface drains, which was established by the dye studies (Section 4.4.3), was confirmed by several aspects of the subsurface drainage chemographs and the chemistry of the water collected by zero-tension samplers.

No clear difference between P in shallow and deep zero-tension samplers was found. Given the considerable variability of the chemistry of replicate zero-tension samplers it was only possible to detect large effects of different treatments (depth, soil P), and the effect of depth on P in zero-tension samples may thus have been lost. An alternative explanation of the lack of effect of depth on P in zero-tension samples is that water and P conducting pores may have reached beyond 50 cm below the soil surface. This was confirmed by the dye studies (Chapter 4.4.3). An abundance of macropores reaching depths greater than 50 cm below the soil surface was further suggested by the

fact that, on all but one sampling occasions, samples could be collected from the zero-tension samplers (i.e. only one occurrence of empty sampler). In a study carried out by Simmons and Baker (1993), on the other hand, empty samplers were a common occurrence. The difference between the findings of the two studies can probably be explained by the fact that their zero-tension samplers collected water at much greater depth (1.2 m) than the samplers used in this study (just over 0.5 m).

P from fresh cattle faeces was observed to move down the soil profile via preferential flow pathways (Jensen et al., 2000). There were no fresh faeces to influence the P levels in zero-tension samplers at the Beef Unit. However, the elevated P and K levels, which were measurable in samples from 1ZB at several sampling occasions, could have been caused by an old (decomposed) cowpat. Animal excreta could be one of the factors responsible for variations in the chemistry of replicate zero-tension samples.

8.4.3 P in Relation to Rates of Flow

As there were no strong correlations between P levels and the rate of overland flow (Section 7.4.2), it is hard to explain that in subsurface drain flow, the P concentrations tended to increase with the rate of flow between about 15 and 40-50 l/s during most events (as noted in Section 8.3.2). Positive relationships between P concentrations and flow rates of single events have been reported (Djodjic et al., 2000; Stamm et al.; 1998) and Stamm et al. (1998) attributed them to a greater proportion of preferential flow at higher rates of flow. As the low flow P concentrations at the Beef Unit station were always below detection, it makes sense that the P enriched water reaching the subsurface drainage system via macropore flow during rainfall events (see above) would drive up the P levels. The effect of preferential P transport on P concentrations in subsurface drains may only have been noticeable above rates of flow of 15 l/s because the low P spring/soil water contributions were dominant at lower rates of flow. Conditions of maximum possible preferential flow contribution to drain flow may have been achieved at subsurface drainage flow rates of 40-50 l/s. Thus P levels levelled out at those flow values.

8.4.4 P in Relation to Other Chemical Parameters

The relationship between DRP and K was stronger in subsurface drain flow than in overland flow. Despite the fact that the PP was of greater importance in drain than in overland flow (Section 5.4.2), there was a lack of an obvious correlation between DRP and ss in drain flow, whereas these parameters were related in overland flow (Section 7.3.3). Furthermore there were weak negative trends between DRP and TON and DRP and conductivity in subsurface but not in overland flow.

All of the above could be due to the fact that overland flow and water in artificial subsurface drains were monitored at different sites. The overall correlations between parameters were furthermore based on data from monitoring periods of varying durations. Monitoring at the Beef Unit, for example, mainly covered wet and/or cool conditions, no artificial P or K fertiliser applications and no grazing cycles. Similar circumstances applied to overland flow monitoring at one (Warren 2), but not the other two (Warren 1 and Cowlands) sites.

However, conductivity and TON in artificial subsurface drainage also tended to decrease with increasing flow (Figures 8.33 and 8.34). The slight negative correlation between these parameters and DRP is therefore probably a reflection of the tendency of DRP to increase with flow, which becomes apparent on an event basis (Section 8.4.3). Regarding the DRP – ss relationships, it is conceivable that some removal of the larger solids but, as indicated by the greater proportion of PP of TP in subsurface than overland flow, not of the fine P rich material did occur as overland flow moved down towards the subsurface drains.

8.4.5 P Exports and Concentrations

The event based sampling programme was adequate for estimating total P exports via the artificial subsurface drains at the monitoring site in the Beef Unit because P levels at spring/low flow conditions were below the limit of detection. Thus, nearly all P losses through the drains happened during storm flow. The accuracy of the P export calculations is affected by the same factors as were discussed in section 7.4.3.

As shown in Table 8.3, phosphorus loss per ha via the subsurface drainage network at the Beef Unit was greater than the P export with overland flow from the Warren 1 but was exceeded by the export at the Cowlands. The environmental significance of the subsurface losses at the Beef Unit site is, however, different to that discussed in connection with the overland flow sites (Section 7.4.3). The drainage system and the spring caught by it form the beginning of a small stream. The P exported from the area by the artificial subsurface drains is thus also delivered to a water body, and the concentrations measured in samples from our monitoring station are P levels which actually occurred in a small stream. The fact that these concentrations were high during some of the storms not only documents that our particular artificial subsurface drainage system delivered environmentally significant (according to Vollenweider and Kerekes, 1980) amounts of P, but it also identified the subsurface drainage system as a source of P in the Dairy Farm stream at high flow (Chapter 9).

How representative our results are of artificial subsurface drainage water in Irish grassland is unknown. The subsurface drainage system reported on here was quite old and very little maintenance work had been carried out on it. There was also the atypical spring contribution. Furthermore, evidence of sagging ground above the main drain in the field upstream of the measuring station suggested the occurrence of bypass flow, and thus a greater risk of P loss, along the soil-backfill interface. The fact that the soil-backfill interface is an area where preferential flow pathways are likely to develop has been shown by Uusitalo et al. (2001). All the above suggests that our results are not transferable to water in other artificial subsurface drainage networks. However, considering that not all subsurface drainage networks are in perfect order and that high P levels due to preferential P transport have been measured elsewhere (Beauchemin et al., 1998; Djodjic et al., 2000; Laubel et al., 1999; Stamm et al., 1998; Turtola and Jaakkola, 1995), our findings identify a need for further investigations into this issue.

CHAPTER 9: P LOSS AT THE SMALL CATCHMENT SCALE: THE DAIRY FARM STREAM

9.1 Introduction

The work at the Dairy Farm was a scale up from the edge of field measurements at the overland flow plots. The Dairy sub-catchment includes areas of different soil types (Figure 3.4) and soil P levels (Figure 3.5), and the stream is made up of a mix of overland flow and water from artificial subsurface drains. The Dairy Farm sub-catchment covers an area of approximately 70 ha, and the stream running through the Dairy Farm is about 1.1 km long (distance between upstream (M1) and downstream (M2) monitoring station). The work at the Dairy Farm was to lead to an estimate of the P losses from an agricultural grassland sub-catchment of mixed characteristics to a small stream, and it was to allow an assessment of the impact of these P exports on the water quality of the stream. Furthermore, the main source areas of P loss and transport pathways were to be identified (Section 1.4).

As land related losses usually occur during heavy rainfall events (Dils and Heathwaite, 1996; Hawkins and Scholefield, 1996), the sampling programme prioritised storm flow. The stream was known to contain a mixture of overland and shallow and deep subsurface flow water during storm events (i.e. high flow conditions). Intensive monitoring with automatic flow meters and samplers was carried out at the point where the stream enters (upstream monitoring station, M1) and the point where it leaves the Dairy Farm sub-catchment (downstream monitoring station, M2) (Section 3.6.1) from 24th November 1996 to 31st May 1997. Grab samples at several locations along the Dairy Farm stream were taken to give some information on P concentrations in different sections of the stream and on P inputs to the stream with overland flow and artificial subsurface drainage discharge. The extension of the grab sampling programme was dictated by the water quality results of the first few high flow events (see below).

Detailed monitoring of the stream during winter 96/97 confirmed fears that the P concentrations at the upstream monitoring station (M1, Figure 3.7) on the Dairy Farm stream may be affected by the land and/or the farmyard of the Beef Unit (Section 3.2), which is located upstream of the Dairy sub-catchment (Figure 3.7). The at times erratic and high P levels at the upstream monitoring station (M1) on the Dairy Farm stream made an accurate assessment of the impact of the sub-catchment land on stream water quality impossible. This and the impact of two construction sites on stream quality led to an abandonment of the Dairy Farm site after 6 months of monitoring (Section 3.2). Therefore many of the questions to be answered by the monitoring of the Dairy

Farm stream (Section 1.4) remained unanswered. Especially data on P source areas and information on pathways of P loss and delivery to stream water were missing. Edge of field measurements (described in Chapter 7) did yield information on the potential of overland flow as a pathway of P export. However, very little data on the possibility of P losses in shallow subsurface flow had been collected. This was one of the main reasons for the subsequent monitoring of water in artificial subsurface drains at the Beef Unit (Section 3.2).

Most TP and TDP results are missing for events 1-5 at the upstream (M1) and events 1-4 at the downstream (M2) monitoring station. As a general discussion of the collected P data can be found in Chapter 5, Chapter 9 mainly relies on the DRP results.

9.2 Methods

9.2.1 Instrumentation at the Dairy Farm Stream

The two flow and water quality monitoring stations at the stream in the Dairy Farm (Figure 3.7) were both equipped with automatic samplers (SIGMA 900 Max) with integrated water velocity (doppler principle) and depth probes (pressure transducers). The stream flows underground at the point where it enters the Dairy Farm sub-catchment. The monitoring equipment was therefore set up in an existing concrete block manhole at the sub-catchment boundary (monitoring station M1) (see Section 3.6.1 and Figure 3.7). The manhole had been constructed in such a way that the inflow and outflow pipes were level with the floor of the hole. A shelf was mounted to accommodate the sampler with integrated data logger. The velocity/depth probe was inserted into the pipe leading into the manhole from upstream (43 cm inner diameter). To ensure that samples were always taken at the same position, the sample uptake tube was fastened along the walls and to the bottom of the manhole.

The downstream monitoring station (M2) was set up at the end of the concrete pipe, which had been inserted into the old stone shore underneath the farm roadway at the downstream end of the Dairy sub-catchment (see Section 3.6.1). The depth/velocity probe was again inserted into the concrete pipe (43 cm inner diameter) and the sample uptake tube was positioned in the centre of the stone shore at the end of the concrete pipe. The sampler/data logger was contained in a purpose built concrete structure at ground level adjacent to the stone shore.

Another project (Bartley, 1996) placed a 90° v-notch weir in the section of stream just downstream of the Bogwood (sampling station weir (G2) Figure 3.7). The weir was damaged at installation.

Thus standard tables or discharge formulae could not be used to obtain reliable estimates of flow for given water levels.

9.2.2 Flow Recording and Sampling Programme

At the beginning of the monitoring period, the flow meters were programmed to take water depth and velocity readings every second and record the 1 minute average flow values. The 5 minute average flow values were calculated from these data and a comparison between the 1 and 5 minute averages showed that 5 minute logging intervals were adequate at both sites (Figures 9.1 to 9.4).

To confirm that the flow figures determined by the meters at the upstream (M1) and downstream (M2) monitoring stations were reasonable, the flow over the weir was gauged on four days during low flow conditions in April and May 1997. This was done by recording the water level upstream of the weir and catching the flow over the weir during a measured time interval in a graduated barrel. Thus, only low flow measurements could be carried out.

The sampling programmes were triggered by a water level rise at the monitoring stations (M1 and M2). Because of the slow drop of the water level in the stream at the end of events, the water level to initiate sampling was not constant. It was adjusted at every visit to the sites. Time related sampling was carried out at both monitoring sites during the first three events. The sampling intervals were small at the beginning of the events (15 or 30 minutes) and gradually increased to a sample every 8 hours towards the end of the events. In February 1997, flow related sampling programmes were worked out on the basis of the experience gained with time related sampling. Grab samples were taken during dry periods to gain information on the water quality at low (i.e. non-event) flow conditions.

Grab samples of stream water were taken at the weir (Section 9.2.1, sampling site G2 in Figure 3.7) during event D1. The weir (G2) is located about 477 m downstream of the upstream monitoring station (M1). Site G2 and the stream at the access hole in the middle of the Dairy Farm (Section 3.6.1, sampling site G3 in Figure 3.7) were also sampled when low flow (non-event) samples were taken at the upstream and downstream monitoring sites (M1 and M2). The distance between the weir (G2) and the stream access hole at the Dairy Farm (G3) amounts to approximately 389 m. In addition to providing access to the culverted stream, the hole in the middle of the Dairy Farm (G3) provided access to two subsurface drains. Overland flow was furthermore observed to flow into the hole during event D1. Thus subsurface drainage water (G3D1 and G3D2) and overland flow samples (G3O) were also taken at this site during event D1.

A spring, which rises just north of the Bogwood and is caught in a land drain, contributes water to the stream at the Dairy Farm (Section 3.6.1). To determine the P concentration in the water of that spring, the drain which catches the spring was sampled during low flow conditions from January onwards (G1 in Figure 3.7).

An examination of the P concentrations at the upstream monitoring site (M1) during event D3 revealed unusually high P levels at the end of the event. This suggested the contamination of the water at that site by other than land related P losses. The generally high concentrations at the upstream site during events D1 and D2 had already been cause for concern. An investigation into the possible causes of high P concentrations at this site was therefore undertaken. During its course, grab samples were taken from existing and additional sites. These sites included the drain and the tank at the Beef Unit (see Section 3.6.1, sites A1 and A2 in Figure 3.7), a discharge pipe into the tank from peat filter beds (site P in Figure 3.7), the stream at the access holes at the castle wall (see Section 3.6.1, site A3 in Figure 3.7) and the end of the Bogwood (site A4 in Figure 3.7). The drain and tank at the Beef Unit (A1 and A2) are located about 512 m upstream of M1 and the access hole at the castle wall about 326 m upstream of M1. The distance between M1 and the end of the Bogwood (A4) is about 389 m.

Sampling at those additional sites evolved in the process of the investigation. The furthest upstream site accessible in early 1997 was the tank at the Beef Unit (site A2). The tank was underground but water from it could be pumped up to the yard of the Beef Unit and sampled from a hose. The first such samples were taken in early February 1997. As the DRP levels in the tank were at times considerable, the big iron slab covering the tank was removed on 18th April 1997. A pipe (A1) carried water from a spring and an artificial subsurface drainage system into the tank (Section 3.6.1). The pipe was half submerged. To take samples from it, the water level in the tank was lowered by turning on the hose in the yard. Once the tank was accessible it was discovered that overland flow from land of the Beef Unit could reach the tank via a gully which had been covered by the iron slab. Furthermore, two small pipes (P) from a project on the treatment of dirty water with peat filtration were found to discharge into that tank. One of those pipes was sampled (the other one being dry at that time).

Towards the end of May 1997, a pollutant, which gave rise to high P levels at the upstream monitoring station (M1), found its way into the stream. In order to determine where the pollutant entered, the underground pipe carrying the stream from the tank at the Beef Unit (A2) to the castle wall (A3) (see Section 3.6.1 and Figure 3.7) and a drain discharging into that pipe were uncovered in June 1997 (451 m upstream of M1). In the hope of gaining more information on the causes of high P concentrations at the upstream monitoring station (M1) at the Dairy Farm, samples from the

pipe and the drain were taken (sites X and XD respectively in Figure 3.7) even though monitoring of the Dairy sub-catchment had stopped at the end of May 1997 (Section 3.2). Overland flow from the road was also sampled because it was observed to run into the access hole to the stream at the castle wall (site XR).

After event D3, grab samples were thus taken at various locations during and between rainfall events (i.e. high and low flow conditions).

9.2.3 Data Treatment and Calculations

The data from the Dairy Farm monitoring stations were processed as described in Section 7.2.4. The separation of the data into events was, like at the artificial subsurface drainage site (Section 8.2.3), arbitrary. Land related P losses were under investigation and it was therefore important that the events would include all days during which these occurred. Because the Warren 1 was the wettest site investigated in this study, it could be used to indicate the maximum number of days on which overland flow was likely to occur. No such indicator was available for the occurrence of subsurface water drainage flow into the stream. Thus, the duration of the events at the upstream (M1) and downstream (M2) monitoring stations at the Dairy Farm sub-catchment was chosen to at least encompass all days included in corresponding events at the Warren 1. An exception of this principle was event D4 at the Warren 1. The amount of rainfall during this event was too small to cause a flow response big enough to trigger the sampling programmes at the stream sites.

The graphs of events D4 and D6 at the Dairy farm site (events 5 and 7/8 at the Warren 1) indicated that the hydrographs at the stream sites had not quite levelled off when the overland flow at the Warren 1 had stopped (Figures 9.9 and 9.11). In those cases, events at the Dairy Farm were defined to be of longer duration than the events at the Warren 1.

Scatterplots were used to investigate the relationships between flow and P concentrations, and between P concentrations and other water quality parameters (see Section 7.2.4).

9.3 Results

9.3.1 Flow

There was good agreement between the flow gauged manually at the weir (G2) and the rates measured by the flow meters at the monitoring stations. The rates of flow at the weir (Table 9.1)

were of the same order of magnitude as the flow measurements taken at the upstream and downstream sites (M1, M2).

Table 9.1: Rates of flow at the weir (G2), the upstream (M1) and downstream (M2) monitoring stations.

Date	Time	Flow upstream (M1)	Flow weir (G2)	Flow downstream (M2)
			l/s	
17-Apr-97	10:30	1	1	1
	11:30	1	1	2
23-Apr-97	10:00	0	2	2
	11:30	0	1	2
24-Apr-97	10:00	0	1	2
	15:00	1	1	1
25-Apr-97	09:30	2	3	4
	12:00	2	2	4

The dates of the events monitored at the Dairy Farm sub-catchment, and the corresponding events at the Warren 1 are listed in Table 9.2.

Table 9.2: Dates and numbers of events at the Dairy Farm and corresponding events at the Warren 1.

No. of event at the Dairy Farm	Date start	Date end	Corresponding event(s) at the Warren 1
D1	24-Nov-96	5-Dec-96	1
D2	17-Dec-96	22-Dec-96	2
D3	10-Jan-97	19-Jan-97	3
D4	1-Feb-97	6-Mar-97	5
D5	24-Apr-97	29-Apr-97	6
D6	4-May-97	28-May-97	7,8

For each event, the flow measured at the upstream monitoring site (M1) amounted to well over half (63-95%) of the discharge at the downstream monitoring site (M2) (Figure 9.5). The quantity of water flowing into the Dairy Farm thus exceeded the contribution of the Dairy Farm sub-catchment to the stream. The hydrographs of the upstream and downstream sites were very similar (Figures 9.6 to 9.11). The timing and the heights of the flow peaks were nearly identical at the two sites. There was a slight tendency for the upstream flow to react stronger than the downstream flow to rainfall early on in events. The flow regime at the upstream station (M1) was, furthermore, more erratic and there was a greater difference between minimum and maximum rates of flow. The baseflow rates were higher at the downstream station (M2). Figure 9.8 illustrates this point very well because it depicts an event with generally low rates of flow.

During low flow, the use of water to clean out the buildings and the yard at the Beef Unit (Section 3.6.1) led to small but clear dips in the hydrographs. These dips were more pronounced at the

upstream site (M1). Figure 9.8 shows a good example of such an occurrence and also illustrates the time delay between the passage of the dip at the two sites. The minimum values at the downstream site (M2) were generally measured about 2 hours after they had been recorded at the upstream site (M1) (distance between the two sites is approximately 1.1 km).

Due to the similarity of the hydrographs at the monitoring stations, it is not surprising that there is a strong positive linear relationship between the amounts of daily flow measured at the two sites during events (Figure 9.12). The highest daily flow values at both sites were measured on 3rd December 1996. The greatest amount of rainfall during the monitoring period, on the other hand, occurred on 19th May 1997. Figure 9.13 indicates that heavy rainfall in April and May resulted in much less flow than smaller amounts of rain in January and February. The Soil Moisture Deficit (SMD) was very low until the middle of March, when it started to increase towards a maximum 23rd April 1997.

9.3.2 Concentrations

DRP Concentrations at the Monitoring Stations (M1, M2) During Events

At both sites, the DRP concentrations varied considerably during events. They generally increased with rising rates of flow and dropped again during the falling limbs of the hydrographs (Figures 9.6-9.11). During events D1 and D4, later flow peaks tended to go along with a smaller increase of the P levels than earlier peaks (Figures 9.6 and 9.9). The course of the P levels during events D1, D2, D4 and D5 was quite similar at the upstream (M1) and downstream (M2) monitoring stations. However, the DRP concentrations tended to be higher at the upstream site (M1). Figure 9.14 illustrates that the flow-weighted average DRP concentrations were always higher at upstream site (M1), and that the maximum concentrations measured at the upstream site (M1) were often more than double those measured at the downstream site (M2). In some samples of event D4, however, DRP at the downstream station (M2) exceeded levels measured at the upstream station (M1) markedly. Figures 9.15 and 9.32 document that, during event D4, the P levels recorded for the downstream monitoring station (M2) were high in comparison with other DRP concentrations measured at that site. The water level rise during event D3 was too small to trigger the sampling programme at the downstream site (M2) and only one grab sample was taken. A comparison of the DRP levels at the two sites during event D3 is thus not possible.

As seen in Figures 9.14 and 9.15, there was a marked overall increase in DRP concentrations at the upstream (M1) site during events D5 and D6. The flow-weighted average DRP concentrations of those events were more than double the one measured during event D4. Elevated DRP levels were

also recorded for the downstream station (M2) during events D5 and D6 but the increase in comparison with previous events was not as marked as at the upstream site (M1). Thus, there was a greater difference between the DRP values at the two sites during the last two events.

This point is illustrated very clearly by the graph of the daily flow-weighted average DRP concentration at the two sites (Figure 9.15). The daily averages of events D5 and D6 formed two distinct groups of points with very little overlap, whereas the daily averages of the previous events were mostly of similar magnitude at the two sites. As suggested by above mentioned differences, there was no clear relationship between the daily flow-weighted average DRP concentrations at the two sites (Figure 9.16).

A clear overall relationship between the rates of flow and the DRP concentrations did not become apparent at either the upstream (M1) or the downstream (M2) monitoring stations (Figures 9.17 and 9.18). However, the data of event D5 at the upstream station (M1) and of events D2 and D5 at the downstream station (M2) suggest the existence of clear, positive linear relationships between DRP and flow during these events (Figures 9.19-9.21).

Grab Samples During Events

The P concentrations at the grab sampling sites were compared with the P levels measured in the samples from the automated monitoring stations (M1, M2) taken closest to the time of grab sampling.

The DRP levels of grab samples taken during event D1 are displayed in Figure 9.22. The only additional stream site sampled during event D1 was the weir (site G2, Figure 3.17). The concentrations measured at this site and at the upstream (M1) and downstream (M2) monitoring stations followed different trends on the two days of grab sampling (Figure 9.22). The P levels at the weir (G2) (0.297 mg P/l DRP) were higher than those at the upstream (M1) and downstream (M2) monitoring sites on 25th November. On 27th November, the highest P levels were measured at the upstream monitoring site (M1) (0.301 mg P/l DRP).

The samples of overland flow running into the access hole in the Dairy Farm (G3O, Figure 3.17) on 25th November (event D1) contained 0.606 mg P/l DRP. The DRP levels in samples from the two drains discharging into the same hole amounted to 0.035 (G3D1) and 0.135 (G3D2) mg P/l on 25th November and to 0.012 (G3D1) and 0.062 (G3D2) mg P/l on 27th November.

The DRP concentrations of water samples taken on grab sampling days during event D4 are displayed in Figures 9.23 and 9.24. Figure 9.23 shows the results of days on which the tank at the Beef Unit (A2) was sampled, Figure 9.24 the data of all other grab sampling days. The tank at the Beef Unit (A2) was sampled on 7 occasions during event D4. The concentrations in the tank (range: 0.019-0.225 mg P/l DRP) exceeded those measured at the upstream monitoring site (M1) (range: 0.055-0.175 mg P/l DRP) on 5 out of the 7 days. On most days there was a drop in DRP levels from the upstream monitoring site (M1) to the weir (G2) (range: 0.055-0.122 mg P/l DRP). The magnitude of this decrease varied considerably. The DRP concentrations then normally decreased slightly from the weir (G2) to the stream at the access hole in the Dairy Farm (G3) (range: 0.046-0.106 mg P/l DRP) and the downstream monitoring site (M2) (range: 0.033-0.099 mg P/l DRP). Reflecting the trend at the automatic monitoring stations (Figure 9.9), the DRP levels in grab samples were generally lower in the second than the first half of event D4.

The drain which catches the spring north of the Bogwood (Section 3.6.1, G1 in Figure 3.7) was sampled 6 times during event D4. The DRP levels ranged from 0.014 to 0.048 mg P/l and the average amounted to 0.035 mg P/l. Drains G3D1 and G3D2 were sampled on 11 and 6 days respectively during event D4. The DRP levels measured in those samples were very low. The maximum concentrations amounted to 0.012 mg P/l at drain G3D1 and to 0.027 mg P/l at drain G3D2.

On the one grab sampling day of event D5, the DRP concentrations in the combined discharge from the spring and the artificial subsurface drainage network at the Beef Unit (site A1) was below the limit of detection. The DRP levels were quite high (0.485 mg P/l) in the tank (A2). They decreased to 0.353 mg P/l at the upstream monitoring site at the Dairy Farm (M1) and to 0.075mg P/l at the downstream monitoring site (M2). The discharge from the peat filter beds (site P) was also sampled during event D5. The DRP concentration amounted to 11.7 mg P/l.

Figure 9.25 displays DRP concentrations of grab sampling days during event D6, up to and including the first day of the pollution incident (Section 9.2.2). On the first four grab sampling days, the DRP concentrations in spring/subsurface drainage water (A1) were very low. The DRP levels were considerably higher in the tank at the Beef Unit (A2) and they then decreased towards the upstream monitoring station at the Dairy Farm (M1) and further towards the downstream monitoring station (M2). The differences in DRP concentrations between the sampling sites were small on 19th and 22nd of May. On 20th of May the DRP levels at the upstream monitoring station (M1) were clearly higher than those at all other sites, and on 23rd May they were substantially higher. On 23rd of May an abundance of fungus was observed to cover the wetted area of the pipe at the upstream monitoring station (M1).

Low Flow (i.e. Non-Event) Sampling

The results of the first four low flow (or non-event) sampling days are displayed in Figure 9.26. Figure 9.27 shows the DRP concentrations in all other low flow samples before the pollution incident (Section 9.2.2). The DRP contents of samples taken at the upstream monitoring station (M1) on 13th December 1996 and 17th January 1997 was very small. The amounts of DRP measured at the weir (G2) were slightly higher than those at the upstream station (M1). The concentrations determined at the downstream monitoring station (M2) were comparable to the ones measured at the weir (G2) on 17th January and below the limit of detection on 13th January. From January 24th onward, the samples taken at the upstream monitoring station (M1) generally contained elevated to considerable amounts of DRP and the concentrations usually exceeded those measured in samples taken at the downstream monitoring station (M2). Only on 14th March were the DRP levels at the upstream station (M1) low again.

The DRP levels in the spring water caught by the artificial subsurface drainage network at the Beef Unit (spring sampled at A1 during non-event flow, Figure 3.7) were below detection both times such samples were taken. Figure 9.27 indicates that the high P levels at the upstream monitoring station (M1) were a consequence of the high P concentrations in the tank at the Beef Unit (A2). The low flow period between events D4 and D5 lasted from 7th March to 23rd April. It is noticeable that the DRP concentrations in the tank tended to increase, the longer after the end of D4 they were taken. Figure 9.28 shows that the flow at the upstream monitoring station (M1) decreased during that period. As the stream at the upstream monitoring station (M1) is fed by the spring led into the artificial subsurface drainage network of the Beef Unit (A1 is end point of network), it can be assumed that the amount of spring water flowing into the tank decreased steadily between events D4 and D5.

Pollution Incident

The samples taken during the pollution incident (see Section 9.2.2) were taken during high and low flow conditions. Event D6 lasted until 28th May and there was heavy rainfall on 5th June. Thus high flow (event flow) conditions prevailed on sampling dates up to 28th May and after 5th June. Low (non-event) flow was sampled from 29th May to 4th June.

On 23rd May 1997 a white fungus was first detected at the upstream monitoring station (M1). It covered the entire wetted perimeter of the pipe. On investigation, fungus was also discovered at the stream access hole at the castle wall (A3) but not in the tank at the Beef Unit (A2). High P levels were measured in a grab sample taken at the upstream monitoring station (M1) early in the morning of 23rd May (Figures 9.11 and 9.25). The DRP levels of a sample taken by the automatic

sampler 15 minutes later were not extremely high for the upstream monitoring station (M1) (0.246 mg P/l), but the TP concentration in that sample still exceeded 1 mg P/l (Figure 9.29).

Consistent with the lack of fungus in the tank at the Beef Unit (A2), the DRP levels in samples taken to investigate the pollution incident were often considerably lower in that tank than at the upstream monitoring station at the Dairy Farm (M1) (Figure 9.30). The underground pipe containing the stream was therefore excavated and made accessible downstream of the tank at the Beef Unit on 6th May. The sections of pipe upstream and downstream of the new stream access hole (site X, Figure 3.7, see Section 9.2.2) were also covered in fungus and the two grab samples taken at that site had higher DRP levels (0.272 and 0.153 mg P/l) than the samples taken from the tank (A2) at about the same time (0.100 and <0.005 mg P/l). The pollutants had thus been flowing into the underground stream between the tank (A2) and the new stream access hole (X).

A 6 inch drain (XD) leading into the underground stream from the direction of the Beef Unit was also uncovered at the new stream access hole (X). This drain was initially thought to contain nothing but roof water. It was sampled after heavy rainfall on 5th and 6th June and the DRP levels measured in the samples amounted to 1.036 and 0.291 mg P/l respectively. Overland flow from the road (XR) was sampled on 5th June and the discharge pipe from the peat filter bed (P) on 6th June. These samples contained 0.306 and 0.599 mg P/l respectively.

On 26th, 27th and 29th May, the DRP concentrations at the downstream monitoring station (M2) at the Dairy Farm were substantially lower than those measured at the upstream monitoring station (M1) (Figure 9.30). On the one day on which a sample was taken just downstream of the Bogwood (A4), the main reduction in DRP levels had occurred between the upstream monitoring station (M1) and the end of the Bogwood (A4).

Other Water Quality Parameters and their Relationships to P

At both sites, all measured water quality parameters varied considerably during events.

In general, the total oxidised nitrogen (TON) levels were slightly higher at the upstream (M1) than the downstream (M2) site (Figures 9.31 and 9.32). However, the only TON concentration which exceeded 10 mg N/l was measured on 21st March 1997 at the downstream site (M2). At both sites, the TON concentrations of the last two events tended to be lower than those measured during previous events.

Overall, the total ammonia (TA) concentrations tended to be higher at the upstream (M1) than the downstream (M2) site (Figures 9.31 and 9.32). At both sites the concentrations reached higher values during events D1, D5 and D6 than during the other events and the low flow periods. The potassium (K) levels were clearly higher at the upstream (M1) than the downstream (M2) site (Figures 9.33 and 9.34). There was a very slight tendency of decreasing K levels from event D1 to the low flow period preceding event D5. From event D5 onward, the K levels tended to rise again. Conductivity was similar at the upstream (M1) and downstream (M2) monitoring stations but lower levels generally occurred at the upstream site (M1) during events (Figures 9.35 and 9.36). The amount of suspended solids (ss) was often higher at the upstream (M1) than the downstream (M2) site but excessive amounts of ss were determined during event 6 at the downstream site (M2) (Figures 9.37 and 9.38).

The levels of nutrients other than P for samples taken from the peat filter bed discharge pipes and from overland flow on the road are summarised in Table 9.3. The K levels were excessively high in the effluent from the filter bed, and the same is true for the TA concentrations of the first two samples.

Table 9.3: TON, TA and K concentrations in samples taken of peat filter bed effluent and overland flow from the road.

Site	Date	TON mg N/l	TA mg N/l	K mg/l
P	18-Apr-97	<0.3	50.56	>80
P	28-Apr-97	<0.3	27.74	>80
P	6-Jun-97	2.4	0.32	41.5
XR	5-Jun-97	5.7	4.60	9.1

At both monitoring sites (M1 and M2) there was a positive linear relationship between the DRP and the K concentrations (Figures 9.39 and 9.40). Figures 9.41 and 9.42 suggest negative relationships between DRP and the TON and DRP and conductivity values at the downstream monitoring station (M2). These relationships are hardly detectable in corresponding figures of data of the upstream monitoring station (M1) (Figures 9.43 and 9.44). There was a small tendency of conductivity to decrease with rising rates of flow at both stations. Upstream TON tended to increase with flow slightly. This weak trend also occurred at the downstream station but there a minor tendency of TON to decrease with flow could further be observed.

The number of samples analysed for both TP and ss was too small to give information on a possible relationship between those parameters.

9.3.3 P Exports

Figure 9.45 shows that the amount of DRP imported into the Dairy Farm with stream water was greater than the amount exported from the Dairy Farm via the stream for all but two events. The net DRP exports (exports minus imports) and the percentage of the net exports in reference to the sum of the DRP loads upstream (M1) and downstream (M2) are plotted in Figure 9.46. The figure shows that the DRP retention (negative DRP net exports) in the Dairy Farm during events D4 and D6 dwarfed the values for retention or net export which were calculated for the other events. During event D3 there was a net P export of greater than 18% but the absolute figure was not very high.

The figure of the daily DRP imports and exports (Figure 9.47) reveals that the maximum values of both occurred during event D1 and that the imports were unusually high in comparison with the exports on some days mid to end of May 1997. Comparatively high DRP imports also occurred on 3rd, 4th and 27th of February and slightly elevated exports in reference to imports were measured on 18th and 19th February.

9.4 Discussion

9.4.1 Overview of Stream Flow and DRP Concentrations in the Dairy Farm Stream

The contribution of the Dairy Farm sub-catchment to peak storm flow in the stream was generally small. The sometimes higher rates of peak flow at the upstream (M1) than the downstream (M2) monitoring station suggest that the Dairy Farm sub-catchment was buffering extreme flow values from upstream. This effect is probably largely attributable to the area of wetland called the Bogwood (Section 3.6.1) as the stream runs through concrete pipes throughout most of the Dairy Farm sub-catchment. The Bogwood contains a complicated network of small, distinct channels, dead waters, small ponds and extended areas of marshy land. Most of the area of the Bogwood is flooded during wet periods. The spring at the beginning of the Bogwood, the water stored in the Bogwood, and probably some soil water then sustained flow in the Dairy Farm stream during a falling hydrograph, and thus maintained clearly higher low flow rates at the downstream station than were measured upstream.

Storm flow from the Dairy Farm sub-catchment was thus more dependent on the water contributed by upstream areas than on water reaching the stream within the sub-catchment. The close relationship between flow measured at the upstream (M1) and downstream (M2) monitoring stations is further underlined by the strong correlation between daily flow values (Figure 9.12).

The response of stream flow to rainfall was greatly affected by the SMD. Such a pattern has already been established for overland flow (Section 7.4.1) and it is therefore not surprising that the maximum daily flow in the stream and at the overland flow monitoring field at the Cowlands were measured on the same day. The similar but disproportional rises and falls of the chemo- and the hydrographs at each site (M1 and M2) during the course of events recalls more the patterns found in connection with overland than shallow subsurface flow. Reflecting the huge variety of factors influencing P concentrations in the stream, clearly perceptible positive relationships between flow and DRP only occurred during 1 event at the upstream (M1) and 2 events at the downstream (M2) monitoring stations (Figures 9.19-9.21).

Not only the majority of storm flow but also the greatest part of the P in it reached the Dairy Farm stream from upstream areas rather than the sub-catchment itself. The DRP concentrations indicated better water quality at the downstream (M2) than the upstream monitoring station (M1), and the DRP exports were generally exceeded by the imports (Figure 9.47). Given the fact that the net export/retention calculations are based on P loading figures of, at best, moderate accuracy (see Section 7.4.3), differences of less than 15% (in reference to the sum of upstream and downstream loadings) between upstream (M1) and downstream (M2) loads can be dismissed, and differences up to 25% should be viewed with caution. Thus the only unambiguous difference between DRP loads at the upstream (M1) and downstream (M2) monitoring stations was the DRP retention by the Dairy Farm sub-catchment during event D6. The DRP retention of 18% during event D5 may reflect reality but the figure for the net export measured during event D3 is unlikely to be reliable because the downstream (M2) DRP load calculation was based on 1 sample. As the upstream (M1) flow-weighted average DRP concentration during event D3 was much higher than the DRP level of the single downstream sample, the greater amount of water at the downstream station (M2) during this very small event led to the P exports exceeding the imports. This raises the question whether there generally was a net P export from the Dairy Farm sub-catchment during periods of low flow. The sampling programme of this study was not geared towards non-storm losses. However, the downstream (M2) baseflow was not normally more than double the upstream (M1) flow but the upstream DRP levels in low flow grab samples commonly exceeded the downstream concentrations multifold. Overall it can therefore be said that the Dairy Farm sub-catchment is more likely to be a DRP sink than a DRP source.

The grab sampling programme helped to pin-point where along the stream the main decrease in P concentrations occurred. From the upstream monitoring station (M1) to the weir (G2) (Figure 3.7) the DRP levels dropped most times but they were also shown to rise on some occasions. Because the drops were normally greater than the increases it can be said that, overall, DRP levels were depressed downstream of the wetland (Bogwood), which ended just upstream of the weir (Figure

3.7). Some of the decrease in DRP concentrations was attributable to dilution by the spring rising in the Bogwood but, at times, large differences in concentration upstream and downstream of the Bogwood strongly suggest that DRP removal in this area of wetland did take place. This finding agrees with work establishing the usefulness of wetlands for P attenuation (Casey and Klaine, 2001; Gale et al., 1994). The usually gentle DRP decrease from the weir (G2) to the stream access hole in the middle of the Dairy Farm and to the downstream monitoring station (M2) was probably caused more by dilution with low DRP subsurface flow than P removal as the stream mainly ran through concrete pipes in that section.

The DRP concentrations of overland flow and flow from one of the subsurface drains discharging into the stream access hole in the middle of the Dairy Farm (G3) show that land related losses did occur in the Dairy Farm sub-catchment. However, these DRP inputs to the stream seemed to be more than offset by the P retention in the Bogwood. As mentioned above though, our sampling programme was aimed at losses during high flow conditions and could have missed net exports from the sub-catchment between events.

The often high DRP levels in the tank at the Beef Unit (A2) documented that the upstream monitoring station (M1) at the Dairy was usually influenced by P losses from the land of the Beef Unit (overland and/or subsurface flow) and/or the discharge from the peat filter beds. The amount of dirty water applied to the filter beds remained constant. The effluent increased with rainfall but the DRP concentration in it decreased accordingly (Table 9.3). Thus, the amount of P discharged from the filter beds was unlikely to have been excessively variable during the monitoring period and the filter beds probably behaved like a point source. This assumption is confirmed by the observation that, during low flow periods when the filter beds were the only DRP source, the concentrations in the tank (A2) increased with declining flow from the spring (Figures 9.27 and 9.28), and therefore with decreasing dilution of the filter bed effluent (P). This type of pattern has generally been associated with point sources of pollution (MacDonald et al., 1995; Muscutt and Withers, 1996; Osborne and Wiley, 1988). During storm events, overland flow from the land of the Beef Unit was observed to flow into the tank (A2) and hence affect the DRP levels. The grab samples taken from the spring/subsurface drains at the Beef Unit (A1) in spring 1997 contained little DRP but intensive monitoring of the combined (spring/subsurface water) discharge pipe in winter 97/98 (Section 8.4.2) showed that DRP entered into the tank (A2) via the artificial subsurface drainage network.

As the peaks in the chemographs coincided with the flow peaks, the high flow and, therefore, land related losses made up the bulk of the P exports from the Beef Unit. The occasional influence of overland flow from the road and leakage from the Beef Unit farmyard and facilities on stream

water quality was revealed by the pollution incident and by the DRP values at the upstream Dairy Farm monitoring station (M1) sometimes significantly exceeding the concentrations in the tank at the Beef Unit (A2).

9.4.2 Management Practices and Water Quality

There is no obvious explanation for the few high (in comparison with upstream measurements) DRP levels at the downstream station during event D4. This event was preceded by a slurry application in the Dairy Farm sub-catchment but as neither the TA, TON nor the K levels were elevated, it is unlikely that slurry spreading influenced the DRP levels in the stream. Moreover, neither N applications in February and March nor N, P, K fertilisation in the Dairy Farm sub-catchment during May led to elevated levels of any of these nutrients in stream water.

An effect of fertilisation at the Beef Unit on water quality may, however, be detectable. The exact date of the P and K application to the land of the Beef Unit in February 1997 was not recorded (Section 3.5.2). However, towards the end of event D4 ($26^{th}/27^{th}$ February) there was a distinct DRP peak during the receding limb of the hydrograph (Figure 9.9). In the same samples K levels were clearly elevated (Figure 9.33). Furthermore, two obvious TA peaks (25^{th} April and 19^{th} May) (Figure 9.31) at the upstream monitoring station (M1) are likely to have resulted from N fertilisation at the Beef Unit in April and May (Section 3.5.2). The TA peaks coincided with DRP peaks in stream water but, as both were recorded during flow peaks when DRP values are usually up anyway, an impact of N fertilisation on DRP levels in stream water cannot be postulated on the basis of these results. The corresponding flow peaks also let us dismiss the hypothesis that the TA peaks were caused by high TA levels in effluent from the filter beds, because the effect of filter bed discharge on stream water quality was shown to decrease with flow (see above).

N fertilisation carried out at the Beef Unit in March did not affect stream water, which is not surprising as March was dominated by non-storm flow. Weak reflections of the aforementioned DRP and TA peaks detected at the upstream monitoring station (M1) were visible at the downstream station (M2). Thus fertilisation at the Beef Unit only had a slight impact on nutrient levels in the stream leaving the Dairy Farm, and the already addressed positive effect of the Dairy Farm sub-catchment on the quality of the stream again becomes apparent.

The above discussion shows that fertiliser applications at the Beef Unit were responsible for some of the enhanced daily flow-weighted average DRP concentrations at the upstream monitoring station (M1) of the Dairy Farm sub-catchment recorded for events D5 and D6. Grazing of the land at the Beef Unit, which started mid April, may also have been a contributory factor. A seasonal,

not management related effect on land related P losses is not proposed by these data because the flow-weighted average DRP concentrations calculated for events D5 and D6 at the downstream monitoring station (M2) were only very slightly elevated in comparison with those calculated for event D4.

The reactions of the stream chemistry to management practices at the Beef Unit are consistent with the connections between management operations and overland and artificial subsurface drain flow quality described in Sections 7.4.2 and 8.4.2. The strong positive relationships between DRP and K concentrations at the upstream (M1) and downstream (M2) monitoring stations are more similar to the ones described for artificial subsurface drainage (Section 8.3.3) than overland flow (Section 7.3.3). This may underline the importance of artificial subsurface drainage as a contributor of nutrients to stream flow at the Beef Unit and the Dairy Farm. However, the stream at the Dairy Farm was monitored in winter 96/97, the artificial subsurface drainage network in winter 97/98 and measurements at the overland flow sites were made during both of these winter half years and throughout the summer between them (summer 1997). Thus the relationships between DRP and K concentrations could be influenced by the differences in monitoring periods and the relationships found at the different sites are therefore not really comparable.

As a result of the investigations carried out (Section 9.2.2), the extraordinarily high P (all fractions) and K values at the upstream monitoring station (M1) at the end of event D6 were discovered to be the result of silage effluent getting into the stream between the tank at the Beef Unit (A2) and the new access hole to the stream (X). The samples taken at various locations along the stream running from the Beef Unit to and through the Dairy Farm indicated the farmyard of the Beef Unit to be the point of origin of the pollutant (Section 9.3.2). It was subsequently discovered that one of the silage pits at the Beef Unit had a cracked floor and the effluent was able to find a subsurface pathway to the stream. Excessive amounts of suspended solids at the downstream station in the second half of May were attributable to the construction of the Department of Agriculture building (Section 3.2). Very turbid overland flow was observed to flow from the building site to the stream access hole in the middle of the Dairy Farm (G3) and into the stream. This happened shortly after construction had began and it illustrated that from then on an unknown and unpredictable, not farming related, influence was going to work on the stream. The Dairy Farm site was therefore abandoned (Section 3.2).

9.4.3 Site Characteristics and Water Quality

Site characteristics or timing in relation to rainfall must have been responsible for the fact that management practices at the Beef Unit but not the Dairy Farm affected the storm flow nutrient

levels in stream water. According to the evidence found in stream water, P and K application and some of the N fertilisation at the Beef Unit was carried out during or near wet periods. The same is true for slurry (just preceding event D4) and fertiliser applications at the Dairy Farm, however (Section 3.6.2), and grazing animals were present in both areas during the last two events. Hence overland and shallow subsurface flow producing areas, and fast hydrological connections between the land and the stream must have been more prevalent at the Beef Unit than the Dairy Farm. The greater proportion of poorly and imperfectly drained soils at the Beef Unit than the Dairy Farm (Figures 3.2 and 3.4) lends support to this interpretation. Wet soils are likely to produce overland flow (Cooke and Dons, 1988) and networks of artificial subsurface drains may furthermore have been installed to improve their drainage. Overland flow is known to be an efficient mechanism of delivering nutrients to water bodies (Correll et al., 1999; Pionke et al., 1988; Sharpley and Syers, 1979), and, in some situations, artificial subsurface drains are thought to foster the development of preferential flow pathways (Dils and Heathwaite, 1996) (Section 4.4.3) and they may thus have limited success in reducing the P losses from some wet areas (Hawkins and Scholefield, 1996). The nutrient loss potential of wet but artificially drained soils is likely to be greater than that of naturally well drained soils.

The drainage characteristics of the land may explain the different impacts the two areas had on water quality but the result that a reasonably intensive farm (Section 3.6.2) could act as a sink for nutrients in stream water is still surprising. The high levels of P in the stream on entering the Dairy Farm and the effect of the Bogwood on water quality were largely responsible for this occurrence. The combination of these elements created a situation where first, elevated levels of nutrients were present in stream water, and second, circumstances which furthered dilution and nutrient removal were provided in the Bogwood. Dilution would have occurred as a consequence of the contributions of water low in P from the spring rising just upstream of the Bogwood (sampled at G1 in Figure 3.7) to the water flow through this area of wetland. Nutrient removal is likely to have occurred due to the fact that flow through the Bogwood occurred through an intricate network of very small channels, ponds and marshy areas. Thus increased opportunities for nutrient attenuation by soil/sediment and plant uptake were given. The above discussion suggests that it was mainly the interactions between the Bogwood and the nutrient losses from the Beef Unit which were responsible for the Dairy Farm sub-catchment to act as a nutrient sink. Moreover, due to the high upstream nutrient levels and the considerable error (30-50%) associated with a result based on a difference of loading figures, moderate nutrient losses from the land of the Dairy Farm sub-catchment were undetectable and their occurrence therefore cannot be dismissed. Still, the effect of the Dairy Farm sub-catchment on DRP concentrations in the stream indicates that the Dairy Farm operation (land and farmyard) probably led to small DRP losses to stream water. Elevated P levels during storm flow conditions have even been measured in extensively managed agricultural

catchments, and the concentrations were shown to increase with more intensive agricultural use (Kilmer et al., 1974; Lambert et al., 1985; Owens et al., 1991). Against this background and considering the P imports from upstream areas, the flow-weighted average high flow DRP concentration of 0.102 mg P/l for the monitoring period is low given the land use characteristics at the Dairy Farm. However, even lower P concentrations in drainage water of agricultural grassland catchments have also been reported (Kilmer et al., 1974; Lambert et al., 1985). Obviously variations in site characteristics (including for example hydrology, soil type and weather), management practices and interactions between these explain the different results.

CHAPTER 10: CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

10.1 Introduction

In this chapter, the research findings detailed in the previous chapters are summarised, with reference to the project aims as outlined in Chapter 1. The research has yielded a substantial amount of data on phosphorus (P) loss from agricultural grassland to water. However, it should be borne in mind that the data presented are typical of the monitoring period of this study because soil chemical and biological processes, management practices and the timing of the above in relation to flow events influence the amount of P mobilised and transported. All the aforementioned then are affected by past and present weather conditions. Our results are furthermore specific to our sites because there are many variables influencing P concentrations and P exports in overland and artificial subsurface flow. At each point in time, the potential of land to enrich overland and subsurface flow with P is affected by site characteristics such as soil chemistry and biology, soil hydrology and agricultural management practices.

10.2 Aim 1: Phosphorus Export with Overland Flow from Agricultural Grassland of Different Soil P Levels

The estimated yearly P exports for the low and the high soil P sites (698 and 4,764 g P/ha respectively as dissolved reactive P (DRP)) are considered to be of environmental significance, provided that the P leaving the fields reaches a water body. As the annual total P (TP) loss from the high soil P site could amount to a figure in the region of 20% of the yearly P fertiliser application, P loss with overland flow may also be important from an agronomic and economic point of view.

The overland flow at the three overland flow monitoring sites (Warren 1, Warren 2 and Cowlands) was undoubtedly enriched with P. At each site, the concentrations measured during an overland flow producing rainfall event were extremely variable, but there was a very clear and consistent trend for the P levels in overland flow to increase from the low soil P (Warren 1) to the medium (Warren 2) and the high soil P site (Cowlands) (Aim 1.1). This establishes an influence of the soil P level, or a related factor such as the P content of dead and live organic matter, on P concentrations in overland flow from gley soils across environmental conditions and across most grassland management practices typical for pastures of the soil P levels studied. The quantities of overland flow produced at the sites, of course, also influence the P concentrations (Sharpley et al., 1977). However, as the P concentrations in overland flow from a wetter site would be higher than those in water from a drier site of equal soil P level (Sharpley et al., 1977), the differences of the

quantities of overland flow at our sites (Warren 1 produced more than Cowlands) strengthen the argument for an effect of soil P status or a related factor on the P levels in overland flow. Rainfall simulation studies by Pote et al. (1996; 1999) suggest that the tendency of the P concentrations in overland flow to increase with rising P status of gley soils can also be found in connection with other soil types.

Even though the amounts of overland flow produced were more comparable between the sites than the P concentrations, the variations in overland flow volume still showed that, overall, the Cowlands was the driest and the Warren 1 the wettest site. The total annual quantity of overland flow from the Warren 1 and the Cowlands amounted to 62% and 36% respectively of the yearly rainfall. The areas studied covered some of the range of drainage patterns associated with gleys. Gley soils in general are of impeded drainage and they are waterlogged for a part of the year (Gardiner and Radford, 1980). In Ireland, gleys make up a large proportion of the wet soils in agricultural use. Wetter soils like peaty gleys and peats moreover sorb P less strongly than mineral soils (Daly et al., 2001), and they therefore have an even greater potential for P loss due to agricultural use than gleys. However, the area of such soils which is farmed intensively is expected to be small. The P concentrations and exports measured in our work thus have some relevance for a large proportion of the land in Ireland from which significant amounts of P are likely to be lost with overland flow.

The monthly P export was generally lowest at the Warren 1 (low soil P site), intermediate at the Warren 2 (medium soil P site) and highest at the Cowlands (highs soil P site). As the variations of the P concentrations between the sites were far greater than the variations of the amounts of overland flow, the P concentrations were responsible for the majority of the inter-site differences in P exports (Aim 1.3).

Due to this principal influence of the P concentrations in overland flow on the differences in P exports between the sites, a relatively rough assessment of soil drainage characteristics, for example the method used by the Soil Survey of Ireland (e.g. Gardiner and Radford, 1980), is likely to be adequate to express, in relative terms, the part of the pollution potential of sites which can be attributed to the amount of overland flow produced. Also in relative terms, the soil P levels of gleys can be used to assign a risk factor associated with P concentrations in overland flow from sites.

Concerning the hydrology of the overland flow sites (Aim 1.2), the data suggest strongly that saturation excess overland flow when soil water levels reached the soil surface was the main mechanism of overland flow production. However, return flow was also observed and the

infiltration capacities measured at the overland flow study sites point towards the occurrence of infiltration excess overland flow. Within each of our overland flow sites, the water table levels were shown to vary spatially and temporally. Thus, saturation excess overland flow was not produced evenly throughout the sites. Overland flow early on during events is likely to have stemmed from areas in which the water table levels had reached the ground surface the quickest. During the course of events, the overland flow producing areas would then have expanded as saturated conditions became more prevalent.

In reference to the total amount of overland flow produced during events, the early parts of events were more important at the Warren 1 than the Cowlands (Aim 1.3). As the P levels in early overland flow were often particularly high, the flow pattern observed at the Warren 1 can be expected to have furthered edge-of-field P losses in comparison with the flow response described for the Cowlands. However, this effect was overshadowed by the overwhelming influence of the soil P level (or a related factor) on the concentrations of P in overland flow at the Warren 1 (low P site) and the Cowlands (high P site).

Weather conditions (present and antecedent) influenced the amount and quality of overland flow (Aim 1.4). However, it was often difficult to separate such effects from the impact of management practices on overland flow quality and quantity. Still, the percentage of rainfall that was turned into overland flow was strongly influenced by the Soil Moisture Deficit (SMD) and therefore by antecedent rainfall and evapotranspiration. At the Warren 1 there was furthermore a detectable, but not management related, increase of P concentrations in overland flow in springtime, which may be due to increased organic P mineralisation at higher temperatures. Overall, the combined effects of the environmental conditions and the management practices on overland flow quality and quantity led to vast variations of P exports between events. This point is well illustrated by the fact that a large rainfall event during summer, when the P levels in overland flow were high, was responsible for nearly half the annual P losses from the Warren 1 and the Cowlands. The high P concentrations in overland flow during summer months suggest that at this time of year the soil, cattle faeces and fertilisers supply enhanced amounts of P available to overland flow.

10.3 Aim 2: P Exports from Agricultural Grassland via Artificial Subsurface Drains

The P concentrations measured in water collected by the artificial subsurface drainage network at the Beef Unit at Johnstown Castle during storm flow ranged from low to high (maximum DRP level of 1.650 mg P/l) (Aim 2.1). During a rainfall event there was often a perceptible trend of the P concentrations to rise with increasing rates of flow (Aim 2.4). The results of the dye studies and

the soil water samples support the interpretation that natural and man-made preferential flow pathways allowed fast movement of overland flow down the soil profile and into the artificial subsurface drainage system (Aim 2.2). P concentrations were shown to remain high in water during bypass flow (zero-tension samples). P mobilised and transferred into water at the soil surface is thought to have reached the artificial subsurface drainage system. The observation that P levels in macropore water were dependent on topsoil P levels is consistent with the higher levels of P in overland flow measured at the high than at the low soil P site.

The elevated P concentrations at high flows suggest that artificial subsurface drain flow may have been dominated by contributions from preferential flow pathways during peak flow. However, an estimate of the relative contributions of matrix and preferential flow to flow in the artificial subsurface drainage network is not possible on the basis of the data presented here.

The information on P in artificial subsurface drainage water is less transferable to other areas than the knowledge gained from the overland flow sites because the prevalence of naturally occurring preferential flow pathways is another factor adding to site-specific variability. The creation of preferential flow pathways can, furthermore, happen as a result of the installation of artificial subsurface drainage networks. The backfill material over the drains takes time to settle and it tends to react differently to environmental conditions (e.g. cold, wet, dry) than the undisturbed soil. Thus preferential flow pathways often develop along the interface between the soil and the backfilled trenches (Uusitalo et al., 2001). A network of macropores, which developed along the excavation walls and the backfilled material over the drains, was thought to still allow the transfer of particulate material from the topsoil to subsurface drainage water 50 years after the installation of the subsurface drainage system (Uusitalo et al., 2001). It is, therefore, likely that bypass flow into artificial subsurface drainage networks is the rule rather than the exception.

10.4 Aim 3: The P loss Potential of an Intensive Dairy Farm

The Dairy Farm at Johnstown Castle is likely to have acted as a P sink rather than a source of P during the events monitored (Aim 3.1). During high flow conditions, the land of the Dairy Farm generally had a buffering effect on flow and P concentration peaks measured at the upstream boundary of the Dairy Farm sub-catchment (Aim 3.4). This occurrence is largely attributed to an area of wetland through which the Dairy Farm stream flows.

The water of the Dairy Farm stream was shown to consist of a mixture of overland and subsurface flow. Information on the importance of the different flow pathways and on source areas of P loss cannot be deduced from the data presented here.

10.5 Aims 1.4, 2.3 and 3.3: Effects of Agricultural Management Practices on P Losses to Water

Effects of agricultural management practices on water quality were picked up in overland flow, artificial subsurface drain flow and stream water. At sites other than the Dairy Farm, the P, K and N levels in water were elevated when these elements were applied to land as organic or inorganic fertiliser just prior to heavy rainfall. The strong response of the stream water quality to slurry application at the Beef Unit in combination with a lack of a response of stream water quality to slurry spreading at the Dairy Farm was interesting. Generally, the same management practices carried out under similar conditions at the Beef Unit and at the Dairy Farm differed considerably in their impact on stream water quality. This suggests that rapid active hydrological connections between the stream and the land were of great importance at the Beef Unit but of minor significance at the Dairy Farm.

Unexpected also was the strong effect of a growth response, triggered by urea application, on P concentrations in overland flow. The drop in P levels was so pronounced that it resulted in the only occasion when maximum P concentrations in overland flow from the high soil P site were lower than those measured at the low soil P site during the same event. The overland flow data left open the question whether nitrogen fertilisation can trigger an increase of P levels in overland flow. The amounts of dissolved organic and condensed P in overland flow were greatly enhanced when an event starting with a period characterised by low rates of flow occurred shortly after animals had grazed an overland flow site. However, in general there still is a lack of information on the impact of grazing animals on P loss with overland and subsurface flow.

10.6 Aim 4: The Different Forms of P Lost

Dissolved forms of P made up the majority of total P in overland flow and subsurface flow (77% and 70%, respectively). There was a tendency for particulate P to be more important in water from artificial subsurface drains than in overland flow. Most of the dissolved P was in reactive from. There was some evidence that dissolved unreactive forms of P (dissolved organic and condensed P) in overland flow were enhanced by the presence of grazing animals in the fields.

The high total P levels in overland flow from the Warren 2 were not representative of overland flow from grassland areas because the source of particulate material at that site was a mound of low P subsoil. The elevated total P concentrations at that site are witness to a rapid uptake of dissolved P by solids suspended in overland flow.

The importance of the different forms of P was very variable in the Dairy Farm stream. Not enough total dissolved P and total P data were available to describe general trends.

10.7 Suggestions for Further Research

The surprisingly high levels of dissolved organic and condensed forms of P in rainwater need further investigation. A study looking at different sampling techniques and spatial variations of rain water quality would yield valuable information on atmospheric depositions and sources of P.

Because of the overruling importance of P concentrations in overland flow for estimating the P exports from soils of impeded drainage, it would be useful to have a way of assessing the P actually released from soil to water at a particular site under field conditions rather than to just estimate the content of P in the soil. The measurements taken at the sites described here show that the variability of the P concentrations in overland flow is enormous during an event and throughout the year. Management practices and probably some seasonal effects contribute to the variations. As past and present weather conditions also affect P concentrations in overland flow, year-to-year variability has to be considered. To reduce this complexity and express the risk of P loss from a site, a P value in overland flow which will mainly change with soil P levels and site specific characteristics such as soil chemistry and hydrology is needed. The data of this study show that the P concentrations in samples taken at the end of sizeable overland flow events, which occurred well into the wet season (winter half year), were comparable between events and years, but clearly different between sites. Targeted sampling could, therefore, be carried out under the conditions described above and records of a variety of sites with varying soil P levels collected. Comprehensive monitoring programmes at some sites could put the point measurements in context of the variability of P concentrations to be expected during events, seasons and years, and due to management operations typically associated with pastures.

At the overland flow sites monitored in this study, the water table levels below the surface often corresponded well to the negative soil moisture deficit (SMD) multiplied by ten. This occurrence is likely to have been a consequence of the air filled pore space (AFPS) at our sites. Work to confirm or dismiss this assumption, and to investigate whether an AFPS measurement in combination with the SMD calculation generally allows a reasonable estimate of the water table levels in gley soils could be of great benefit. As the SMD model based on Brereton and Hope-Cawdery (1988) can be used with automatic hourly weather data recorded at several locations in Ireland, a local up to date SMD value is available. In connection with the amount of rainfall expected, the SMD in combination with an AFPS measurement may indicate how likely it is that overland flow on gley soils in the locality will occur. As gley soils make up a large proportion of

the wet but relatively intensively farmed land in Ireland, losses due to spreading of slurry or fertiliser just before the occurrence of overland flow could thus largely be avoided as long as the long range (several days) weather forecast is reliable.

More information is also needed on the occurrence of preferential flow and elevated P levels in shallow subsurface flow (natural and artificial drainage), and there is clearly great scope for research on the impact of agricultural management practices on edge of field P losses and P concentrations in water bodies. Work needs to be carried out on the effects various agricultural management practices can have when carried out on land of various drainage classes and throughout the year.

The data on the Dairy Farm stream showed up another set of research needs. It concerns the spatial integration of P sources, the P delivery to water bodies, the dynamic interactions of these with present and past weather conditions, and the impacts of stream characteristics, like for example small natural wetlands, on hydrology and water quality. In other words: does P, once mobilised from a particular area and transported in overland or shallow subsurface flow, reach a freshwater body? To what degree do parameters such as storm size influence the hydrological connection between source area and water body? And what happens to P after its delivery to a small stream draining agricultural land?

REFERENCES

Addiscott, T.M., D. Brockie, J.A. Catt, D.G. Christian, G.L. Harris, K.R. Howse, N.A. Mirza, and T.J. Pepper. 2000. Phosphate losses through field drains in a heavy cultivated soil. Journal of Environmental Quality 29: 522-532.

Ahl, T. 1988. Background yield of phosphorus from drainage area and atmosphere: an empirical approach. Hydrobiologia 170: 35-44.

Ahuja, L.R., A.N. Sharpley, M. Yamamoto, and R.G. Menzel. 1981. The depth of rainfall-runoff-soil interaction as determined by ^{32}P. Water Resources Research 17: 969-974.

Ahuja, L.R., A.N. Sharpley, and O.R. Lehman. 1982. Effect of soil slope and rainfall characteristics on phosphorus runoff. Journal of Environmental Quality 11: 9-13.

Alberts, E.E., W.H. Neibling, and W.C. Moldenhauer. 1981. Transport of sediment nitrogen and phosphorus in runoff through cornstalk residue strips. Soil Science Society of America Journal 45: 1177-1184.

Anderson, G., E. G. Williams and J. O. Moir. 1974. A comparison of the sorption of inorganic orthophosphate and iniositol hexaphosphate by six acid soils. Journal of Soil Science 25: 51-62.

Anderson, M.G., and T.P. Burt 1990. Subsurface runoff. pp. 365-400. *In* M.G. Anderson, and T.P. Burt (ed.) Process Studies in Hillslope Hydrology. John Wiley & Sons, Chichester.

Andraski, B.J., D.H. Mueller, and T.C. Daniel. 1985. Phosphorus losses in runoff as affected by tillage. Soil Science Society of America Journal 49: 1523-1527.

Angulo-Jaramillo, R., F. Moreno, B.E. Clothier, J.L. Thony, G. Vachaud, E. Fernandez-Boy, and J.A. Cayuela. 1997. Seasonal variation of hydraulic properties of soils measured using a tension disk infiltrometer. Soil Science Society of America Journal 61: 27-32.

Anon. 1986. The analysis of agricultural materials. Ministry of Agriculture, Fisheries and Food, reference book 427. Her Majesty's Stationary Office, London.

Anon. 1991. Continuous flow analysis manual. M. B. Scientific Services Ltd, Cambridge.

Anon. 1995. Standard methods for the examination of water and wastewater, 19th edition. American Public Health Association, Washington.

Anon. 1996. A nutrient export study of one farm unit in the Dripsey catchment – Development of a baseline for nutrient management planning. A report by the Aquatic Services Unit and Civil Engineering UCC, commissioned under the LIFE programme by Teagasc, Johnstown Castle, Wexford.

Anon. 1997. Managing Ireland's rivers and lakes. Department of the Environment, Dublin.

Armstrong, A.C., and E.A. Garwood. 1991. Hydrological consequences of artificial drainage of grassland. Hydrological Processes 5: 157-174.

Arya, L.M., and J.F. Paris. 1981. A physicomempirical model to predict the soil moisture characteristic from particle-size distribution and bulk density data. Soil Science Society of America Jouranl 45: 1023-1030.

Austin, N.R., J.B. Prendergast, and M.D. Collins. 1996. Phosphorus loss in irrigation runoff from fertilized pasture. Journal of Environmental Quality 25: 63-68.

Bache, B.W., C.A. Frost, and R.H.E. Inkson. 1981. Moisture release characteristics and porosity of twelve Scottish soil series and their variability. Journal of Soil Science 32: 505-520.

Baker, J.L., and J.M. Laflen. 1982. Effects of corn residue and fertilizer management on soluble nutrient runoff losses. Transactions of the American Society of Agricultural Engineers 25: 344-348.

Baldwin, D.S. 1998. Reactive 'organic' phosphorus revisited. Water Research 32: 2265-2270.

Ball, R.C., and Hooper, F.F. 1963. Translocation of phosphorus in a trout stream ecosystem. pp. 217-228. *In* V. Schultz, and A.W. Klement, Jr., (ed.) Radioecology. Reinhold, New York.

Balls, P.W., A. Macdonald, K.B. Pugh, and A.C. Edwards. 1997. Rainfall events and their influence on nutrient distributions in the Ythan estuary (Scotland). Estuarine, Coastal and Shelf Science 44: 73-81.

Barberis, E., F. Ajmone Marsan, R. Scalenghe, A. Lammers, U. Schwertmann, A.C. Edwards, R. Maguire, M.J. Wilson, A. Delgado, and J. Torrent. 1996. European soils overfertilised with phosphorus: Part 1. Basic properties. Fertiliser Research 45: 199-207.

Barnett, G.M. 1994. Phosphorus forms in animal manure. Bioresource Technology 49: 139-147.

Barrow, N.J. 1983a. A mechanistic model for describing the sorption and desorption of phosphate by soil. Journal of Soil Science 34: 733-750.

Barrow, N.J. 1983b. On the reversibility of phosphate sorption by soils. Journal of Soil Science 34: 751-758.

Bartley, P. 1996. Groundwater investigations at Johnstown Castle. Dissertation submitted in partial fulfilment of the requirements for the degree of M.Sc. to the Department of Civil, Structural and Environmental Engineering, Trinity College, Dublin.

Basta, N.T., R.J. Zupancic, and E.A. Dayton. 2000. Evaluating soil tests to predict bermudagrass growth in drinking water treatment residuals with phosphorus fertilizer. Journal of Environmental Quality 29: 2007-2012.

Beauchemin, S., R.R. Simard, and D. Cluis. 1998. Forms and concentration of phosphorus in drainage water of twenty-seven tile-drained soils. Journal of Environmental Quality 27: 721-728.

Beaulac, M.N., and K.H. Reckhow. 1982. An examination of land use – nutrient export relationships. Water Resources Bulletin 18: 1013-1024.

Bekele, T., B.J. Cino, P.A.I. Ehlert, A.A. Van der Maas, and A. Van Diest. 1983. An evaluation of plant-borne factors promoting the solubilization of alkaline rock phosphates. Plant and Soil 75: 361-378.

Bengston, R.L., C.E. Carter, H.F. Morris, and S.A. Barkiewicz. 1988. The influence of subsurface drainage practices on nitrogen and phosphorus losses in a warm, humid climate. Transactions of the ASAE 31: 729-733.

Beven, K., and P. Germann. 1982. Macropores and water flow in soils. Water Resource Research 18: 1311-1325.

Birr, A.S., and D.J. Mulla. Evaluation of the phosphorus index in watersheds at the regional scale. Journal of Environmental Quality 30: 2018-2025.

Bodman, G.B., and E.A. Colman. 1943. Moisture and energy conditions during downward entry of water into soils. Soil Science Society of America Proceedings 8: 116-122.

Bolan, N.S., and N.J. Barrow. 1984. Modelling the effect of adsorption of phosphate and other anions on the surface charge of variable charge oxides. Journal of Soil Science 35: 273-281.

Bolton, E.F., J.W. Aylesworth, and F.R. Hore. 1970. Nutrient losses through tile drains under three cropping systems and two fertility levels on a Brookston clay soil. Canadian Journal of Soil Science 50: 275-279.

Bootlink, H.W.G., and J. Bouma. 1991. Physical and morphological characterization of bypass flow in a well-structured clay soil. Soil Science Society of America Journal 55: 1249-1254.

Borström, B., G. Persson, and B. Broberg. 1988. Bioavailability of different phosphorus forms in freshwater systems. Hydrobiologia 170: 133-155.

Bosch, D.D., R.K. Hubbard, L.T. West, and R.R. Lowrance. 1994. Subsurface flow patterns in a riparian buffer system. Transactions of the American Society of Agricultural Engineers, 37: 1783-1790.

Bottcher, A. B., E. J. Monke, and L. F. Huggins. 1981.Nutrient and sediment loadings from a subsurface drainage system. Transactions of the ASAE 24: 1221-1226.

Bottcher, A.B., L.W. Miller, and K.L. Campbell. 1984. Phosphorus adsorption in various soil-water extraction cup materials: effect of acid wash. Soil Science 137: 239-244.

Bouma, J. 1982. Measuring the hydraulic conductivity of soil horizons with continuous macropores. Soil Science Society of America Journal 46: 438-441.

Bouma, J., and L.W. Dekker. 1978. A case study on infiltration into dry clay soil. I. Morphological observations. Geoderma 20: 27-40.

Bouma, J., and J.H.M. Wösten. 1979. Flow patterns during extended saturated flow in two, undisturbed swelling clay soils with different macrostructures. Soil Science Society of America Journal 43: 16-22.

Bouma, J., A. Jongerius, O. Boersma, A. Jager, and D. Schoonderbeek. 1977. The function of different types of macropores during saturated flow through four swelling soil horizons. Soil Science Society of America Journal 41: 945-950.

Bouma, J., L.W. Dekker, and J.C.F.M. Haans. 1979. Drainability of some Dutch clay soils: a case study of soil survey interpretation. Geoderma 22: 193-203.

Bouwer, H. 1986. Intake Rate: Cylinder Infiltrometer. pp. 825-844. *In* A. Klute (ed.) Methods of soil analysis, part 1, physical and mineralogical methods, second edition. American Society of Agronomy and Soil Science Society of America, Madison, Wisconsin.

Bowman, J.J., and K.J. Clabby. 1998. Water quality of rivers and lakes in the Republic of Ireland. pp. 55-63. *In* J.G. Wilson (ed.) Eutrophication in Irish waters. Royal Irish Academy, Dublin.

Bowman, J.J., K.J. Clabby, J. Lucey, M.L. McGarrigle, and P.F. Toner. 1996. Water quality in Ireland 1991-1994. Environmental Protection Agency, Wexford.

Bowman, R.A., J.B. Rodriguez, and J.R. Self. 1998. Comparison of methods to estimate occluded and resistant soil phosphorus. Soil Science of America Journal 62: 338-342.

Bradford, M.E., and R.H. Peters. 1987. The relationship between chemically analysed phosphorus fractions and bioavailable phosphorus. Limnology and Oceanography 32: 1124-1137.

Brennan, D. Unpublished. A micro pipette method for mechanical analysis of soil containing organic matter and lime. Johnstown Castle Research and Development Centre, Wexford.

Brennan, M. T., J. Khan, D. W. Jeffrey, E. Jennings, and J. G. Wilson. 1998. The impact of nutrients in an estuarine system. pp. 115-125. *In* J.G. Wilson (ed.) Eutrophication in Irish waters. Royal Irish Academy, Dublin.

Brereton, A.J., and M. Hope-Cawdery. 1988. Drumlin soils – the depression of herbage yield by shallow water table depth. Irish Journal of Agricultural Research 27: 167-178.

Brink, N. 1968. Self-purification in an open ditch. Water Research 2: 481-503.

Broberg, O. 1984. Phosphate removal in acidified and limed lake water. Water Research 18: 1273-1278.

Brookes, P.C., J.A. Catt, R. Farina, G. Heckrath, K.R. Howse, and D. Thomas. 1996. The movement of phosphate from soil to water. Soil Use and Management 12: 224.

Brookes, P.C., G. Heckrath, J. De Smet, G. Hofman, and J. Vanderdeelen. 1997. Losses of phosphorus in drainage water. pp. 253-271. *In* H. Tunney et al. (ed.) Phosphorus loss from soil to water. CAB Int., Oxon, UK.

Brown, S., H. Schreier, and P.B. Shah. 2000. Soil phosphorus fertility degradation: a geographic information system-based approach. Journal of Environmental Quality 29: 1152-1160.

Brunet, R.-C., and K.B. Astin. 1998. Variation in phosphorus flux during a hydrological season: the River Adour. Water Research 32: 547-558.

Bundy, L.G., T.W. Andraski, and J.M. Powell. 2001. Management practice effects on phosphorus losses in runoff in corn production systems. Journal of Environmental Quality 30: 1822-1828.

Burke, W., J. Mulqueen, and P. Butler. 1974. Fertiliser losses in drainage water from a surface water gley. Irish Journal of Agricultural Research 13: 203-214.

Burke, W., J.C.I. Dooge, G.J. Mullen, and F.J. Larney. 1986. The moisture balance. pp. 61-84. In T. Keane et al. (ed.) Climate, weather and Irish agriculture. AGMET, Dublin.

Burt, R., T.G. Reinsch, and W.P. Miller. 1993. A micro-pipette method for water dispersible clay. Communications in Soil Science and Plant Analysis 24: 2531-2544.

Burt, T.P., and D.P. Butcher. 1985. On the generation of delayed peaks in stream discharge. Journal of Hydrology 78: 361-378.

Burt, T.P., D.P. Butcher, N. Coles, and A.D. Thomas. 1983. The natural history of Slapton Ley nature reserve XV: Hydrological processes in the Slapton Wood catchment. field Studies 5: 731-752.

Byrne, E. 1979. Chemical analysis of agricultural materials. An Foras Taluntais, Dublin.

Caffrey, J.M., and Allison, J.P. 1998. Eutrophication in canals. pp. 71-81. *In* J.G. Wilson (ed.) Eutrophication in Irish waters. Royal Irish Academy, Dublin.

Calvert, D.V. 1975. Nitrate, phosphate, and potassium movement into drainage lines under three soil management systems. Journal of Environmental Quality 4: 183-186.

Caraco, N.F. 1995. Influence of human populations on P transfers to aquatic systems: a regional scale study using large rivers. *In*: H. Tiessen (ed.) Phosphorus in the global environment. John Wiley and Sons Ltd., Chichester.

Carr, O.J., and R. Goulder. 1990. Fishpfarm effluents in rivers-II. Effects on inorganic nutrients, algae and the macrophyte *Ranunculus penicillatus*. Water Research 24: 639-647.

Casey, H., and I.S. Farr. 1982. The influence of within stream disturbance on dissolved nutrient levels during spates. Hydrobiologia 92: 447-462.

Casey, R.E., and S.J. Klaine. 2001. Nutrient attenuation by riparian wetland during natural and artificial runoff events. Journal of Environmental Quality 30: 1720-1731.

Castillo, M.M., J.D. Allan, and S. Brunzell. 2000. Nutrient concentrations and discharges in a Midwestern agricultural catchment. Journal of Environmental Quality 29: 1142-1151.

CEC (Commission of the European Communities). 1991. Council Directive of 21 May concerning urban waste water treatment (91/271/EEC). Official Journal of the European Communities, No L 135/40-No L 135/52.

Chambers, B.J., D.B. Davies, and S. Holmes. 1992. Monitoring of water erosion on arable farms in England and Wales, 1989-90. Soil Use and Management 8: 163-170.

Chambers, B.J., T.W.D. Garwood, and R.J. Unwin. 2000. Controlling soil water erosion and phosphorus losses from arable land in England and Wales. Journal of Envrionmental Quality 29: 145-150.

Champ, W.S.T. 1998. Phosphorus/chlorophyll relationships in selected Irish lakes: Ecological consequences and suggested criteria for ecosystem management. pp. 91-105. *In* J.G. Wilson (ed.) Eutrophication in Irish waters. Royal Irish Academy, Dublin.

Chang, S.C., and M.L. Jackson. 1957. Fractionation of soil phosphorus. Soil Science 84: 133-144.

Chapman, P.J., A.C. Edwards, and C.A. Shand. 1997. The phosphorus composition of soil solutions and soil leachates: Influence of soil:solution ratio. European Journal of Soil Science 48: 703-710.

Chessman, B.C., P.E. Hutton, and J.M. Burch. 1992. Limiting nutrients for periphyton growth in sub-alpine, forest, agricultural and urban streams. Freshwater Biology 28: 349-361.

Chevallier, P., and O. Planchon. 1993. Hydrological processes in a small humid savanna basin (Ivory Coast). Journal of Hydrology 151: 173: 191.

Chichester, F.W., R.W. Van Keuren, and J.L. McGuinness. 1979. Hydrology and chemical quality of flow from small pastured watersheds: II. Chemical quality. Journal of Environmental Quality 8: 167-171.

Childs, F.D., and E.M. Jencks. 1967. Effect of time and depth of sampling upon soil test results. Agronomy Journal 59: 537-540.

Church, M., and M.-K. Woo. 1990. Geography of surface runoff: some lessons from research. pp. 299-326. *In* M.G. Anderson, and T.P. Burt (ed.) Process Studies in Hillslope Hydrology. John Wiley & Sons, Chichester.

Clausen, J.C., K. Guillard, C.M. Sigmund, and K.M. Dors. 2000. Water quality changes from riparian buffer restoration in Conneticut. Journal of Environmental Quality 29: 1751-1761.

Clenaghan, C., C. Collins, and M. Crowe. 2001. Phosphorus regulations national implementation report, 2001. Environmental Protection Agency, Wexford.

Codling, E.E., R.L. Chaney, and C.L. Mulchi. 2000. Use of aluminium- and iron-rich residues to immobilize phosphorus in poultry litter and litter-amended soils. Journal of Environmental Quality 29: 1924-1931.

Cooke, G.W., and R.J.B. Williams. 1970. Losses of nitrogen and phosphorus from agricultural land. Water Treatment Examination 19: 253-274.

Cooke, I.J. 1966. A kinetic approach to the description of soil phosphate status. Journal of Soil Science 17: 56-64.

Cooke, J.G. 1988. Sources and sinks of nutrients in a New Zealand hill pasture catchment. II. Phosphorus. Hydrological Processes 2: 123-133.

Cooke, J. G. and T. Dons. 1988. Sources and sinks of nutrients in a New Zealand hill pasture catchment. I. Stormflow generation. Hydrological Processes 2: 109-122.

Correll, D.L., T.E. Jordan, and D.E. Weller. 1999. Effects of precipitation and air temperature on phosphorus fluxes from the Rhode River watersheds. Journal of Environmental Quality 28: 144-154.

Coulter, B.S. 2001. Nutrient and trace element advice for grassland and tillage crops. Teagasc, Johnstown Castle, Wexford.

Cox, F.R. 1992. Range in soil phosphorus critical levels with time. Soil Sciences Society of America Journal 56: 1504-1509.

Cox, F.R., and S.E. Hendricks. 2000. Soil test phosphorus and clay content effects on runoff water quality. Journal of Environmental Quality 29: 1582-1586.

Cullen, P., and R.S. Roisch. 1979.Effects of rural and urban sources of phosphorus of Lake Burely Griffin. Progresses in Water Technology 11: 219-230.

Culleton, E.B. 1976. Pleistocene deposits in South Wexford and their classification as soil parent materials. Ph.D. thesis, Dublin University (UCD).

Culleton, E.B., and J. Diamond. In print. Soils and land use – Johnstown Castle Estate. Teagasc, Wexford.

Culleton, N., and J. Murphy. 1996. The evaluation of environmental, agronomic and economic implications of high and low input diary systems. pp. 3-4. *In* Johnstown Castle Research Centre, Research Report 1996. Teagasc, Wexford.

Culleton, N., E. Byrne, and B. Coulter. 1996. Soil Sampling. pp 65-75. *In* O.T. Carton et al. (ed.) Phosphorus recommendations for grassland. Teagasc, Dublin.

Culleton, N., W.E. Murphy, O. T. Carton, and A. Cuddihy. 1999a. An assessment of the long term effects of three phosphorus fertiliser regimes on soil phosphorus and sward composition. Teagasc, Dublin.

Culleton, N., J. Murphy, and W.E. Murphy. 1999b. The evaluation of environmental, agronomic and economic implications of high and low input dairy systems. Teagasc, Dublin.

Culley J. L. B., E. F. Bolton, and V. Bernyk. 1983. Suspended solids and phosphorus loads from a clay soil: I. Plot studies. Journal of Environmental Quality 12: 493-503.

D'Angelo, D.J., and J.R. Webster. 1991. Phosphorus retention in streams draining pine and hardwood catchments in the southern Appalachian Mountains. Freshwater Biology 26: 335-345.

Dalal, R.C. 1977. Soil organic phosphorus. Advances in Agronomy 29: 83-323.

Dalal, R.C. 1997. Long-term phosphorus trends in Vertisols under continuous cereal cropping. Australian Journal of Soil Research 35: 327-339.

Dalton, J.D., G.C. Russell, and D.H. Sieling. 1952. Effect of organic matter on phosphate availability. Soil Science 73: 173-181.

Daly, D. 1991. Impact of landspreading of manures and other organic wastes on groundwater. Geological Survey of Ireland, Dublin.

Daly, K. 1999. An environmental appraisal of the phosphorus dynamics of Irish grassland soils. PhD thesis, School of Botany, Trinity College, Dublin.

Daly, K., D. Jeffery, and H. Tunney. 2001. The effect of soil type on phosphorus sorption capacity and desorption dynamics in Irish grassland soils. Soil Use and Management 17: 12-20.

Daniel, T.C., D.R. Edwards, and A.N. Sharpley. 1993. Effect of extractable soil surface phosphorus on runoff water quality. Transactions of the ASAE 36: 1079-1085.

Daniel, T.C., A.N. Sharpley, D.R. Edwards, R. Wedepohl, and J.L. Lemunyon. 1994. Minimizing surface water eutrophication from agriculture by phosphorus management. Journal of Soil and Water Conservation 49: 30-38.

Daniels, M.B., P. Delaune, P.A. Moore, Jr., A. Mauromoustakos, S.L. Chapman, and J.M. Langston. 2001. Soil phosphorus variability in pastures: Implications for sampling and environmental management strategies. Journal of Environmental Quality 30: 2157-2165.

Dao, T.H., L.J. Sikora, A. Hamasaki, and R.L. Chaney. 2001. Manure phosphorus extractability as affected by aluminium- and iron by-products and aerobic composting. Journal of Environmental Quality 30: 1693-1698.

David, M.B., and L.E. Gentry. 2000. Anthropogenic inputs of nitrogen and phosphorus and riverine export for Illinois, USA. Journal of Environmental Quality 29: 494-508.

Derby, N.E., and R. E. Knighton. 2001. Field-scale preferential transport of water and chloride tracer by depression-focused recharge. Journal of Environmental Quality 30: 194-199.

Descy, J.-P. 1991. Eutrophication in the River Meuse. pp 132-142. *In* D. W. Sutcliffe, and J. G. Jones (ed.) Eutrophication research and application to water supply. Freshwater Biological Association, London.

DeWalle, D.R., and H.B. Pionke. 1994. Streamflow generation on a small agricultural catchment during autumn recharge: II. Stormflow periods. Journal of Hydrology 163: 23-42.

DeWalle, D.R., B.R. Swistock, and W.E. Sharpe. 1988. Three-component tracer model or stromflow on a small Appalachian forested catchment. Journal of Hydrology 104: 301-310.

Diamond, J. and T. Shanley. 1998. Infiltration rate assessment of some major soils. End of Project Report 4102. Teagasc, Dublin.

Diamond, J. and T. Shanley. In print. Infiltration rate assessment of some major soils. Irish Geography.

Diamond, J., and P. Sills. 1998. The measurement of soil water regimes of three representative soils and implications for run-off. Teagasc, Dublin.

Dick, W. A., R. J. Roseberg, E. L. McCoy, W. M. Edwards and F. Haghiri. 1989. Surface hydrologic response of soils to no-tillage. Soil Science of America Journal 53: 1520-1526.

Dils, R.M., and A.L. Heathwaite. 1996. Phosphorus fractionation in hillslope hydrological pathways contributing to agricultural runoff. pp: 229-251. *In* M.G. Anderson and S.M. Brooks (ed.) Advances in hillslope processes. John Wiley and Sons Ltd., Chichester.

Dils, R.M., and A.L. Heathwaite. 1997. Phosphorus fractionation in grassland hill-slope hydrological pathways. pp. 349-351. *In* H. Tunney et al. (ed.) Phsophorus losss from soil to water. CAB Int., Wallingford, UK.

Djodjic, F., B. Ulén, and L. Bergström. 2000. Temporal and spatial variations of phosphorus losses and drainage in a structured clay soil. Water Research 34: 1687-1695.

Dodds, W.K., V.H. Smith, and B. Zander. 1997. Developing nutrient targets to control benthic chlorophyll levels in streams: a case study of the Clark Fork river. Water Research 31: 1738-1750.

Doesburg, J.D.J. 1996. Particle-size analysis and mineralogical analysis. pp. 251-278. *In* P. Buurman et al. (ed.) Manual for soil and water analysis. Backhuys Publishers, Leiden, The Netherlands.

Dorich, R.A., D.W. Nelson, and L.E. Sommers. 1985. Estimating algal available phosphorus in suspended sediments by chemical extraction. Journal of Envrionmental Quality 14: 400-405.

Dou, Z., J.D. Thoth, D.T. Galligen, C.F. Ramberg, Jr., and J.D. Ferguson. 2000. Laboratory procedures for characterizing manure phosphorus. Journal of Environmental Quality 29: 508-514.

Drewry, J.J., and R.J. Paton. 2000. Effects of cattle treading and natural amelioration on soil physical properties and pasture under dairy farming in Southland, New Zealand. New Zealand Journal of Agricultural Research 43: 377-386.

Drewry, J.J., R.P. Littlejohn, and R.J. Paton. 2000. A survey of soil physical properties on sheep and dairy farms in southern New Zealand. New Zealand Journal of Agricultural Research 43: 251-258.

Duda, A.M., and D.S. Finan. 1983. Influence of livestock on nonpoint source nutrient levels of streams. Transactions of the ASAE 26: 1410-1416.

Dunne, T. 1983. Relation of field studies and modelling in the prediction of storm runoff. Journal of Hydrology 65: 25-48.

Dunne, T., and R. Black. 1970a. An experimental investigation of runoff production in permeable soils. Water Resources Research 6: 478-490.

Dunne, T., and R. Black. 1970b. Partial area contributions to storm runoff in a small New England watershed. Water Resources Research 6: 1296-1311.

Edwards, W.M., L.D. Norton, and C.E. Redmond. 1988. Characterizing macropores that affect infiltration into nontilled soil. Soil Science Society of America Journal 52: 483-487.

Ehlers, W. 1975. Observations on earthworm channels and infiltration on tilled and untilled loess soil. Soil Science 119: 242-249.

Ekholm, P. 1998. Algal-available phosphorus originating from agriculture and municipalities. Monograph 11 of the Boreal Environment Research. Finnish Environment Institute, Helsinki.

Elliot, J.A., A.J. Cessna, K.B. Best, W. Nicholaichuk, and L.C. Tollefson. 1998. Leaching and preferential flow of clopyralid under irrigation: field observations and simulation modeling. Journal of Environmental Quality 27: 124-131.

Eshleman, K.N., J.S. Pollard, and A. Kuebler O'Brien. 1993. Determination of contributing areas for saturation overland flow from chemical hydrograph separations. Water Resources Research 29: 3577-3587.

Fernandes, M.L.V., R. Indiati, J. Coutinho, and A. Buondonno. 1999. Soil properties affecting phosphorus extraction from Portuguese soils by conventional and innovative methods. Communications in Soil Science and Plant Analysis 30: 921-936.

Fingleton, W.A., and Cushion, M. 1999. Irish agriculture in figures. Teagasc, Dublin.

Fitzgerald, G.P. 1970. Evaluations of the availability of sources of nitrogen and phosphorus for algae. Journal of Phycology 6: 239-247.

Fitzgerald, G.P., and S.L. Faust. 1967. Effect of water sample preservation methods on the release of phosphorus from algae. Limnology and Oceanography 12: 332-334.

Flanagan, P.J. 1992. Parameters of water quality, interpretation and standards. Environmental Research Unit, Dublin.

Fleming, N.K., and J.W. Cox. 1998. Chemical losses off dairy catchments located on a texture-contrast soil: carbon, phosphorus, sulfur, and other chemicals. Australian Journal of Soil Research 36: 979-995.

Flury, M., H. Flühler, H., Jury, W.A., and J. Leuenberger. 1994. Susceptibility of soils to preferential flow of water: A field study. Water Resources Research 30: 1945-1954.

Foster, I. D. L. and J. A. Dearing. 1987. Lake-catchments and environmental chemistry: A comparative study of contemporary and historical catchment processes in Midland England. GeoJournal 14.3: 285-297.

Fox, I., M.A. Malati, and R. Perry. 1989. The adsorption and release of phosphate from sediments of a river receiving sewage effluent. Water Research 23: 725-732.

Fox, R.L., and E.J. Kamprath. 1971. Adsorption and leaching of P in acid organic soils and high organic matter sand. Soil Science Society of America Proceedings 35: 154-156.

Foy, R.H., and P.J.A. Withers. 1995. The contribution of agricultural phosphorus to eutrophication. The Fertiliser Society, London.

Foy, R.H., R.V. Smith, C. Jordan, and S.D. Lennox. 1995. Upward trend in soluble phosphorus loadings to Lough Neagh despite phosphorus reduction at sewage treatment works. Water Research 29: 1051-1063.

Foy, R.H., H. Tunney, M.J. Carroll, E. Byrne, T. Gately, J. Bailey, and S.D. Lennox. 1997. A comparison of Olsen and Morgan soil phosphorus test results from the cross-border region of Ireland. Irish Journal of Agricultural and Food Research 36: 185-194

Fransson, A.-M., and B. Bergkvist. 2000. Phosphorus fertilisation causes durable enhancement of phosphorus concentrations in forest soil. Forest Ecology and Management 130: 69-76.

Freeze, R.A. 1974. Streamflow generation. Review of Geophysics and Space Physics 12: 627-647.

Fried, M., C.E. Hagen, J.F. Saiz del Rio, and J.E. Leggert. 1957. Kinetics of phosphate uptake in the soil-plant system. Soil Science 84: 427-437.

Friesen, D.K., G.J. Blair, and M. Duncan. 1985. Temporal fluctuations in soil test values under permanent pasture in New England, N.S.W. Australian Journal of Soil Research 23: 181-193.

Froehlich, P. N. 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. Limnology and Oceanography 33: 649-668.

Frossard, E., L.M. Condron, A. Oberson, S. Sinaj, and J.C. Fardeau. 2000. Processes governing phosphorus availability in temperate soils. Journal of Environmental Quality 29: 15-23.

Furumai, H., and S. Ohgaki. 1988. Radiochemical analysis of phosphorus exchange kinetics between sediments and water under aerobic conditions. Journal of Environmental Quality 17: 205-212.

Gale, P.M., K.R. Reddy, and D.A. Graetz. 1994. Phosphorus retention by wetland soils used for treated wastewater disposal. Journal of Environmental Quality 23: 370-377.

Gallagher, P.A., and M. Herlihy. 1963. An evaluation of errors associated with soil testing. Irish Journal of Agricultural Research 2: 149-167.

Garbouchev, I.P. 1966. Changes occurring during a year in the soluble phosphorus and potassium in soil under crops in rotation experiments at Rothamsted, Woburn and Saxmundham. Journal of Agricultural Science 66: 399-412.

García-Rodeja, I., and F. Gil-Sotres. 1997. Prediction of parameters describing phosphorus-desorption kinetics in soils of Galicia (Northwest Spain). Journal of Environmental Quality 26: 1363-1369.

Gardiner, M.J. 1986. Soil, site and climatic factors in slurry disposal. Irish Journal of Agricultural Research 25: 273-284.

Gardiner, M.J., and T. Radford. 1980. Soil associations of Ireland and their land use potential. Soil Survey Bulletin no. 36, An Foras Talúntais, Dublin.

Garrido, F., M. Ghodarti, C.G. Campbell, and M. Chendorain. 2001. Detailed characterization of solute transport in a heterogeneous field soil. Journal of Environmental Quality 30: 573-583.

Gaynor, J. D. and W. I. Findlay. 1995. Soil and phosphorus loss from conservation and conventional tillage in corn production. Journal of Environmental Quality 24: 734-741.

Gburek, W.J. 1983. Hydrologic delineation of nonpoint source contributing areas. Journal of the Environmental Engineering Division of the ASCE: 1035-1048.

Geelhoed, J.S., W.H. Van Riemsdijk, and G.R. Findenegg. 1999. Simulation of the effect of citrate exudation from roots on the plant availability of phosphate adsorbed on goethite. European Journal of Soil Science 50: 379-390.

Gentry, L.E., M.B. David, K.M. Smith-Starks, and D.A. Kovacic. 2000. Nitrogen fertilizer and herbicide transport from tile drained fields. Journal of Environmental Quality 29: 232-240.

Germann, P.F. 1990. Macropores and hydrologic hillslope processes. pp. 327-364. *In* M.G. Anderson, and T.P. Burt (ed.) Process Studies in Hillslope Hydrology. John Wiley & Sons, Chichester.

Germann, P.F., and L. DiPietro. 1996. When is porous-media flow preferential? A hydromechanical perspective. Geoderma 74: 1-21.

Germann, P.F., W.M. Edwards, and L.B. Owens. 1984. Profiles and increased soil moisture after infiltration into soils with macropores. Soil Science Society of America Journal 48: 237-244.

Gertis, J.J.P., J.L.M.P. de Lima, and T.M.W. van den Broek. 1990. Overland flow and erosion. pp. 173-214. *In* M.G. Anderson, and T.P. Burt (ed.) Process Studies in Hillslope Hydrology. John Wiley & Sons, Chichester.

Ghadiri, H., and C.W. Rose. 1991. Sorbed chemical transport in overland flow: II. Enrichment ratio variation with erosion processes. Journal of Environmental Quality 20: 634-641.

Ghodarti, M., and W.A. Jury. 1990. A field study using dyes to characterize preferential flow of water. Soil Science Society of America Journal 54: 1558-1563.

Gibson, C.E., Y. Wu, and D. Pinkerton. 1995. Substance budgets of an upland catchment: the significance of atmospheric phosphorus inputs. Freshwater Biology 33: 385-392.

Gill, H. 1996. Industrial water resource management. pp. 23-25. *In* M. Cresser and K. Pugh (ed.) Multiple land use and catchment management. Proceedings of an International Conference 11-13 September 1996. Macaulay land use research institute, Aberdeen.

Gleeson, T., and J. Kiely. 1995. Soil water and pollution. Irish Grassland and Animal Production Association Journal 29: 40-48.

Government Supplies Agency. 1998. Statutory Instruments, S.I. No. 258 of 1998, Local Government (Water Pollution Act), 1977 (Water Quality Standards for Phosphorus) Regulations, 1998.

Grant, R., A. Laubel, B. Kronvang, H.E. Anderson, L.M. Svendsen, and A. Fuglsang. 1996. Loss of dissolved and particulate phosphorus from arable catchments by subsurface drainage. Journal of Environmental Quality 30: 2633-2642.

Grayson, R.B., B.L. Finlayson, C. J. Gippel, and B. T. Hart. 1996. The potential of field turbidity measurements for the computation of total phosphorus and suspended solids loads. Journal of Environmental Management 47: 257-267.

Green, D.B., T.J. Logan, and N.E. Smeck. 1978. Phosphate adsorption-desorption characteristics of suspended sediments in the Maumee River Basin of Ohio. Journal of Environmental Quality 7: 208-212.

Greenwood, D.J., T.J. Cleaver, M.K. Turner, J. Hunt, K.B. Niendorf, And S.M.H. Loquens. 1980. Comparison of the effects of phosphate fertilizer on the yield, phosphate content and quality of

22 different vegetable and agricultural crops. Journal of agricultural Science, Cambridge 95: 457-469.

Habib, L., S. Hayfa, and J. Ryan. 1994. Phosphorus solubility changes with time in organically amended soil in a Mediterranean environment. Communications in Soil Science and Plant Analysis 25: 3281-3290.

Haines, B.L., J.B. Waide, and R.L. Todd. 1982. Soil solution nutrient concentrations sampled with tension and zero-tension lysimeters: report of discrepancies. Soil Science Society of America Journal 46: 658-661.

Hanley, K. 1965. Phosphorus in some Irish soils. pp: 103-129. Ministry of Agriculture, Fisheries and Food, Technical Bulletin 13. Her Majesty's Stationary Office, London.

Hansen, E.A., and A.R. Harris. 1975. Validity of soil-water samples collected with porous cups. Soil Science Society of America Journal 39: 528-536.

Hansen, N.C., S.C. Gupta, and J.F. Moncrief. 2000. Herbicide and tillage effects on runoff, sediment, and phosphorus losses. Journal of Environmental Quality 29: 1555-1560.

Hanway, J.J., and J.M. Laflen. 1974. Plant nutrient losses from tile-outlet terraces. Journal of Envrionmental Quality 3: 351-356.

Harris, G.L., M.J. Goss, R.J. Dowdell, K.R. Howse, and P. Morgan. 1984. A study of mole drainage with simplified cultivation for autumn-sown crops on clay soil. Journal of Agricultural Science, Cambridge 102: 561-581.

Haustein, G.K., T.C. Daniel, D.M. Miller, P.A. Moore, Jr., and R.W. McNew. 2000. Aluminium-containing residuals influence high-phosphorus soils and runoff water quality. Journal of Environmental Quality 29: 1954-1959.

Havis, R.N., and E.E. Alberts. 1993. Nutrient leaching from field-decomposed corn and soybean residue under simulated rainfall. Soil Science Society of America Journal 56: 211-218.

Hawkins, J.M.B., and D. Scholefield. 1996. Molybdate-reactive phosphorus losses in surface and drainage water from permanent grassland. Journal of Environmental Quality 25: 727-732.

Hayes, C.R., and L.A. Greene. 1984. The evaluation of eutrophication impact in public water supply reservoirs in East Anglia. Water Pollution and Control 83: 42-51.

Haygarth, P.M., and S.C. Jarvis. 1997. Soil derived phosphorus in surface runoff from grazed grassland lysimeters. Water Research 31: 140-148.

Haygarth, P.M., C.D. Ashby, and S.C. Jarvis. 1995. Short-term changes in molybdate reactive phosphorus of stored soil waters. Journal of Environmental Quality 24: 1133-1140.

Haygarth, P.M., M.S. Warwick, and W.A. House. 1997. Biogeochemical significance of membrane and ultrafilter separation of low-molecular-weight molybdate-reactive phosphorus in soil and river water. pp. 386-389. *In* H. Tunney et al. (ed.) Phosphorus loss from soil to water. CAB Int., Wallingford, UK.

Haygarth, P.M., L. Hepworth, and S.C. Jarvis. 1998. Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland. European Journal of Soil Science 49: 65-72.

Haynes, R.J., and P.H. Williams. 1992. Long-term effect of superphosphate on accumulation of soil phosphorus and exchangeable cations on a grazed, irrigated pasture site. Plant and Soil 142: 123-133.

He, Z.L., X. Yang, K.N. Yuan, and Z.X. Zhu. 1994. Desorption and plant-availability of phosphate sorbed by some important minerals. Plant and Soil 162:89-97.

He, Z.L., M.J. Wilson, C.O. Campbell, A.C. Edwards, and S.J. Chapman. 1995. Distribution of phosphorus in soil aggregate fractions and its significance with regard to phosphorus transport in agricultural runoff. Water, Air and Soil Pollution 83: 69-84.

Heathwaite, A.L. 1993. The impact of agriculture on dissolved nitrogen and phosphorus cycling in temperate ecosystems. Chemistry and Ecology 8: 217-231.

Heathwaite, A.L. 1997. Sources and pathways of phosphorus loss from agriculture. pp. 205-223. *In* H. Tunney et al. (ed.) Phsophorus losss from soil to water. CAB Int., Wallingford, UK.

Heathwaite, A.L., and T.P. Burt. 1991. Predicting the effect of land use on stream water quality in the UK. pp. 209-218. *In* N.E. Peters, and D.E. Walling (ed.) Sediment and stream water quality in a changing environment: trends and explanation. IAHS Publication no. 203, IAHS Press, Wallingford.

Heathwaite, A.L., and P.J. Johnes. 1996. Contribution of nitrogen species and phosphorus fractions to stream water quality in agricultural catchments. Hydrological Processes 10: 971-983.

Heathwaite, A. L., Burt, T. P., and Trudgill, S. T. 1989. Runoff, sediment and solute delivery in agricultural drainage basins: A scale-dependent approach. pp 175-190. *In* S. Ragone (ed.) Regional characterization of water quality. IAHS Publication No. 182, IAHS Press, Wallingford.

Heathwaite, A.L., T.P. Burt, and S.T. Trudgill. 1990a. The effect of land use on nitrogen, phosphorus and suspended sediment delivery to streams in a small catchment in southwest England. pp: 161-177. In J.B. Thornes (ed.) Vegetation and Erosion. John Wiley & Sons Ltd., Chichester.

Heathwaite, A.L., Burt, T.P., and Trudgill, S.T. 1990b. Land-use controls on sediment production in a lowland catchment, south-west England. pp: 69-86. *In* J. Boardman et al. (ed.) Soil erosion on agricultural land. John Wiley & Sons Ltd., Chichester.

Heckrath, G., P.C. Brookes, P.R. Poulton, and K.W.T. Goulding. 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. Journal of Environmental Quality 24: 904-910.

Hendershot, W.H., and F. Courchesne. 1991. Comparison of soil solution chemistry in zero tension and ceramic-cup tension lysimeters. Journal of Soil Science 42: 577-583.

Hendrickx, J.M.H. 1990. Determination of hydraulic soil properties. pp. 43-92. *In* M.G. Anderson, and T.P. Burt (ed.) Process Studies in Hillslope Hydrology. John Wiley & Sons, Chichester.

Henninger, D.L., G.W. Petersen, and E.T. Engman. 1976. Surface soil moisture within a watershed – Variations, factors influencing, and relationship to surface runoff. Soil Science Society of America Journal 40: 773-776.

Henriksen, A. 1969. Preservation of water samples for phosphorus and nitrogen determination. Vatten 25: 247-254.

Hera, C. 1996. The role of inorganic fertilizers and their management practices. Fertilizer Research 43: 63-81.

Hergert, G.W., S.D. Klausner, D.R. Boulding, and P.J. Zwerman. 1981. Effects of dairy manure on phosphorus concentrations and losses in tile effluent. Journal of Environmental Quality 10: 354-349.

Herlihy, M., W.E. Murphy, T. Hegarty, M. Ryan, and M.D. Murphy. 1996. Soil-testing for phosphorus: Requirements and constrains. pp. 16-33. *In* O.T. Carton et al. (ed.) Phosphorus recommendations for grassland. Teagasc, Wexford.

Herve, S., and L. Kauppi. 1986. Effects of filtration on the determination of phosphate phosphorus in runoff waters. Aqua Fennica 16: 151-155.

Hesketh, N., and P.C. Brookes. 2000. Development of an indicator for risk of phosphorus leaching. Journal of Environmental Quality 29: 105-110.

Higgs, B., A.E. Johnston, J.L. Salter, and C.J. Dawson. 2000. Some aspects of achieving sustainable phosphorus use in agriculture. Journal of Environmental Quality 29: 80-87.

Hills, R.C. 1970. The determination of the infiltration capacity of field soils using the cylinder infiltrometer. British Geomorphologica Research Group, Technical Bulletin No. 3.

Hirose, T., and N. Kuramoto. 1981. Stream water quality as influenced by land use patterns in the Kakioka basin, Japan. Journal of Environmental Quality 10: 184-188.

Hodgson, J.M. 1976. Soil Survey Handbook. Soil Survey Technical Monograph No. 5, Harpenden.

Holford, I.C.R. 1980. Effects of phosphate buffer capacity on critical levels and relationships between soil tests and labile phosphate in wheat-growing soils. Australian Journal of Soil Research 18: 405-414.

Holford, I.C.R. 1983. Differences in the efficacy of various soil phosphate testes for white clover between very acid and more alkaline soils. Australian Journal of soil Research 21: 173-182.

Holford, I.C.R. 1988. Buffering of phosphate in the soil solution during growth of ryegrass compared with buffering by sorption. Plant and Soil 111: 3-9.

Holford, I.C.R. 1997. Soil phosphorus: its measurement, and its uptake by plants. Australian Journal of Soil Research 35: 227-239.

Holford, I.C.R., and G.E.G. Mattingly. 1975. The high- and low-energy phosphate adsorbing surfaces in calcareous soils. Journal of Soil Science 26: 407-417.

Holford, I.C.R., and G.E.G. Mattingly. 1976a. A model for the behaviour of labile phosphate in soil. Plant and Soil 44: 219-229.

Holford, I.C.R., and G.E.G. Mattingly. 1976b. Phosphate adsorption and availability plant of phosphate. Plant and Soil 44: 377-389.

Holford, I.C.R., R.W.M. Wedderburn, and G.E.G. Mattingly. 1974. A Langmuir two-surface equation as a model for phosphate adsorption by soils. Journal of Soil Science 25: 242-255.

Holford, I.C.R. and G.E.G. Mattingly. 1979. Effects of phosphate buffering on the extraction of labile phosphate by plants and by soil tests. Australian Journal of Soil Research 17: 511-514.

Holford, I.C.R., C. Hird, and R. Lawrie. 1997. Effects of animal effluents on the phosphorus sorption characteristics of soils. Australian Journal of Soil Research 35: 365-373.

Holtan, H, L. Kamp-Nielsen and A. O. Stuanes. 1988. Phosphorus in soil, water and sediment: an overview. Hydrobiologia 170: 19-34.

Hooda, P.S., Moynagh, M., and I.F. Svoboda. 1996. A comparison of phosphate losses in drainage water from two different grassland systems. Soil Use and Management 12: 224.

Hooda, P.S., M. Moynagh, I.F. Svoboda, M. Thurlow, M. Stewart, M. Thomson, and H.A. Anderson. 1997. Soil and land use effects on phosphorus in six streams draining small agricultural catchments in Scotland. Soil Use and Management 13: 196-204.

Hooda, P.S., M. Moynagh, I.F. Svoboda, A.C. Edwards, H.A Anderson, and G. Sym. 1999. Phosphorus loss in drainflow from intensively managed grassland soils. Journal of Environmental Quality 28: 1235-1242.

Hooda, P.S., A.R. Rendell, A.C. Edwards, P.J.A. Withers, M.N. Aitken, and V.W. Truesdale. 2000. Relating soil phosphorus indices to potential phosphorus release to water. Journal of Environmental Quality 29: 1166-1171.

Hortenstine, C.C., and R.B. Forbes. 1972. Concentrations of nitrogen, phosphorus, potassium, and total soluble salts in soil solution samples from fertilized and unfertilised Hisosols. Journal of Environmental Quality 1: 446-449.

Horton, R.E. 1933. The role of infiltration in the hydrologic cycle. Transactions of the American Geophysical Union 14: 446-460.

House, W.A. 1990. The prediction of phosphate coprecipitation with calcite in freshwaters. Water Research 24: 1017-1023.

House, W.A., and F.H. Denison. 1998. Phosphorus dynamics in a lowland river. Water Research 32: 1819-1830.

House, W.A., and M.S. Warwick. 1998. Hysteresis of the solute concentration/discharge relationship in rivers during storms. Water Research 32: 2279-2290.

House, W.A., H. Casey, L. Donaldson, and S. Smith. 1986. Factors affecting the coprecipitation of inorganic phosphate with calcite in hardwaters-I. Water Research 20: 917-922.

House, W.A., F.H. Denison, and P.D. Armitage. 1995a. Comparison of the uptake of inorganic phosphorus to a suspended and stream bed-sediment. Water Research 29: 767-779.

House, W.A., F.H. Denison, J.T. Smith, and P.D. Armitage. 1995b. An investigation of the effects of water velocity on inorganic phosphorus influx to a sediment. Environmental Pollution 89: 263-271.

House, W.A., D. Leach, M.S. Warwick, B.A Whitton, S.N. Pattinson, G. Ryland, A. Pinder, J. Ingram, J.P. Lishman, S.M. Smith, E. Rigg, and F.H. Denison. 1997. Nutrient transport in the Humber rivers. The Science of the Total Environment 194/195: 303-320.

Hsu, P.H. 1964. Adsorption of phosphate by aluminium and iron in soils. Soil Science Society Proceedings 28: 474-478.

Humphreys, J. H. Tunney, and P. Duggan. 1998. Soil phosphorus determination using three extraction procedures, the effect of sampling depth and comparison of phosphorus fertiliser recommendations for grassland. Irish Journal of Agricultural and Food Research 37: 29-38.

Hunsaker, C.T., and D.A. Levine. 1995. Hierarchical approaches to the study of water quality in rivers. BioScience 45: 193-203.

Hyde, J.E., and T.F. Morris. 2000. Phosphorus availability in soils amended with dewatered water treatment residual and metal concentrations with time in residual. Journal of Environmental Quality 29: 1896-1904.

Ingram, J.J., and D.A. Woolhiser. 1980. Chemical transfer into overland flow. pp: 40-53. Proceedings of the ASCE Symposium on watershed management, 21-23 July, Boise, Idaho.

Irvine, K., N. Allott, P. Mills, and G. Free. 2000. The use of empirical relationships and nutrient export coefficients for predicting phosphorus concentrations in Irish lakes. Verhandlungen der Internationalen Vereinigung für Limnologie 27: 1127-1131.

Istvanovics, V. 1988. Seasonal variation of phosphorus release from the sediments of shallow Lake Balaton (Hungary). Water Research 22: 1473-1481.

Jawson, M.D., L.F. Elliott, K.E. Saxton, and D.H. Fortier. 1982. The effect of cattle grazing on nutrient losses in a Pacific Northwest setting. Journal of Environmental Quality 11: 628-631.

Jensen, M.B., T.B. Olsen, H.C.B. Hansen, and J. Magid. 2000. Dissolved and particulate phosphorus in leachate from structured soil amended with fresh cattle faeces. Nutrient Cycling in Agroecosystems 56: 253-261.

Johnes, P.J., and Heathwaite, A.L. 1992. A procedure for the simultaneous determination of total nitrogen and total phosphorus in freshwater samples using persulphate microwave digestion. Water Research 26: 1281-1287.

Johnes, P.J., and A.L. Heathwaite. 1997. Modelling the impact of land use change on water quality in agricultural catchments. Hydrological Processes 11: 269-286.

Johnes, P.J. and R.A. Hodgkinson. 1998. Phosphorus loss from agricultural catchments: pathways and implications for management. Soil Use and Management 14: 175-185.

Johnes, P.J., B. Moss and G. Phillips, 1996. The determination of total nitrogen and total phosphorus concentrations in freshwaters from land use, stock headage and population data: testing of a model for use in conservation and water quality management. Freshwater Biology 36: 451-473.

Johnson, A.H., D.R. Bouldin, and G.W. Hergert. 1975. Some observations concerning preparation and storage of stream samples for dissolved inorganic phosphate analysis. Water Resources Research 11: 559-562.

Johnson, A.H., D.R. Bouldin, E.A. Goyette, and A.M. Hedges. 1976. Phosphorus loss by stream transport from a rural watershed: quantities, processes and sources. Journal of Environmental Quality 5: 148-157.

Johnston, A. E., P. W. Lane, G. E. G. Mattingly, P. R. Poulton and M. V. Hewitt. 1986. Effects of soil and fertilizer P on yields of potatoes, sugar beet, barley and winter wheat on a sandy clay loam soil at Saxmundham, Suffolk. Journal of Agricultural Science 106: 155-167.

Jones, R.A., and G.F. Lee. 1982. Recent advances in assessing impact of phosphorus loads on eutrophication-related water quality. Water Research 16: 503-515.

Jones, R.I. 1990. Phosphorus transformations in the epilimnion of humic lakes: biological uptake of phosphate. Freshwater Biology 23: 323-337.

Jordan, C. 1997. Mapping of rainfall chemistry in Ireland 1972-94. Biology and the Environment 97B: 53-73.

Jordan, C., and R.V. Smith. 1985. Factors affecting leaching of nutrients from an intensively managed grassland in Country Antrim, Northern Ireland. Journal of Environmental Management 20: 1-15.

Jordan, C., S.O. McGuckin, and R.V. Smith. 2000. Increased predicted losses of phosphorus to surface waters from soils with high Olsen-P concentrations. Soil Use and Management 16: 27-35.

Kaila, A., and P. Hänninen. 1961. Response of winter rye to hyperphosphate and superphosphate. The Journal of the Scientific Agricultural Society of Finland 33: 39-50.

Kamprath, E.J. 1999. Changes in phosphate availability of Ultisols with long-term cropping. Communications in Soil Science and Plant Analysis 30: 909-919.

Karlovsky, J. 1958. Pasture responses to phosphatic fertilisers. New Zealand Journal of agricultural Research 1: 51-60.

Kedziora, A., L. Ryszkowski, and Z. Kundzewicz. 1995. Phosphate transport and retention in a riparian meadow – a case study. pp. 229-234. *In* H. Tiessen (ed.) Phosphorus in the global environment. John Wiley & Sons Ltd., Chichester.

Ketcheson, J.W., and J.J. Onderdonk. 1973. Effect of corn stover on phosphorus in run-off from nontilled soil. Agronomy Journal 65: 69-71.

Keup, L.E. 1968. Phosphorus in flowing waters. Water Research 2: 373-386.

Khalid, R.A., W.H. Patrick, Jr., and R.D. DeLaune. 1977. Phosphorus sorption characteristics of flooded soils. Soil Science Society of America Journal 41: 305-310.

Kilmer, V.J., J.W. Gilliam, J.F. Lutz, R.T. Joyce, and C.D. Eklund. 1974. Nutrient losses from fertilized grassland watersheds in Western North Carolina. Journal of Environmental Quality 3: 214-219.

Kilroy, G. 2001. Phosphorus in Irish aquifers: implications for input to surface waters. PhD thesis, Department of Geology, Trinity College, Dublin.

Kimmel, R.J., G.M. Pierzyinski, K.A. Janssen, and P.L. Barnes. 2001. Effects of tillage and phosphorus placement on phosphorus runoff losses in a grain sorghum-soybean rotation. Journal of Environmental Quality 30: 1324-1329.

Kirkby, C.A., L.J. Smythe, J.W. Cox, and D.J. Chittleborough. 1997. Phosphorus movement down a toposequence from a landscape with texture contrast soils. Australian Journal of Soil Research 35: 399-417.

Kladivko, E.J., A.D. Mackay, and J.M. Bradford. 1986. Earthworms as a factor in the reduction of soil crusting. Soil Science Society of America Journal 50: 191-196.

Kladivko, E.J., G.E. Van Scoyoc, E.J. Monke, K.M. Oates, and W. Pask. 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. Journal of Environmental Quality 20: 264-270.

Klausner, S.D., P.J. Zwerman, and D.F. Ellis. 1974. Surface runoff losses of soluble nitrogen and phosphorus under two systems of soil management. Journal of Environmental Quality 3: 42-46.

Klausner, S.D., P.J. Zwerman, and D.F. Ellis. 1976. Nitrogen and phosphorus losses from winter disposal of diary manure. Journal of Environmental Quality 5: 47-49.

Knapp, B.J. 1978. Infiltration and storage of soil water. *In* M.J. Kirkby (ed.) Hillslope Hydrology. John Wiley & Sons, Chichester.

Koblenz, A.O. 1980. Gewässerbelastung durch Land- und Forstwirtschaft. Wasser und Boden 1: 26-31.

Korevaar, H., and D.J. den Boer. 1990. Practical measures to reduce nutrient losses from grassland systems. The Fertiliser Society, London.

Koski-Vähälä , J., and H. Hartikainen. 2001. Assessment of the risk of phosphorus loading due to resuspended sediment. Journal of Environmental Quality 30: 960-966.

Kotlash, A.R., and B.C. Chessman. 1998. Effects of water sample preservation and storage on nitrogen and phosphorus determinations: implications for the use of automated sampling equipment. Water Research 32: 3731-3737.

Kovacic, A., M.B. David, L.E. Gentry, K.M. starks, and R.A. Cooke. 2000. Effectiveness of constructed wetlands in reducing nitrogen and phosphorus export from agricultural tile drainage. Journal of Environmental Quality 29: 1262-1274.

Kronvang, B. 1990. Sediment-associated phosphorus transport from two intensively farmed catchment areas. pp: 313-330. *In* J. Boardman et al. (ed.) Soil erosion on agricultural land. John Wiley & Sons Ltd., Chichester.

Kronvang, B. 1992. The export of particulate matter, particulate phosphorus and dissolved phosphorus from two agricultural river basins: implications on estimating the non-point phosphorus load. Water Research 26: 1347-1358.

Kronvang, B., G. Ærtebjerg, R. Grant, P. Kristensen, M. Hovmand, and J. Kirkegaard. 1993. Nationwide monitoring of nutrients and their ecological effects: state of the Danish aquatic environment. Ambio 22: 176-187.

Kung, K.-J.S. 1990. Preferential flwo in a sandy vadose zone: 2. Mechanism and implications. Geoderma 46: 59-71.

Kuntze, H. 1975. Meliorationen – Gewässer ent- oder belastend? Zeitschrift für Kulturtechnik und Flurbereinigung 16:212-220.

Lambert, M.G., B.P. Devantier, P. Nes, and P.E. Penny. 1985. Losses of nitrogen, phosphorus, and sediment in runoff from hill country under different fertiliser and grazing management regimes. New Zealand Journal of Agricultural Research 28: 371-379.

Larsen, S. 1967. Soil phosphorus. Advances in Agronomy 19:151-210.

Larsen, S., D. Gunray, and C.D. Sutton. 1965. The rate of immobilisation of applied phosphate in relation to soil properties. Journal of Soil Science 16: 141-148.

Larson, W.E., C.E. Clapp, W.H. Pierre, and Y.B. Morachan. 1972. Effects of increasing amounts of organic residues on continuous corn: II. Organic carbon, nitrogen, phosphorus, and sulfur. Agronomy Journal 64: 204-208.

Larsson, M.H., and N.J. Jarvis. 1999. Evaluation of a dual-porosity model to predict field-scale solute transport in a macroporous soil. Journal of Hydrology 215: 153-171.

Larsson, M.H., N.J. Jarvis, G. Torstensson, and R. Kasteel. 1999. Quantifying the impact of preferential flow on solute transport to tile drains in a sandy field soil. Journal of Hydrology 215: 116-134.

Laubel, A., O.H. Jacobsen, B. Kronvang, R. Grant, and H.E. Anderson. 1999. Subsurface drainage loss of particles and phosphorus from field plot experiments and a tile-drained catchment. Journal of Environmental Quality 28: 576-584.

Laverdière, M. R. and A. Karam. 1984. Sorption of phosphorus by some surface soils from Quebec in relation to their properties. Communications in Soil Science and Plant Analysis 15: 1215-1230.

Le Bissonnais, Y., and M.J. Singer. 1993. Seal formation, runoff, and interrill erosion from seventeen California soils. Soil Science Society of America Journal 57L 224-229.

Lean, D.R.S. 1973. Movements of phosphorus between its biologically important forms in lake water. Journal Fisheries Research Board of Canada 30: 1525-1536.

Lee, K.-H., T.M. Isenhart, R.C. Schultz, and S.K. Mickelson. 2000. Multispecies riparian buffers trap sediment and nutrients during rainfall simulation. Journal of Environmental Quality 29: 1200-1205.

Lehmann, O. R. and L. R. Ahuja. 1985. Interflow of water and tracer chemical on sloping field plots with exposed seepage faces. Journal of Hydrology 76: 307-317.

Leinweber, P., F. Lünsmann, and K.U. Eckhardt. 1997. Phosphorus sorption capacities and saturation of soils in two regions with different livestock densities in northwest Germany. Soil Use and Management 13: 82-89.

Leinweber, P., R. Meissner, K.-U. Eckhardt and J. Seeger. 1999. Management effects of phosphorus and leaching losses. European Journal of Soil Science 50: 413-424.

LeMare, P.H. 1981. Exchangeable phosphorus, estimates of it from amorphous iron oxides, and soil solution phosphorus, in relation to phosphorus taken up by maize. Journal of Soil Science 32: 185-299.

Lemunyon, J.L., and R.G. Gilbert. 1993. The concept and need for a phosphorus assessment tool. Journal of Production Agriculture 6: 483-486.

Lennaretz, B., J. Michaelsen, W. Wichtmann, and P. Widmoser. 1999. Time variance analysis of preferential solute movement at a tile-drained field site. Soil Science Society of America Journal 63: 39-47.

Lennox, L.J. 1984. Sediment-water exchange in Lough Ennell with particular reference to phosphorus. Water Research 18: 1483-1485.

Levine, S.N., and D.W. Schindler. 1980. Radiochemical analysis of orthophosphate concentrations and seasonal changes in the flux of orthophosphate to seston in two Canadian Shield lakes. Canadian Journal of Fishery and Aquatic Science 37: 479-487.

Levine, S.N., and D.W. Schindler. 1989. Phosphorus, nitrogen, and carbon dynamics of experimental lake 303 during recovery from eutrophication. Canadian Journal and Fishery and Aquatic Science 46: 2-10.

Ling, C.C. 1982. Einführung in die Meteorologie. Verlag der Fachvereine, Zürich.

Liu, F., C.C. Mitchell, D.T. Hill, J.W. Odom, and E.W. Rochester. 1997. Phosphorus recovery in surface runoff from swine lagoon effluent by overland flow. Journal of Environmental Quality 26: 995-1001.

Loehr, R.C. 1979. Potential pollutants from agriculture – an assessment of the problem and possible control approaches. Progress in Water Technology 11: 169-193.

Logan, T.J. 1982. Mechanisms for release of sediment-bound phosphate to water and the effects of agricultural land management on fluvial transport of particulate and dissolved phosphate. Hydrobiologia 92: 519-530.

Logan, T.J., and E. O. McLean. 1973. Nature of phosphorus retention and adsorption with depth in soil columns. Soil Science Society of America Proceedings 37: 351-355.

Logan, T.J., T.O. Oloya and S.M. Yaksich. 1979. Phosphate characteristics and bioavailability of suspended sediments from streams draining into Lake Erie. Journal of Great Lakes Research 5: 112-123.

Lord, E.I., and M.A. Shepherd. 1993. Developments in the use of porous ceramic cups for measuring nitrate leaching. Journal of Soil Science 44: 435-449.

Lowrance, R.R., R.L. Todd, and L.E. Asmussen. 1984. Nutrient cycling in an agricultural watershed: II. Streamflow and artificial drinage. Journal of Environmental Quality 13: 27-32.

Lund, J.W.G. 1972. Eutrophication. Proceedings of the Royal Society London B 180: 371-382.

Luxmoore, R.J. 1981. Micro-, meso- and macroporosity of soil. Soil Science Society of America Journal 45: 671-672.

MacDonald, A.M., A.C. Edwards, K.B. Pugh, and P.W. Balls. 1995. Soluble nitrogen and phosphorus in the river Ythan system, U.K.: Annual and seasonal trends. Water Research 29: 837-846.

Macklon, A.E.S., S.J. Grayston, C.A. Shand, A. Sim, S. Sellars, and B.G. Ord. 1997. Uptake and transport of phosphorus by Agrostis capillaries seedlings from rapidly hydrolosed organic sources extracted from ^{32}P-labelled bacterial cultures. Plant and Soil 190: 163-167.

Magette, W.L., and T.H. Ifft. 1989. Error control in pollutant mass load estimation. American Society of Agricultural Engineers meeting presentation, paper no. 89-2517.

Magette, W.L., R.B. Brinsfield, R.E. Palmer, and J.D. Wood. 1989. Nutrient removal by vegetated filter strips. Journal of the ASAE 32: 663-667.

Magid, J., and N.E. Nielsen. 1992. Seasonal variation in organic and inorganic phosphorus fractions of temperate-climate sandy soils. Plant and Soil 144: 155-165.

Magid, J., N. Christensen, and H. Nielsen. 1992. Measuring phosphorus fluxes through the root zone of a layered sandy soil: comparisons between lysimeter and suction cell solution. Journal of Soil Science 43: 739-747.

Maguire, R.O., A.C. Edwards, and M.J. Wilson. 1998. Influence of cultivation on the distribution of phosphorus in three soils from NE Scotland and their aggregate size fractions. Soil Use and Management 14: 147-153.

Maguire, R.O., J.T. Sims, and F.J. Coale. 2000. Phosphorus solubility in biosolids-amended farm soils in the Mid-Atlantic region of the USA. Journal of Environmental Quality 29: 1225-1233.

Malmqvist, S-O., and L. Göransson. 1997. Animal feed – an important fertiliser input source. The Fertiliser Society, York.

Martin, J.K., and L.F. Molloy. 1971. A comparison of the organic phosphorus compounds extracted from soil, sheep faeces, and plant material collected at a common site. New Zealand Journal of Agricultural Research 14: 329-333.

Massey, H.F., and M.L. Jackson. 1952. Selective erosion of soil fertility constituents. Soil Science Society America Proceedings 16: 353-356.

Massik, Z., and M.J. Costello. 1995. Bioavailability of phosphorus in fish farm effluents to freshwater phytoplankton. Aquaculture Research 26: 607-616.

Mattingly, G.E.G., and A. Penny. 1968. Evaluation of phosphate fertilizers. I. Immediate value of dicalcium phosphate, nitrophosphates, Gafsa rock phosphate, basic slag and potassium metaphosphate for barley and ryegrass. Journal of Agricultural Science, Cambridge 70: 131-138.

Mayer, T.D., and W.M. Jarrell. 1995. Assessing colloidal forms of phosphorus and iron in the Tualatin River basin. Journal of Environmental Quality 24: 1117-1124..

McCallister, D.L., and T.J. Logan. 1978. Phosphate adsorption-desorption characteristics of soils and bottom sediments in the Maumee River Basin of Ohio. Journal of Environmental Quality 7: 87-92.

McColl, R.H.S. 1979. Factors affecting downslope movement of nutrients in hill pasture. Progress in Water Technology 11: 271-285.

McColl, R.H.S., and A.R. Gibson. 1979. Downslope movement of nutrients in hill pastures, Taita, New Zealand. New Zealand Journal of Agricultural Research 22: 151-161.

McColl, R.H.S., E. White and J.R. Waugh. 1975. Chemical run-off in catchments converted to agricultural use. New Zealand Journal of Science 18: 67-84.

McColl, R.H.S., D.J. McQueen, A.R. Gibson, and J.C. Heine. 1985. Source areas of storm runoff in a pasture catchment. Journal of Hydrology New Zealand 24: 1-19.

McCollum, R.E. 1991. Buildup and decline in soil phosphorus: 30-year trends on a Typic Umprabuult. Agronomy Journal 83: 77-85.

McConaghy, S. 1965. Studies on the availability of phosphorus in the soils of Northern Ireland. pp: 38-47. Ministry of Agriculture, Fisheries and Food, Technical Bulletin 13. Her Majesty's Stationary Office, London.

McCoy, E.L., C.W. Boast, R.C. Stehouwer, and E.J. Kladivko. 1994. Macropore hydraulics: taking a sledgehammer to classical theory. pp. 303-348. *In* R. Lal, and B.A. Stewart (ed.) Advances in Soil Science: soil properties and water quality. Lewis Publishers, London.

McDowell, R.W., and A.N. Sharpley. 2001. Approximating phosphorus release from soils to surface runoff and subsurface drainage. Journal of Environmental Quality 30: 508-520.

McDowell, R., and A. Sharpley. 2002. Phosphorus transport in overland flow in response to position of manure application. Journal of Environmental Quality 31: 217-227.

McDowell, R., A. Sharpley, and G. Folmar. 2001. Phosphorus export from an agricultural watershed: linking source and transport mechanisms. Journal of Environmental Quality 30: 1587-1595.

McGarrigle, M.L. 1998. Impact of eutrophication on Irish river water quality. pp 82-90. *In* J.G. Wilson (ed.) Eutrophication in Irish waters. Royal Irish Academy, Dublin.

McGarrigle, M. L., W. S. T. Champ, R. Norton, P. Larkin, and M. Moore. 1993. The trophic status of Lough Conn. Mayo County Council, Castlebar.

McGarrigle, M.L., L. Kilmartin, and R. Hallissey. 1997. Phosphorus loss from agriculture to water – a twin-catchment analysis in the Lough Conn catchment. Irish Journal of Agriculture and Food Research 36: 93.

McGarrigle, M.L., J.J. Bowman, K.J. Clabby, J. Lucey, P. Cunningham, M. MacCárthaigh, M. Keegan, B. Cantrell, M. Lehane, C. Clenaghan, and P.F. Toner. 2002. Water Quality in Ireland 1998-2000. Environmental Protection Agency, Wexford.

McKercher, R. B. and G. Anderson. 1989. Organic phosphate sorption by neutral and basic soils. Communications in Soil Science and Plant Analysis 20: 723-732.

Miller, M.H., E.G. Beauchamp, and J.D. Lauzon. 1994. Leaching of nitrogen and phosphorus from the biomass of three cover crop species. Journal of Environmental Quality 23: 267-272.

Miller, W.P., and D.M. Miller. 1987. A micro-pipette method for soil mechanical analysis. Communications in Soil Science and Plant Analysis 18: 1-15.

Misselbrook, T.H., B.F. Pain, A.C. Stone, and D. Scholefield. 1995. Nutrient run-off following application of livestock wastes to grassland. Environmental Pollution 88: 51-56.

Mitchell, D.J. 1990. The use of vegetation and land use parameters in modelling catchment sediment yields. pp. 289-316. *In*: J.B. Thornes (ed.) Vegetation and erosion. John Wiley & Sons Ltd., Chichester.

Mohr, C.O. 1943. Cattle droppings as ecological units. Ecological Monographs 13: 278-298.

Monaghan, R.M., R.J. Paton, L.C. Smith, and C. Binet. 2000. Nutrient losses in drainage and surface runoff from a cattle-grazed pasture in Southland. Proceedings of the New Zealand Grassland Association 62: 99-104.

Moog, O. 1984. Stream phosphorus exports from prealpine watersheds with respect to geology and land use. Verhandlungen der Internationalen Vereinigung für Limnologie 22: 1071-1076.

Moog, O., H. Nesemann, T. Ofenböck, and C. Stundner. 1993. Grundlagen zum Schutz der Flussperlmuschel in Österreich. Bristol-Stiftung, Zürich.

Moore, P.A., Jr., and D.M. Miller. 1994. Decreasing phosphorus solubility in poultry litter with aluminium, calcium, and iron amendments. Journal of Environmental Quality 23: 325-330.

Moore, P.A. and K. R. Reddy. 1994.Role of Eh and pH on phosphorus geochemistry in sediments of Lake Okeechobe, Florida. Journal of Environmental Quality 23: 955-964.

Moore, P.A., Jr., T.C. Daniel, and D.R. Edwards. 2000. Reducing phosphorus runoff and inhibiting ammonia loss from poultry manure with aluminium sulfate. Journal of Environmental Quality 29: 37-49.

Moorkens, E.A., and Costello, M. 1994. Imminent extinction of a species unique to Ireland: Phillip's freshwater pearl mussel *Margaritifera durrovensis* Phillips. Aquatic Conservation: Marine and Freshwater Ecosystems 4: 363-365.

Morel, C., H. Tunney, D. Plénet, and S. Pellerin. 2000. Transfer of phosphate between soil and solution: Perspectives in soil testing. Journal of Environmental Quality 29: 50-59.

Morgan, M.A. 1997. The behaviour of soil and fertilizer phosphorus. pp. 137-149. *In* H. Tunney et al. (ed.) Phsophorus losss from soil to water. CAB Int., Wallingford, UK.

Mosley, M.P. 1982. Subsurface flow velocities through selected forest soils, South Island, New Zealand. Journal of Hydrology 55: 65-92.

Mozaffari, M. and J. T. Sims. 1994. Phosphorus availability and sorption in an Atlantic coastal plain watershed dominated by animal-based agriculture. Soil Science 157: 97-107.

Mueller, D. H., R. C. Wendt and T. C. Daniel. 1984. Phosphorus losses as affected by tillage and manure application. Soil Science Society of America Journal 48: 901-905.

Mullen, G.J., R.M. Jelley, and D.M. McAleese. 1974. Effects of animal treading on soil properties and pasture production. Irish Journal of Agricultural Research 13: 171-180.

Munk, H. 1985. Ermittlung wirtschaftlich optimaler Phosphatgaben auf Löss- und Geschiebelehmböden auf Basis der CAL-Methode. Zeitschrift für Pflanzenernährung und Bodenkunde 148: 193-213.

Munk, H., and M. Rex. 1990. Zur Eichung von Bodenuntersuchungsmethoden auf Phosphat. Agribiological Research 43: 164-174.

Murphy, J., and J. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27: 31-36.

Murphy, W.E., and N. Culleton, 1997. Distribution of available phosphorus in soil under long-term grassland. pp. 448-449. *In* H. Tunney et al. (ed.) Phsophorus losss from soil to water. CAB Int., Wallingford, UK.

Muscutt, A.D., and P.J.A. Withers. 1996. The phosphorus content of rivers in England and Wales. Water Research 30: 1258-1268.

Nair, P.S., T.J. Logan, A.N. Sharpley, L.E. Sommers, M.A. Tabatabai, and T.L. Yuan. 1984. Interlaboratory comparison of a standardized phosphorus adsorption procedure. Journal of Environmental Quality 13: 591-595.

Nash, D. and C. Murdoch. 1997. Phosphorus in runoff from a fertile dairy pasture. Australian Journal of Soil Research 35: 419-429.

Nash, D., M. Hannah, D. Halliwell, and C. Murdoch. 2000. Factors affecting phosphorus export from a pasture-based grazing system. Journal of Environmental Quality 29: 1160-1166.

Nelson, P.N., E. Cotsaris, and J.M. Oades. 1996. Nitrogen, Phosphorus, and organic carbon in streams draining two grazed catchments. Journal of Environmental Quality 25: 1221-1229.

Netto, A.M., R.A. Pieritz, and J.P. Gaudet. 1999. Field study on the local variability of soil water content and solute concentration. Journal of Hydrology 215: 23-37.

Newbold, J.D., J.W. Elwood, R.V. O'Neill, and A.L. Sheldon. 1983. Phosphorus dynamics in a woodland stream ecosystem: A study of nutrient spiralling. Ecology 64: 1249-1265.

Newson, M.D., and M. Robinson. 1983. Effects of agricultural drainage on upland streamflow: case studies in mid-Wales. Journal of Environmental Management 17: 333-348.

Novak, J.M., D.W. Watts, P.G. Hunt, and K.C. Stone. 2000. Phosphorus movement through a coastal plain soil after a decade of intensive swine manure application. Journal of Environmental Quality 29: 1310-1315.

O'Connor, P.W. and J.K. Syers. 1975. Comparison of ,methods for the determination of total phosphorus in waters containing particulate material. Journal of Environmental Quality 4: 347-350.

Ogaard, A.F. 1996. Effect of phosphorus fertilization on the concentration of total and algal-available phosphorus in different particle-size fractions in Norwegian agricultural soils. Acta Agriculturae Scandinavica 46: 24-29.

Ogunkoya, O. O. and A. Jenkins. 1993. Analysis of storm hydrograph and flow pathways using a three-component hydrograph separation model. Journal of Hydrology 142: 71-88.

Olness, A., S.J. Smith, E.D. Rhoades, and R.G. Menzel. 1975. Nutrient and sediment discharge from agricultural watersheds in Oklahoma. Journal of Environmental Quality 4: 331-336.

Oloya, T.O. and T.J. Logan. 1980. Phosphate desorption from soils and sediments with varying levels of extractable phosphate. Journal of Environmental Quality 9: 526-531.

Olsen, S.R., and F.S. Watanabe. 1970. Diffusive supply of phosphorus in relation to soil textural variations. Soil Science 110: 318-327.

Osborne, L.L., and D.A. Kovacic. 1993. Riparian vegetated buffer strips in water-quality restoration and stream management. Freshwater Biology 29: 243-258.

Osborne, L.L., and M.J. Wiley. 1988. Empirical relationships between land use/cover and stream water quality in an agricultural watershed. Journal of Environmental Management 26: 9-27.

Owens, L.B., W.M. Edwards, and R.W. Van Keuren. 1989. Sediment and nutrient losses from an unimproved, all-year grazed watershed. Journal of Environmental Quality 18: 232-238.

Owens, L.B., W.M. Edwards, and R.W. Van Keuren. 1991. Baseflow and stromflow transport of nutrients from mixed agricultural watersheds. Journal of Environmental Quality 20: 407-414.

Owens, M. 1970. Nutrient Balances in rivers. Water Treatment Examination 19: 239-247.

Owens, M., and G. Wood. 1968. Some aspects of the eutrophication of water. Water Research 2: 151-159.

Ozanne, P.G., D.J. Kirton, and T.C. Shaw. 1961. The loss of phosphorus from sandy soils. Australian Journal of Agricultural Research 12: 410-423.

Pearce, A.J., M.K. Stewart, and M.G. Sklash. 1986. Strom runoff generation in humid headwater catchments 1. Where does the water come from? Water Resources Research 22: 1263-1272.

Peech, M., and L. English. 1944. Rapid microchemical soil tests. Soil Science 57: 167-194.

Pesant, A.R., J.L. Dionne, and J. Genest. 1987. Soil and nutrient losses in surface runoff from conventional and no-till corn systems. Canadian Journal of Soil Science 67: 835-843.

Petch, R.A. 1988. Soil saturation patterns in steep, convergent hill-slopes under forest and pasture vegetation. Hydrological Processes 2: 93-103.

Peterjohn, W.T., and D.L. Correll. 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. Ecology 65: 1466-1475.

Philip, J. R. 1957. The theory of infiltration: 5. The influence of initial moisture content. Soil Science 84: 329-339.

Pierzynski, G.M., T.J. Logan, S.J. Traina, and J.M. Bigham. 1990. Phosphorus chemistry and mineralogy in excessively fertilized soils: descriptions of phosphorus-rich particles. Soil Science Society of America Journal 54: 1583-1589.

Pionke, H.B., and D.R. DeWalle. 1994. Streamflow generation on a small agricultural catchment during autumn recharge: I. Nonstormflow periods. Journal of Hydrology 163: 1-22.

Pionke, H.B., R.R. Schnabel, J.R. Hoover, W.J. Gburek, J.B. Urban, and A.S. Rogowski. 1986. Mahantango Creek watershed – fate and transport of water and nutrients. pp. 108-134. *In* D.L. Correll (ed.) Watershed research perspectives. Smithsonian Institution Press, Washington.

Pionke, H.B., J.R. Hoover, R.R. Schnabel, W.J. Gbured, J.B. Urban, and A.S. Rogowski. 1988. Chemical-hydrologic interactions in the near-stream zone. Water Resources Research 24: 1101-1110.

Pionke, H.B., W.J. Gburek, and G.J. Folmar. 1993. Quantifying stormflow components in a Pennsylvania whatershed when ^{18}O input and storm conditions vary. Journal of Hydrology 148: 169-187.

Pionke, H. B., W. J. Gburek, A. N. Sharpley, and R. R. Schnabel. 1996. Flow and nutrient export patterns for an agricultural hill-land watershed. Water Resources Research 32: 1795-1804.

Pote, D. H., T. C. Daniel, A. N. Sharpley, P. A. Moore, Jr., D. R. Edwards, and D. J. Nichols. 1996. Relating extractable phosphorus to phosphorus in runoff. Soil Science Society of America Journal 60: 855-859.

Pote, D.H., T.C. Daniel, D.J. Nichols, A.N. Sharpley, P.A. Moore, Jr., D.M. Miller and D.R. Edwards. 1999. Relationship between phosphorus levels in three Ultisols and phosphorus concentrations in runoff. Journal of Environmental Quality 28: 170-175.

Poulsen, H.D. 2000. Phosphorus utilization and excretion in pig production. Journal of Environmental Quality 29: 24-27.

Powell, H. K. J., and Taylor, M. C. 1979. Nutrient concentrations in runoff from a gley podzol soil. Progress in Water Technology 11: 295-301.

Quinton, J.N., J.A. Catt, J.A., and T.M. Hess. 2001. The selective removal of phosphorus from soil: Is event size important? Journal of Environmental Quality 30: 538-545.

Radulovich, R., P. Sollins, P. Baveye, and E. Solórzano. 1992. Bypass water flow through unsaturated microaggregated tropical soils. Soil Science Society of America Journal 56: 721-726.

Randall, G.W., T.K. Iragavarapu, and M.A. Schmitt. 2000. Nutrient losses in subsurface drainage water from dairy manure and urea applied for corn. Journal of Environmental Quality 29: 1244-1252.

Rao, P.S.C., D.E. Rolston, R.E. Jessup, and J.M. Davidson. 1980. Solute transport in aggregated porous media: theoretical and experimental evaluation. Soil Science Society of America Journal 44: 1139-1146.

Reid, I., R. Parkinson, S. Twomlow, and A. Clarke. 1990. The impact of agricultural landuse changes on soil conditions and drainage. pp. 199-215. *In* J.B. Thornes (ed.) Vegetation and Erosion. John Wiley & Sons Ltd., Chichester.

Reith, J.W.S., R.H.E. Inkson, N.M. Scott, K.S. Caldwell, J.A.M. Ross, and W.E. Simpson. 1987. Estimates of soil phosphorus for different soil series. Fertilizer Research 11: 123-142.

Reynolds, J.V. 1998. The impact of algae on water use – Cork County Council's experience. pp. 146-155. *In* J.G. Wilson (ed.) Eutrophication in Irish waters. Royal Irish Academy, Dublin.

Reynolds, W.D., and W.D. Zebchuk. 1996. Hydraulic conductivity in a clay soil: two measurement techniques and spatial characterization. Soil Science Society of America Journal 60: 1679-1685.

Richards, K., C. Coxon, and M. Ryan. 1998. Movement of phosphorus down the soil profile, as indicated by Morgan phosphorus value. pp. 102-103. *In* R.H. Foy, and R. Dils (ed.) Practical and innovative measures for the control of agricultural phosphorus losses to water. OECD sponsored workshop 16th-19th June, Greenmount College of Agriculture and Horticulture, Northern Ireland.

Rigler, R.H. 1964. The phosphorus fractions and the turnover time of inorganic phosphorus in different types of lakes. Limnology and Oceanography 9: 511-518.

Roberts, A.M., J.A. Hudson, and G. Roberts. 1989. A comparison of nutrient losses following grassland improvement using two different techniques in an upland area of mid-Wales. Soil Use and Management 5: 174-179.

Robinson, D.A., and R. Naghizadeh. 1992. The impact of cultivation practice and wheelings on runoff generation and soil erosion on the South Downs: some experimental results using simulated rainfall. Soil use and management 8: 151-156.

Rodda, J.C. 1967. The systematic error in rainfall measurement. Journal of the Institute of Water Engineers 21: 173-177.

Rohan, P.K. 1986. The climate of Ireland. The Stationary Office, Dublin.

Römkens, M.J.M., and D.W. Nelson. 1974. Phosphorus relationships in runoff from fertilised soils. Journal of Environmental Quality 3: 10-13.

Römkens, M.J.M., S.N. Prasad, and F.D. Whisler. 1990. Surface sealing and infiltration. pp. 127-172. *In* M.G. Anderson, and T.P. Burt (ed.) Process Studies in Hillslope Hydrology. John Wiley & Sons, Chichester.

Ron Vaz, M.D., A.C. Edwards, C.A. Shand, and M.S. Cresser. 1993. Phosphorus fractions in soil solution: Influence of soil acidity and fertiliser additions. Plant and Soil 148: 175-183.

Rose, S.C., G.L. Harris, A.C. Armstrong, J.R. Williams, K.R. Howse, and N. Tranter. 1991. The leaching of agrochemicals under different agricultural land uses and its effect on water quality. pp. 249-258. *In* N.E. Peters, and D.E. Walling (ed.) Sediment and stream water quality in a changing environment: trends and explanation. IAHS Publication no. 203, IAHS Press, Wallingford.

Ruan, H.D., and R.J. Gilkes. 2000. Phosphorus accumulation in farm ponds and dams in Southwestern Australia. Journal of Environmental Quality 29: 1875-1881.

Rubaek, G.H., and E. Sibbesen. 1995. Soil phosphorus dynamics in a long-term field experiment at Askov. Biology and Fertility of Soils: 20: 86-92.

Russell, R.D. 1965. Phosphate relationships of calcareous soils. pp: 130-141. Ministry of Agriculture, Fisheries and Food, Technical Bulletin 13. Her Majesty's Stationary Office, London.

Ryan, D. 1998. SWAMP Task C, progress report 96-97, Teagasc, Oakpark, Carlow.

Ryan, D., J. Bennett, and I. Kurz 1999. Using a water table model to identify fields prone to overland flow. Irish Journal of Agricultural and Food Research 38: 281.

Ryan, M. 1990. Properties of different grades of soiled water and strategies for safe disposal. pp. 43-58. Seminar on environmental impact of landspreading of wastes, Johnstown Castle, Wexford.

Ryan, M., and D. Noonan. 1995. Using dyes to measure flow patterns of water in soil. Farm & Food Jan/June: 9-11.

Ryden, J.C., J.R. McLaughlin, and J.K. Syers. 1977. Time-dependent sorption of phosphate by soils and hydrous oxides. Journal of Soil Science 28: 585-595.

Saarela, I. 1992. A simple diffusion test for soil phosphorus availability. Plant and Soil 147: 115-126.

Sanderson, M.A., R.M. Jones, M.J. McFarland, J. Stroup, R.L. Reed, and J.P. Muir. 2001. Nutrient movement an removal in a switchgrass biomass-filter strip system treated with dairy manure. Journal of Environmental Quality 30: 210-216.

Sauer, T.J., T.C. Daniel, D.J. Nichols, C.P. West, P.A. Moore, Jr., and G.L. Wheeler. 2000. Runoff water quality from poultry litter-treated pasture and forest sites. Journal of Environmental Quality 29: 515-521.

Saunders, W.M.H., and A.J. Metson. 1971. Seasonal variation of phosphorus in soil and pasture. New Zealand Journal of Agricultural Research 14: 307-328.

Sawyer, C.N. 1947. Fertilization of lakes by agricultural and urban drainage. New England Waterworks Association 61: 109-127.

Schachtschabel, P., H.-P. Blume, G. Brümmer, K.-H. Hartge, and U. Schwertmann. 1992. Lehrbuch der Bodenkunde, 13. Auflage. Enke, Stuttgart.

Schepers, J.S., M.R. Schlemmer, and R.B. Ferguson. 2000. Site-specific considerations for managing phosphorus. Journal of Environmental Quality 29: 125-130.

Schoen R., J.P. Gaudet, and T. Bariac. 1999. Preferential flow and solute transport in a large lysimeter, under controlled boundary conditions. Journal of Hydrology 215: 70-81.

Schofield K., J. Seager, and R.P. Merriman. 1990. The impact of intensive dairy farming activities on river quality: the Eastern Cleddau catchment study. Journal of IWEM 4: 176-186.

Schofield, R.K. 1955. Can a precise meaning be given to available soil phosphorus? Soils and Fertilisers 18: 373-375.

Schoumans, O.F., and A. Breeuwsma. 1997. The relation between accumulation and leaching of phosphorus: laboratory, field and modelling results. pp. 361-361. *In* H. Tunney et al. (ed.) Phosphorus loss from soil to water. CAB Int., Oxon, UK.

Schreiber, J.D. 1988. 1. Estimating soluble phosphorus (PO_4-P) in agricultural runoff. Journal of the Mississippi Academy of Sciences 33: 1-15.

Schreiber, J.D., and L.L. McDowell. 1985. Leaching of nitrogen, phosphorus, and organic carbon from wheat straw residues: I. rainfall intensity. Journal of Environmental Quality 14: 251-256.

Service, M., A.E. Durrant, D. Faughey, J.A. Mills, and J.E. Taylor. 1998. Sources of nutrient inputs to the coastal waters of Northern Ireland. pp. 64-70. *In* J.G. Wilson (ed.) Eutrophication in Irish waters. Royal Irish Academy, Dublin.

Seyfried, M.S., and P.S.C. Rao. 1987. Solute transport in undisturbed columns of an aggregated tropical soil: preferential flow effects. Soil Science Society of America Journal 51: 1434-1444.

Shaffer, K.A., D.D. Fritton, and D.E. Baker. 1979. Drainage water sampling in a wet, dual-pore soil system. Journal of Environmental Quality 8: 241-246.

Shand, C.A., A.E.S. Macklon, A.C. Edwards, and S. Smith. 1994. Inorganic and organic P in soil solutions from three upland soils. Plant and Soil 159: 255-264.

Sharpley, A.N. 1985a. Depth of surface soil-runoff interaction as affeced by rainfall, soil slope, and management. Soil Science Society of America Journal 49: 1010-1015.

Sharpley, A.N. 1985b. The selective erosion of plant nutrients in runoff. Soil Science Society of America Journal 49: 1527-1534.

Sharpley, A.N. 1993. An innovative approach to estimate bioavailable phosphorus in agricultural runoff using iron oxide-impregnated paper. Journal of Environmental Quality 22: 597-601.

Sharpley, A.N. 1995a. Dependence of runoff phosphorus on extractable soil phosphorus. Journal of Environmental Quality 24: 920-926.

Sharpley, A.N. 1995b. Identifying sites vulnerable to phosphorus loss in agricultural runoff. Journal of Environmental Quality 24: 947-951.

Sharpley, A., and B. Moyer. 2000. Phosphorus forms in manure and compost and their release during simulated rainfall. Journal of Environmental Quality 29: 1462-1469.

Sharpley, A.N., and S.J. Smith. 1989. Mineralization and leaching of phosphorus from soil incubated with surface-applied and incorporated crop residue. Journal of Environmental Quality 18: 101-105.

Sharpley, A.N., and S.J. Smith. 1990. Phosphorus transport in agricultural runoff: The role of soil erosion. p. 351-366. *In* J. Boardman et al. (ed.) Soil erosion on agricultural land. John Wiley & Sons, Chichester.

Sharpley, A.N., and S.J. Smith. 1992. Prediction of bioavailable phosphorus loss in agricultural runoff. Journal of Environmental Quality 21: 32-37.

Sharpley, A.N., and J.K. Syers. 1976. Phosphorus transport in surface run-off as influenced by fertiliser and grazing cattle. New Zealand Journal of Science 19: 277-282.

Sharpley, A.N., and J.K. Syers. 1979. Phosphorus inputs into a stream draining an agricultural watershed: II. Amounts contributed and relative significance of runoff types. Water, Air, and Soil Pollution 11: 417-428.

Sharpley, A.N., and P.J.A. Withers. 1994. The environmentally-sound management of agricultural phosphorus. Fertilizer research 39: 133-146.

Sharpley, A.N., J.K. Syers, and P.W. O'Connor. 1976. Phosphorus inputs into a stream draining an agricultural watershed: I. sampling. Water, Air, and Soil Pollution 6: 39-52.

Sharpley, A.N., R.W. Tillman, and J.K. Syers. 1977. Use of laboratory extraction data to predict losses of dissolved inorganic phosphate in surface runoff and tile drainage. Journal of Environmental Quality 6: 33-36.

Sharpley, A.N., J.K. Syers, and R.W. Tillman. 1978. An improved soil-sampling procedure for the prediction of dissolved inorganic phosphate concentrations in surface runoff from pasture. Journal of Environmental Quality 3: 455-456.

Sharpley, A.N., L.R. Ahuja, M. Yamamoto, and R.G. Menzel. 1981a. The kinetics of phosphorus desorption from soil. Soil Science Society of America Journal 45: 493-496.

Sharpley, A.N., R.G. Menzel, E.D. Rhoades, and A.E. Olness. 1981b. The sorption of soluble phosphorus by soil material during transport in runoff from cropped and grassed watersheds. Journal of Environmental Quality 10: 211-215.

Sharpley, A.N., L.R. Ahuja, R.G. Menzel. 1981c. The Release of soil phosphorus to runoff in relation to the kinetics of desorption. Journal of Environmental Quality 10: 386-391.

Sharpley, A.N., C.A. Jones, C. Gray, and C.V. Cole. 1984. A simplified soil and plant phosphorus model: II. prediction of labile, organic, and sorbed phosphorus. Soil Science Society of America Journal 48: 805-809.

Sharpley, A., S.J. Smith and R.G. Menzel. 1986. Phosphorus criteria and water quality management for agricultural watersheds. Lake and Reservoir Management: 2: 177-182.

Sharpley, A.N., S.J. Smith, and J.W. Naney. 1987. Environmental impact of agricultural nitrogen and phosphorus use. Journal of Agricultural Food Chemistry 35: 812-817.

Sharpley, A.N., S.J. Smith, and J.R. Williams. 1988. Nonpoint source pollution impacts of agricultural land use. Lake and Reservoir Management 4: 41-49.

Sharpley, A.N., S.J. Smith, O.R. Jones, W.A. Berg, and G.A. Coleman. 1992. The transport of bioavailable phosphorus in agricultural runoff. Journal of Environmental Quality 21: 30-35.

Sharpley, A.N., J.S. Robinson, and S.J. Smith. 1995. Assessing environmental sustainability of agricultural systems by simulation of nitrogen and phosphorus loss in runoff. European Journal of Agronomy 4: 453-464.

Sharpley, A.N., R.W. McDowell, J.L. Weld, and P.J.A. Kleinmann. 2001. Assessing site vulnerability to phosphorus loss in an agricultural watershed. Journal of Environmental Quality 30: 2026-2036.

Shaw, E.M. 1994. Hydrology in practice. Chapman & Hall, London.

Sherwood, M. 1990. Runoff of nutrients following landspreading of slurry. pp. 111-117. Seminar on environmental impact of landspreading of wastes, Johnstown Castle, Wexford.

Shipitalo, M.J., and W.M. Edwards. 1993. Seasonal patterns of water and chemical movement in tilled and no-till column lysimeters. Soil Science Society of America Journal 57: 218-223.

Shipitalo, M.J., W.M. Edwards, W.A. Dick, and L.B. Owens. 1990. Initial storm effects on macropore transport of surface-applied chemicals in no-till soil. Soil Science Society of America Journal 54:1530-1536.

Sibbesen, E. 1983. Phosphate soil tests and their suitability to assess the phosphate status of soil. Journal of Science Food and Agriculture 34: 1368-1374.

Sibbesen, E., and A.N. Sharpley. 1997. Setting and justifying upper critical limits for phosphorus in soils. pp. 151-176. *In* H. Tunney et al. (ed.) Phsophorus losss from soil to water. CAB Int., Wallingford, UK.

Simard, R.R., S. Beauchemin, and P.M. Haygarth. 2000. Potential for preferential pathways of phosphorus transport. Journal of Environmental Quality 29: 97-105.

Simmons, K.E., and D.E. Baker. 1993. A zero-tension sampler for the collection of soil water in macropore systems. Journal of Environmental Quality 22: 207-212.

Simpson, K. 1965. The significance of effects of soil moisture and temperature on phosphorus uptake. pp: 19-29. Ministry of Agriculture, Fisheries and Food, Technical Bulletin 13. Her Majesty's Stationary Office, London.

Sims, J.T., A.C. Edwards, O.F. Schoumans, and R.R. Simard. 2000. Integrating soil phosphorus testing into environmentally based agricultural management practices. Journal of Environmental Quality 29: 60-71.

Singh, P., and R.S. Kanwar. 1991. Preferential solute transport through macropores in large undisturbed saturated soil columns. Journal of Environmental Quality 20:295-300.

Sklash, M.G., and R.N. Farvolden. 1979. The role of groundwater in storm runoff. Journal of Hydrology 43: 45-65.

Smith, C.M. 1992. Riparian afforestation effects on water yields and water quality in pasture catchments. Journal of Environmental Quality 21: 237-245.

Smith, D.R., P.A. Moore, Jr., C.L. Griffis, T.C. Daniel, D.R. Edwards, and D.L. Boothe. 2001. Effects of alum and aluminium chloride on phosphorus runoff from swine manure. Journal of Environmental Quality 30: 992-998.

Smith, K.A., A.G. Chalmers, B.J. Chambers, and P. Christie. 1998. Organic manure phosphorus accumulation, mobility and management. Soil Use and Management 14: 154-159.

Smith, R.V., R.H. Foy, and S.D. Lennox. 1994. Mathematical modelling techniques to evaluate the impact of phosphorus reduction on phosphate loads to Lough Neagh. pp. 271-284. *In*: V. Barnett, and K.F. Turkman (ed.) Statistics for the environment 2: water related issues. John Wiley & Sons Ltd., Chichester.

Smith, R.V., S.D Lennox, C. Jordan, R.H. Foy, and E. McHale. 1995. Increase in soluble phosphorus transported in drainflow from a grassland catchment in response to soil phosphorus accumulation. Soil Use and Management 11:204-209.

Smith, R.V., R.H. Foy and S.D. Lennox. 1997. Increase in soluble reactive phosphorus transport in grassland catchments in response to soil phosphorus accumulation. pp. 356-358. *In* H. Tunney et al. (ed.) Phsophorus losss from soil to water. CAB Int., Wallingford, UK.

Sonzogni, W.C., S.C. Chapra, D.E. Armstrong, and T.J. Logan. 1982. Bioavailability of phosphorus inputs to lakes. Journal of Envrionmental Quality 11: 555-563.

Stainton, M.P. 1980. Errors in molybdenum blue methods for determining orthophosphate in freshwater. Canadian Journal of Fishery and Aquatic Science 37: 472-478.

Stamm, C. 1995. Causes of eutrophication in a rural watershed. Pp. 377-381. *In*: J.F.Th. Schoute et al. (ed.) Scenario studies for the rural environment. Kluwer Academic Publishers, Dordrecht.

Stamm, C., H. Flühler, R. Gächter, J. Leuenberger, and H. Wunderli. 1998. Preferential transport of phosphorus in drained grassland soils. Journal of Environmental Quality 27: 515-522.

Starr, J.L., H.C. DeRoo, C.R. Frink and J.-Y. Parlange. 1978. Leaching characteristics of a layered field soil. Soil Science Society of America Journal 42: 386-391.

Steegen, A., G. Govers, I. Takken, J. Nachtergaele, J. Poesen, and R. Merckx. 2001. Factors controlling sediment and phosphorus export from two Belgian agricultural catchments. Journal of Environmental Quality 30: 1249-1258.

Steenhus, T.S., and R.E. Muck. 1988. Preferred movement of nonadsorbed chemicals on wet, shallow, sloping soils. Journal of Environmental Quality 17: 376-384.

Stevens, R.J. 1980. Different forms of phosphorus in freshwater. Analytical Proceedings 17: 375-376.

Stevens, R.J., and B.M. Stewart. 1982a. Some components of particulate phosphorus in river water entering Lough Neagh. Water Research 16: 1591-1596.

Stevens, R.J., and B.M. Stewart. 1982b. Concentration, fractionation and characterisation of soluble organic phosphorus in river water entering Lough Neagh. Water Research 16: 1507-1519.

Sticher, H. 1988. Allgemeine Bodenkunde. ETH Zurich, Zurich.

Stoltenberg, N.L. and J.L. White. 1953. Selective loss of plant nutrients by erosion. Soil Science Society Proceedings 17: 406-410.

Stout, W.L., A.N. Sharpley, and J. Landa. 2000. Effectiveness of coal combustion by-products in controlling phosphorus export from soils. Journal of Environmental Quality 29: 1239-1244.

Strong, W.M., E.K. Best, and J.E. Cooper. 1997. Phosphate fertiliser residues in wheat-growing soils of the Western Downs, Queensland. Australian Journal of Soil Research 35: 341-354.

Svendsen, L.M., B. Kronvang, P. Kristensen, and P. Graesbol. 1995. Dynamics of phosphorus compounds in a lowland river system: importance of retention and non-point sources. Hydrological Processes 9: 119-142.

Swarzendruber, D., and T.C. Olsen. 1961. Sand-model of buffer effects in the double-ring infiltrometer. Soil Science Society of America Proceedings 25: 5-8.

Syers, J. K., R. Shah and T. W. Walker. 1969. Fractionation of phosphorus in two alluvial soils and particle-size separates. Soil Science 108: 283-289.

Tarafdar, J.C., and N. Claasen. 1988. Organic phosphorus compounds as a phosphorus source for higher plants through the activity of phosphatases produced by plant roots and microorganisms. Biology and Fertility of Soils 5: 308-312.

Tariq Siddique, M., J. S. Robinson, and B.J. Alloway. 2000. Phosphorus reactions and leaching potential in soils amended with sewage sludge. Journal of Environmental Quality 29: 1931-1938.

Tate, K.R., T.W. Speir, D.J. Ross, R.L. Parfitt, K.N. Whale, and J.C. Cowling. 1991. Temporal variations in some plant and soil P pools in two pasture soils of widely different P fertility status. Plant and Soil 132: 219-232.

Taylor, C.H., and A.J. Pearce. 1982. Storm runoff processes and subcatchmnt characteristics in a New Zealand hill country catchment. Earth surface processes and landforms 17: 439:447.

Terman, G.L., J.C. Noggle, and C.M. Hunt. 1977. Growth rate-nutrient concentration relationships during early growth of corn as affected by applied N, P, and K. Soil Science Society of America Journal 41: 363-368.

Tiessen, H., J. W. B. Stewart and J. O. Moir. 1983. Changes in organic and inorganic phosphorus composition of two grassland soils and their particle size fractions during 60 to 90 years. Journal of Soil Science 34: 815-823.

Tietzsch-Tyler, D., A.G. Sleeman, M.A. Boland, E.P. Daly, A.M. Flegg, P.J. O'Connor, and W.P. Warren. 1994. Geology of South Wexford. Geological Survey of Ireland, Dublin.

Timmons, D.R., R.F. Holt, and J.J. Latterell. 1970. Leaching of crop residues as a source of nutrients in surface runoff water. Water Resource Research 6: 1367-1375.

Torpey, P. and M.A. Morgan. 1999. P profile of water, soil and sediment in a farm drainage system. pp. 25-26. *In* P. O'Kiely et al. (ed.) Summary of papers presented at the Agricultural Research Forum. UCD Belfield, Dublin.

Tricker, A.S. 1978. The infiltration cylinder: some comments on its use. Journal of Hydrology 36: 383-391.

Trojan, M.D., and D.R. Linden. 1992. Microrelief and rainfall effects on water and solute movement in earthworm burrows. Soil Science Society of America Journal 56: 727-733.

Tufford, D.L., H.N. McKellar, Jr., and J.R. Hussey. 1998. In-stream nonpoint source nutrient prediction with land-use proximity and seasonality. Journal of Environmental Quality 27: 100-111.

Tunney. H. 1990. A note on a balance sheet approach to estimating the phosphorus fertiliser needs of agriculture. Irish Journal of Agricultural Research 29: 149-154.

Tunney, H., T. O'Donnell, and A. Fanning. 1997. Phosphorus loss to water from a small low-intensity grassland catchment. pp. 358-360. *In* H. Tunney et al. (ed.) Phosphorus loss from soil to water. CAB Int., Wallingford, UK.

Tunney, H., R.H. Foy, and O.T. Carton. 1998. Phosphorus inputs to water from diffuse agricultural sources. pp. 25-39. *In* J.G. Wilson (ed.) eutrophication in Irish waters. Royal Irish Academy, Dublin.

Tunney, H., B. Coulter, K. Daly, I. Kurz, C. Coxon, D. Jeffrey, P. Mills, G. Kiely, and G. Morgan. 2000. Quantification of phosphorus loss from soil to water. Final report and literature review. EPA, Wexford.

Turner, B.L., and P.M. Haygarth. 2000. Phosphorus forms and concentrations in leachate under four grassland soil types. Soil Science Society of America Journal 64: 1090-1099.

Turner, B.L., and P.M. Haygarth. 2001. Phosphorus solubilization in rewetted soils. Nature 411: 258.

Turner, M.A., R.W. Tillman, and J.K. Syers. 1979. Losses of phosphorus and nitrogen forms in subsurface drainage water as influenced by phosphate fertilizer, grazing animals, and irrigation treatments. Progresses in Water Technology 11: 287-294.

Turtola, E., and A. Jaakkola. 1995. Loss of phosphorus by surface runoff and leaching from a heavy clay soil under barley and grass ley in Finland. Acta Acticuturae Scandinavica 45: 159-165.

Turtola, E., and A. Paajanen. 1995. Influence of improved subsurface drainage on phosphorus losses and nitrogen leaching from a heavy clay soil. Agricultural Water Management 28: 295-310.

Uusitalo, R., E. Turtola, T. Kauppila, and T. Lilja. 2001. Particulate phosphorus and sediment in surface runoff and drainflow from clayey soils. Journal of Environmental Quality 30: 589-595.

Vaithiyanathan, P., and D.L. Correll. 1992. The Rhode river watershed: Phosphorus distribution and export in forest and agricultural soils. Journal of Environmental Quality 21: 280-288.

Valk, H. J.A. Metcalf, and P.J.A. Withers. 2000. Prospects for minimizing phosphorus excretion in ruminants by dietary manipulation. Journal of Environmental Quality 29: 28-36.

Van Keuren, R.W., J.L. McGuiness, and F.W. Chichester. 1979. Hydrology and chemical quality of flow from small pastured watersheds: I. Hydrology. Journal of Environmental Quality 8: 162-166.

Vieira, S.R., D.R. Nielsen, and J.W. Biggar. 1981. Spatial variability of filed-measured infiltration rate. Soil Science Society of America Journal 45: 1040-1048.

Vighi, M., S. Soprani, P. Puzzarini, and G. Menghi. 1991. Phosphorus loads from selected watersheds in the drainage area of the Northern Adriatic Sea. Journal of Environmental Quality 20: 439-444.

Viner, A.B. 1988. Phosphorus on suspensoids from the Tongariro River (North Island, New Zealand) and its potential availability for algal growth. Archiv für Hydrobiologie 111: 481-489.

Vollendweider, R.A. 1971. Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication. OECD, Paris.

Vollenweider, R.A., and J. Kerekes. 1980. The loading concepts as basis for controlling eutrophication philosophy and preliminary results of the OECD programme on eutrophication. Progresses in Water Technology 12: 5-38.

Waldorf, N. 1995. Geographical data analysis. John Wiley & Sons, Chichester.

Ward, R.C., and M. Robinson. 1990. Principles of hydrology. McGraw Hill Book Company, London.

Weaver, D.M., G.S.P. Ritchie, G.C. Anderson, and D.M. Deeley. 1988a. Phosphorus leaching in sandy soils. I. Short-term effects of fertilizer applications and environmental conditions. Australian Journal of Soil Research 26: 177-190.

Weaver, D.M., G.S.P. Ritchie, and G.C. Anderson. 1988b. Phosphorus leaching in sandy soils. II. Laboratory studies of the long-term effects of phosphorus sources. Australian Journal of Soil Research 26: 191-200.

Webber, M.D., and G.E.G. Mattingly. 1970. Inorganic soil phosphorus II. Changes in monocalcium phosphate and lime potentials on mixing and liming soils. Journal of Soil Science 21: 121-126.

Webster, R., and P.H.T. Beckett. 1972. Matric suction to which soils in South Central England drain. Journal of agricultural Science, Cambridge 78: 379-387.

Wehrli, B., A. Wüest. H. Bührer, R. Gächter, and J. Zobrist. 1996. Überdüngung der Schweizer Seen – erfreulicher Trend nach unten. EAWAG News 42D: 12-14.

Wendt, R.C. and R.B. Corey. 1980. Phosphorus variations in surface runoff from agricultural lands as a function of land use. Journal of Environmental Quality 9: 130-136.

Whalen, J.K., and C. Chang. 2001. Phosphorus accumulation in cultivated soils from long-term annual applications of cattle feedlot manure. Journal of Environmental Quality 30: 229-237.

White, R.E., and A.W. Taylor. 1977a. Reactions of soluble phosphate with acid soils: The interpretation of adsorption-desorption isotherms. Journal of Soil Science 28: 314-328.

White, R.E., and A.W. Taylor. 1977b. Effect of pH on phosphate adsorption and isotopic exchange in acid soils at low and high additions of soluble phosphate. Journal of Soil Science 28: 48-61.

White, R.E., G.W. Thomas, and M.S. Smith. 1984. Modelling water flow through undisturbed soil cores using a tranfer function model derived from HOH and Cl transport. Journal of Soil Science 35: 159-168.

White, R.E., J.S. Dyson, Z. Gerstl, and B. Yaron. 1986. Leaching of herbicides through undisturbed cores of structured clay soil. Soil Science Society of America Journal 50: 277-283.

Wild, A., and I.A. Babiker. 1976. The asymmetric leaching pattern of nitrate and chloride in a loamy sand under field conditions. Journal of Soil Science 27: 460-466.

Williams, A.R.I.C. 1965. pp: 49-63. Ministry of Agriculture, Fisheries and Food, Technical Bulletin 13. Her Majesty's Stationary Office, London.

Williams, E.G. 1959. Influence of parent material and drainage conditions of soil phosphorus relationships. Agrochimica 3: 279-309.

Wilson, G.V., and R.J. Luxmoore. 1988. Infiltration, and macroporosity distributions in two forested watersheds. Soil Science Society of America Journal 52: 329-335.

Wilson, G.V., P.M. Jardine, R.J. Luxmoore, L.W. Zelazany, D.A. Lietzke, and E.D. Todd. 1991. Hydrogeochemical processes controlling subsurface transport from an upper subcatchment of Walker branch watershed during storm events. 1. Hydrologic transport processes. Journal of Hydrology 123: 297-316.

Winterbourn, M.J. 1990. Interactions among nutrients, algae and invertebrates in a New Zealand mountain stream. Freshwater Biology 23: 463-474.

Withers, P.J.A. 1996. Phosphorus cycling in UK agriculture and implications for water quality. Soil Use and Management 12: 221.

Withers, P.J.A., and S.C. Jarvis. 1998. Mitigation options for diffuse phosphorus loss to water. Soil Use and Management 14: 186-192.

Withers, P.J.A., S.D. Clay, and V.G. Breeze. 2001. Phosphorus transfer in runoff following application of fertilizer, manure, and sewage sludge. Journal of Environmental Quality 30: 180-188.

Witmer, M.C.H. 1984. Surface water quality in relation to soil type, land use and discharge in a rural catchment area. Science and Technology 17: 1155-1164.

Wolf, A. M., D. E. Baker, H. B. Pionke, and H. M. Kunishi. 1985. Soil tests for estimating labile, soluble, and algae-available phosphorus in agricultural soils. Journal of Environmental Quality 14: 341-348.

Xue, Y., M.B. David, L.E. Gentry, and D.A. Kovacic. 1998. Kinetics and modeling of dissolved phosphorus export from a tile-drained agricultural watershed. Journal of Envrionmental Quality 27: 917-922.

Yli-Halla, M., and H. Hartikainen. 1996. Release of soil phosphorus during runoff as affected by ionic strength and temperature. Agriculture and Food Science in Finland 5: 193-202.

Yli-Halla, M., H. Hartikainen, P. Ekholm, E. Turtola, M. Puustinen, and K. Kallio. 1995. Assessment of soluble phosphorus load in surface runoff by soil analyses. Agriculture, Ecosystems and Environment 56: 53-62.

Young, R.A., and C.K. Mutchler. 1976. Pollution potential of manure spread on frozen ground. Journal of Environmental Quality 5: 174-179.

Zachmann, J.E., and D.R. Linden. 1989. Earthworm effects on corn residue breakdown and infiltration. Soil Science Society of America Journal 53: 1846-1849.

Zhao, S.L., C. Gupta, D.R. Huggins, and J.F. Moncrief. 2001. Tillage an nutrient source effects on surface and subsurface water quality at corn planting. Journal of Environmental Quality 30: 998-1008.

Zimmermann, C.F., M.T. Price, and J.R. Montgomery. 1978. A comparison of ceramic and Teflon in situ samplers for nutrient pore water determinations. Estuarine and Coastal Marine Science 7: 93-97.

Zollweg, J.A., W.J. Gburek, H.B. Pionke, and A.N. Sharpley. 1995. GIS-based modeling of phosphorus output from a northeastern upland agricultural watershed. pp. 251-257. *In* C. Heatwole (ed.) Water quality modeling , proceedings of the international symposium. American Society of Agricultural Engineers, Orlando.

Zou, X., D. Binkley, and K.G. Doxtader. 1992. A new method for estimating gross phosphorus mineralization and immobilization rates in soils. Plant and Soil 147: 243-250.