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 IN IRISH AQUIFERS: IMPLICATIONS FOR INPUT TO SURFACE WATERS

**Presented in fulfilment**
**of the requirements for the degree of**
**Doctor of Philosophy**
**October 2001**

**by Garrett Kilroy**
**Department of Geology**
**Trinity College Dublin**

**Supervised by:**
**Dr. C.E. Coxon**
**Trinity College Dublin**

TRINITY COLLEGE
11 APR 2002
LIBRARY DUBLIN
THESIS 6733

**For**

**Charlie and Mary**

**my parents**

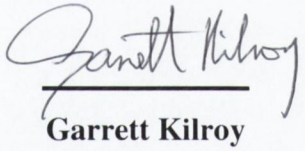
**for all their love and support**

# DECLARATION

**This thesis has not been submitted for a degree to this or any other university and, with acknowledged exception, is entirely my own work.**

I give permission for the Library to lend or copy this thesis upon request.

**Trinity College Dublin regulations.**



**Garrett Kilroy**

**October 2001**

# SUMMARY

This project examines phosphorus levels in a range of Irish hydrogeological situations, both to fill this gap in basic scientific knowledge, and to determine the circumstances in which concentrations likely to trigger eutrophication in surface waters are prone to occur. This research comprised an assessment of phosphorus (P) levels in a national dataset from the Environmental Protections Agency's national groundwater quality monitoring program and the detailed assessment of three catchment areas in the west of Ireland. The study areas were the Robe catchment in Co. Mayo, the Fergus catchment in Co. Clare and Co. Limerick.

Nationally groundwater levels were generally low with a median value 17 $\mu g\ l^{-1}$ of unfiltered molybdate reactive P. However, one quarter of the data were higher than the eutrophication threshold for Irish river (30 $\mu g\ l^{-1}$). Groundwater P concentrations were evenly distributed across the country but sites with elevated groundwater P concentrations were generally located in the eastern half of the country.

Highest median total phosphorus (TP) levels were reported in the Fergus and Robe catchment, where the aquifers were influenced to varying degrees by karstification. The Limerick sites had lowest median TP levels. Approximately one third of the sites had TP levels higher than concentrations which result in adverse conditions in Irish lakes (20 $\mu g\ l^{-1}$ TP). Extreme P levels (1-2 mg $l^{-1}$) were rare and generally occurred at boreholes. Springs and dug wells appear less vulnerable to such extremes in P concentrations.

Total dissolved P (TDP) and dissolved reactive P (DRP) comprised the majority of TP (greater than 80%) in groundwater. Particulate P levels were low, but greatest in the Fergus and Robe catchments, and especially at springs. Karstification in these catchments would facilitate rapid, turbulent flow along conduits, which would best provide the required energy to transport particulates. Temporally particulate P (PP) and dissolved organic P (DOP) exhibited greatest hydrological response, with DRP displaying a more dulled reaction. Greatest increases in P concentrations occurred after the first major autumnal rains in September 1999. Subsequent rainfall peaks appeared to have a lesser impact on P levels. This response to the first autumnal rains probably reflects a

hydrological switch where the catchments change from a soil moisture deficit to a soil moisture surplus situation.

Sites with greater abstraction rates had lower TP levels, which probably represent a dilution effect. Quaternary deposits and karstification appear to be the key hydrogeological factors influencing groundwater P levels. Groundwater under Gley soils had lower P levels than the free-draining Grey Brown Podzolics and Brown Earths.

Groundwater P loading appears less important than other P transfer mechanisms in the catchments studied in Co. Limerick. The contribution of groundwater P to surface waters was greatest in the karstic systems. Both the Fergus and Robe catchments experienced significant groundwater P contributions to their surface waters. In the upper Fergus catchment, during low flow conditions, groundwater P provided the majority of the P load to surface water. Point source P loads in the karstic aquifers, as experienced in the Robe catchment, can provide rapid linkages to river and lakes from on land P sources which may be remote from surface water.

# ACKNOWLEDGEMENTS

I would like to sincerely thank my supervisor Dr. Catherine Coxon for the opportunity of this research and all her valuable support and guidance throughout the project. I am also grateful to Dr. Norman Allott for all help particularly with regard to analytical chemistry.

I am very grateful to Brian O'Neill and Lynne Preston for collecting samples, while I was overseas. I also am very thankful to Mark Kavanagh for analysing DRP during this period and his general expertise in the laboratory. I would like to thank Gareth, Anthony and Brian for assistance in field in all weather.

I am especially grateful to Micheal MacCarthaigh of the Environmental Protection Agency for providing the phosphorus data from the National Groundwater Monitoring Programme and Dr. Martin McGarrigle for all his help with the Robe catchment. From Teagasc I would like to thank Dr. Karen Daly for permission to study and present the soil P desorption model. Dr. Brian Coulter for the national soil P coverage and Dr. Eddie MacDonald for preparing the catchment general soil maps. I appreciate all help given to me by Donal Daly and all at the groundwater section of the Geological Survey of Ireland.

A special thanks to all the landowners of the Robe and Fergus catchment for allowing me access to springs and wells on their land during my sampling programme. I am very grateful for their hospitality and assistance. This thanks also extends especially to Cait Gleeson of the Limerick County Council and for organising access to the Limerick public supply wells and group water schemes, and to all the caretakers involved. Without the generous assistance of all these individuals this research would not have been possible.

In the Geology Department I would like to thank all my colleagues for their help and especially to Neil, Declan and Frank for all their technical assistance. I am very thankful to Tale, Pat and Krysia in the Geography Department for assistance in all aspects of GIS. I am also very grateful to Paul Mills of Compass Informatics for GIS assistance.

To those in the Centre for the Environment, I would like to express a special thank you for all help and fun during the project. In the final throes of this thesis, I am very grateful for help from Alice, Gary, and Ric. Thanks to my office mates Eddy and Dave, my old office mate Karl, and to Micheal for all his help, not all phosphorus related.

A very special thanks to all my brothers; Patrick, Karl, Darragh and Declan for their support and companionship. Thank you Neeta for all your support and understanding throughout the project. Finally, I would like to thank my parents, to whom this thesis is dedicated, for everything.

# TABLE OF CONTENTS


**Title Page** i
**Dedication** ii
**Declaration and permission to copy** iii
**Summary** iv
**Acknowledgements** vi
**Table of contents** vii
**List of figures** xii
**List of tables** xvii

**CHAPTER 1. CONTEXT OF RESEARCH** 1
**1.1 General introduction** 1
**1.2 Surface water quality in Ireland** 2
**1.3 Sources of phosphorus in Irish surface waters** 4
**1.4 Nomenclature in phosphorus analysis of freshwaters** 4
**1.5 Why groundwater phosphorus has been neglected** 6
1.5.1 Regulatory requirements 6
1.5.2 International studies of phosphorus in groundwater 7
**1.6 Movement of phosphorus to groundwater** 10
**1.7 Groundwater phosphorus derived from geological materials** 13
**1.8 National strategies to deal with eutrophication** 15
**1.9 Aims and Objectives** 16
**1.10 Thesis Structure** 16

**CHAPTER 2. PHOSPHORUS IN IRISH GROUNDWATERS** 19
**2.1 Introduction** 19
**2.2 Materials and methods** 20
2.2.1 Structure of the monitoring network for groundwater phosphorus 20
2.2.2 Available datasets 24
2.2.3 Factors affecting the quality of spatial data 25
2.2.4 Summary of GIS methods used in assessment of the national dataset 25
2.2.5 Boxplots for graphical presentation 26
**2.3 Results** 26
2.3.1 Introduction 26
2.3.2 Phosphorus concentrations in the NGQMP 26
2.3.3 Spatial distribution of phosphorus levels in Irish aquifers. 29
2.3.4 Groundwater site location characteristics 29
2.3.5 Soil phosphorus 30
2.3.6 Soil phosphorus desorption model 31
2.3.7 Stocking densities 35
2.3.8 CORINE land use classification 37
2.3.9 Geology 40
2.3.10 Hydrometric regions 42
**2.4 Discussion** 48
2.4.1 Relationships. 48

2.4.2 Sources of error 50
2.4.3 National versus catchment scale assessment 51

**CHAPTER 3. CATCHMENT DESCRIPTIONS 53**
**3.1 Introduction 53**
**3.2 Fergus Catchment 56**
3.2.1 Introduction 56
3.2.2 Bedrock geology 56
3.2.3 Quaternary deposits (subsoils) 58
3.2.4 Hydrogeology 58
3.2.5 Hydrology 59
3.2.6 Surface water quality 63
**3.3 Robe Catchment 64**
3.3.1 Introduction 64
3.3.2 Bedrock geology 64
3.3.3 Quaternary deposits (subsoils) 66
3.3.4 Hydrogeology 66
3.3.5 Hydrology 67
3.3.6 Surface water quality 68
**3.4 Limerick Catchments 69**
3.4.1 Introduction 69
3.4.2 Bedrock geology 70
3.4.3 Quaternary deposits (subsoils) 70
3.4.4 Hydrogeology 70
3.4.5 Hydrology 72
3.4.6 Surface water quality 72

**CHAPTER 4. HYDROCHEMISTRY 74**
**4.1 Introduction 74**
**4.2 Methods 75**
4.2.1 Monitoring Regime 75
4.2.2 Sampling Procedures 76
4.2.3 Sample Preparation and storage 78
4.2.4 Phosphorus analysis 78
4.2.5 Other analytes 79
4.2.6 Quality control and quality assurance 80
4.2.7 Field Meaurements 80
**4.3 Phosphorus Results 81**
4.3.1 Quality control and quality assurance 81
4.3.2 Total Phosphorus 82
4.3.3 Phosphorus fractions 86
**4.4 Basic hydrochemical descriptions of each catchment 89**
4.4.1 Ion balance errors 89
4.4.2 Major ionic composition 92
**4.5 Field parameters distribution maps 97**
**4.6 Relationships between phosphorus fractions and other water chemistry parameters 102**
4.6.1 Introduction 102
4.6.2 Assessment of total phosphorus and EC, DO and Ph 103

4.6.3 Assessment of phosphorus fractions and EC, DO and pH at selected sites in each catchment. 107
4.6.4 Phosphorus fractions and major ions at selected sites in the Fergus catchments. 111
4.6.5 Coefficient of variation of EC and TP 114
4.6.6 Saturation Indices of Calcite and Hydroxyapatite. 116
**4.7 Discussion 119**
4.7.1 Total phosphorus concentrations 119
4.7.2 Phosphorus fractions in groundwater 119
4.7.3 Groundwater type and its influence on phosphorus levels 120
4.7.4 The influence of specific chemical parameters on groundwater phosphorus 121
4.7.5 Dissolved solids variability and groundwater phosphorus 122
4.7.6 Calcite and hydroxyapatite saturation indices 122

**CHAPTER 5. HYDROGEOLOGICAL CONTROLS ON PHOSPHORUS IN GROUNDWATER 124**
**5.1 Introduction 124**
**5.2 Abstraction rates and depth to standing water 126**
5.2.1 Introduction and methods 126
5.2.2 Abstraction rates results 127
5.2.3 Depth to standing water 128
5.2.4 Discussion 133
**5.3 Quaternary deposits 134**
5.3.1 Introduction and methods 134
5.3.2 Limerick Quaternary deposits results 135
5.3.3 Fergus Quaternary deposits results 135
5.3.4 Robe Quaternary deposits results 136
5.3.5 Depth to bedrock results 136
5.3.6 Discussion 137
**5.4 Bedrock geology and aquifer classification 139**
5.4.1 Introduction and methods 139
5.4.2 Co. Limerick results 140
5.4.3 Fergus catchment results 144
5.4.4 Geological phosphorus in the Fergus catchment 146
5.4.5 Robe catchment results 147
5.4.6 Discussion 147
**5.5 Aquifer vulnerability 149**
5.5.1 Introduction and methods 149
5.5.2 Co. Limerick 149
5.5.3 Fergus catchment 150
5.5.4 Robe catchment 151
5.5.5 Discussion 151
**5.6 Overall discussion 152**

**CHAPTER 6. TEMPORAL ANALYSIS** **153**
**6.1 General Introduction** **153**
**6.2 Materials and Methods** **155**
6.2.1 Sampling Procedures and analytical techniques 155
6.2.2 Rainfall in the Study Catchments 156
6.2.3 Effective rainfall and soil moisture deficits 157
**6.3 Long Term Changes in Groundwater P** **159**
6.3.1 Introduction 159
6.3.2 Fergus catchment 159
6.3.3 Robe catchment 160
6.3.4 Limerick sites 161
6.3.5 Boreholes with gross levels of TP 161
**6.4 Medium Term Changes in Groundwater P** **164**
6.4.1 Introduction 164
6.4.2 Robe Catchment 164
6.4.3 Fergus Catchment 167
**6.5 Short Term Changes in Groundwater P** **169**
6.5.1 Introduction 169
6.5.2 RS06 spring: Robe catchment short term changes 170
6.5.3 RS13 spring: Fergus catchment short term changes 172
6.5.4 FS05 spring: Fergus catchment short term changes 173
**6.6 Discussion** **174**

**CHAPTER 7. LAND COVER** **178**
**7.1 General introduction** **178**
**7.2 Soil Cover** **178**
7.2.1 Introduction 178
7.2.2 Methods 180
7.2.3 Limerick Catchments Results 181
7.2.4 Fergus Catchment Results 187
7.2.5 Robe Catchment Results 194
7.2.6 Discussion 196
**7.3 CORINE Landcover Classes** **198**
7.3.1 Introduction 198
7.3.2 Methods 199
7.3.3 Limerick Catchments Results 199
7.3.4 Fergus Catchment Results 201
7.3.5 Robe Catchment Results 204
7.3.6 Discussion 206
**7.4 Agricultural Statistics** **207**
7.4.1 Introduction 207
7.4.2 Methods 207
7.4.3 Limerick Catchments Results 208
7.4.4 Fergus Catchment Results 209
7.4.5 Robe Catchment Results 211
7.4.6 Discussion 212

**CHAPTER 8. IMPLICATIONS OF GROUNDWATER PHOSPHORUS TO SURFACE WATER** **214**
**8.1 Introduction** **214**
**8.2 Methods for measuring flow at springs and rivers** **215**
**8.3 Fergus catchment** **216**
8.3.1 Introduction 216
8.3.2 Results 216
8.3.3 Groundwater phosphorus loadings 221
8.3.4 Discussion 225
**8.4 Robe catchment** **227**
8.4.1 Introduction 227
8.4.2 Results 228
8.4.3 Groundwater Phosphorus Loadings 231
8.4.4 Discussion 233
**8.5 Limerick Catchments (Deel and Maigue)** **234**
8.5.1 Introduction 234
8.5.2 Material and Methods 234
8.5.3 Baseflow estimates 235
8.5.4 Phosphorus results 236
8.5.5 Discussion 239
**8.6 Overall conclusions** **240**

**CHAPTER 9. CONCLUSIONS** **242**
**9.1 Review of thesis objectives** **242**
**9.2 Overall Conclusions** **243**
**9.3 Recommendations and scope for further research** **249**

**REFERENCES** **251**

**APPENDICES** **259**
**Appendix A: Site Characteristics** **259**
**Appendix B: Groundwater Protection Schemes** **268**
**Appendix C: Analytical Methods** **270**
**Appendix D: Analytical Data** **274**

# LIST OF FIGURES


Figure 1.1 Phosphorus pathways from land to surface waters including groundwater inputs at springs and as river baseflow. 2
Figure 1.2 Percentage of channel length in four Biological Quality Classes (Adapted from Lucey *et al.*, 1999). 3
Figure 2.1 Location map of public, group and private schemes used in the EPA's national groundwater quality monitoring program. 22
Figure 2.2 County boundaries of the Republic of Ireland. 23
Figure 2.3 Source type of public, private and group groundwater supplies. 24
Figure 2.4 Explanation of the components of boxplots. 26
Figure 2.5 Frequency distribution histogram of mean MRP (unf.) data from the EPA NGQMP. The line plots the cumulative percent for each column. 27
Figure 2.6 EPA groundwater MRP (unf.) (A) and log-transformed MRP (unf.) (B). 27
Figure 2.7 Spatial distribution of phosphorus levels in Irish aquifers. 28
Figure 2.8 Mean MRP (unf.) levels at different source types of the EPA NGQMP (error bars denote plus and minus one standard error). 29
Figure 2.9 Mean MRP (unf.) levels at different ownership types of the EPA NGQMP (error bars denote plus and minus one standard error). 30
Figure 2.10 MRP (unf.) and daily abstraction rates of NGQMP sites 30
Figure 2.11 Groundwater MRP (unf.) and (i) mean Morgans P (1993-97) from 10 km grid and (ii) mean Morgans P (1996) from interpolated polygons. 31
Figure 2.12 Mean soil P and groundwater P levels. 32
Figure 2.13 Predicted MRP levels in surface waters in dry and wet catchments. NGQMP data is superimposed. 33
Figure 2.14 Boxplots for the natural log of NGQMP MRP (unf.) and for group A (dry) and group B (wet) predicted MRP classes. 34
Figure 2.15 Total stocking density by county (after, Coulter *et al.*, 1999). 36
Figure 2.16 Median county groundwater P levels and (A) overall stocking density (B) cows & replacement density (C) other cattle density and (D) sheep density. 37
Figure 2.17 CORINE land cover classes for Co. Limerick, with groundwater P levels from the EPA national monitoring programme. 38
Figure 2.18 CORINE land cover classes for EPA groundwater MRP (unf.) data. The CORINE class code is explained in Table 2.5 below 39
Figure 2.19 The geology of Ireland with groundwater P levels from the EPA national monitoring programme. 41
Figure 2.20 Boxplots of Log transformed MRP (unf.) data for each geological Strata with five or more sites. 42
Figure 2.21 Hydrometric regions of the Republic of Ireland (source: EPA). 43
Figure 2.22 Percentage of river length with class A water quality (unpolluted) in each hydrometric region and groundwater P data from the EPA NGQMP. 44
Figure 2.23 Scatterplots of percentage river length with water quality class A, B, C, and D, and mean unf. MRP for each hydrometric region. 45
Figure 2.24 Interpolated groundwater P data compared with soil P data for hydrometric region 26 (Upper Shannon). 47
Figure 2.25 Mean interpolated MRP (unf.) for soil P levels hydrometric region 26. 48
Figure 3.1 Catchment location map of the groundwater phosphorus study areas. 54
Figure 3.2 Fergus catchment sampling locations. 57
Figure 3.3 Springs, sinkholes and underground connections of the upper Fergus catchment. 61
Figure 3.4 Springs, sinkholes and underground connections of the lower Fergus catchment 62
Figure 3.5 River quality trends in Hydrometric Region 27 (Lucey *et al.*, 1999). 63
Figure 3.6 Robe catchment sampling locations. 65
Figure 3.7 River quality trends in Hydrometric Region 30 68

Figure 3.8 Co. Limerick sampling locations. 71
Figure 3.9 River quality trends in Hydrometric Region 24 (after Lucey *et al.*, 1999). 73
Figure 4.1 Measured and calculated fractions of phosphorus is water. 79
Figure 4.2 Quality control chart for dissolved reactive P. Solid line is the mean result, minor gridlines represent 2 standard deviations. 82
Figure 4.3 Quality control chart for total phosphorus. Solid line is the mean result, minor gridlines represent 2 standard deviations. 82
Figure 4.4 Frequency distribution histogram of mean total P for groundwater sites. 83
Figure 4.5 Total P Frequency distribution histograms for each catchment area. 84
Figure 4.6 Log-log TP/DRP plot using all catchment groundwater P data. 87
Figure 4.7 Log-log TP/TDP plot using all catchment groundwater P data. 87
Figure 4.8 Median phosphorus fraction levels for boreholes and springs. 88
Figure 4.9 Histograms illustrating Ion balance error (IBE) percentages for sites in the Fergus/Robe catchments (A) and sites in Co. Limerick (B). 89
Figure 4.10 Fergus and Robe sites which were subject to anion/cation analysis. 90
Figure 4.11 Actual versus calculated alkalinity for the Fergus & Robe Sept. 1999 run. 91
Figure 4.12 Hydrogeochemical classification system for natural waters using the trilinear diagram. 92
Figure 4.13 Limerick Trilinear Diagram 94
Figure 4.14 $Na^+/Cl^-$ and $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ plots for the Limerick sites. Note: $Na^+$ on log axis; Clear diamonds are LB19 and LB12. 94
Figure 4.15 Fergus and Robe Trilinear diagram 95
Figure 4.16 Fergus Trilinear diagram temporal. Solid symbols are surface water. 96
Figure 4.17 $Na^+/Cl^-$ and $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ plots for the Fergus (♦) and Robe (▲) sites. Note: open diamond is FB11; the open triangle is RS06. 96
Figure 4.18 Limerick distribution map. 99
Figure 4.19 Robe distribution maps 100
Figure 4.20 Fergus distribution maps. 101
Figure 4.21 Mean EC and Log TP in the Fergus catchment. The correlation is improved when five boreholes (open diamonds) are removed. 103
Figure 4.22 Mean EC and Log TP in the Co. Limerick. 103
Figure 4.23 Mean EC and Log TP in the Robe catchment. 104
Figure 4.24 Mean pH and Log TP in the Fergus catchment. 105
Figure 4.25 Mean pH and Log TP in the Co. Limerick sites. 105
Figure 4.26 Mean pH and Log TP in the Robe catchment. 105
Figure 4.27 Mean DO and Log TP in the Fergus catchment. 106
Figure 4.28 (A) As above Figure with boreholes (x) springs (o) and dug wells (+). (B) DO frequency distribution histogram. 106
Figure 4.29 Mean DO and Log TP in the Limerick catchment. 107
Figure 4.30 Mean DO and Log TP in the Robe catchment. 107
Figure 4.31 Mean TP, TDP, DRP and pH at selected sites in the Fergus catchment. Regression lines shown. 108
Figure 4.32 Mean TP, TDP, DRP and EC at selected sites in the Fergus catchment. Regression lines shown. 108
Figure 4.33 Mean TP, TDP, DRP and DO at selected sites in the Fergus catchment. 109
Figure 4.34 Mean TP, TDP and DRP with pH, EC and DO. (TP = diamonds, TDP = squares, DRP = triangles). 109
Figure 4.35 Mean TP, TDP, DRP and pH at the Co. Limerick sites. 110
Figure 4.36 Mean TP, TDP, DRP and EC at the Co. Limerick sites. 110
Figure 4.37 Mean TP, TDP, DRP and DO at the Co. Limerick sites. 111
Figure 4.38 Coefficient of variation of EC and TP for Robe Springs and Boreholes. 114
Figure 4.39 Coefficient of variation of EC and TP for combined Robe Springs (▲) and Boreholes (◆). 115
Figure 4.40 Coefficient of variation of EC and TP for Fergus Springs and Boreholes. 115

Figure 4.41 Coefficient of variation of EC and TP for combined Fergus springs (▲) and boreholes (◆). 116
Figure 4.42 Calcite and hydroxyapatite saturation indices in the Fergus catchment downstream to Lough Inchquin (see Table 4.10 for codes of sites). 117
Figure 4.43 Fergus (◆)and Robe (▲) sites plotting (A) Calcite versus hydroxyapatite saturation indices and (B) hydroxyapatite versus pH. RS06 (△). 118
Figure 4.44 Dissolved reactive P (DRP) and hyroxyapatite saturation indices for Robe (▲) and Fergus (◆) springs. 118
Figure 5.1 Abstraction rate and mean total P levels at the 19 Limerick sites that have source protection reports prepared. 127
Figure 5.2 Log-log graph of mean total P and daily abstraction rates for the 19 Limerick sites that have source protection reports prepared. 128
Figure 5.3 Known below ground level static water levels and average measured depth to standing water for 15 of the Limerick boreholes. 129
Figure 5.4 Static water levels and groundwater TP in Limerick sites. 130
Figure 5.5 Depth to standing water (DSW) and total P concentrations for boreholes and dug wells in the Fergus (◇) and Robe (+) catchments. 130
Figure 5.6 Total P (solid line) and depth to standing water (DSW; dashed line) time series for Robe boreholes. 132
Figure 5.7 Total P (solid line) and depth to standing water (DSW; dashed line) time series for Fergus boreholes. 133
Figure 5.8 Boxplots showing groundwater log TP levels for Quaternary deposit types in the Limerick sites. 135
Figure 5.9 Boxplots showing groundwater log TP levels for Quaternary deposit types in the Fergus sites. 136
Figure 5.10 Mean TP boxplots of Quaternary deposits for the Robe sites. 136
Figure 5.11 Limerick borehole depth to bedrock data and mean TP levels. (A) presents all borehole data. (B) presents borehole data < 100 $\mu g\ l^{-1}$ TP. 137
Figure 5.12 General geology of Co. Limerick 141
Figure 5.13 Mean TP boxplots for bedrock lithologies of Limerick sites. See Table 5.2 for explanation of bedrock types. 143
Figure 5.14 Mean TP boxplots of Limerick sites. (See Table 5.1 for aquifer details). 143
Figure 5.15 General geology of the Fergus catchment. 145
Figure 5.16 Bedrock lithologies for the Fergus catchment. 146
Figure 5.17 Mean TP boxplots of Fergus sites. (See Table 5.3 for aquifer details). 146
Figure 5.18 Vulnerability of all Limerick groundwater sites. 150
Figure 5.19 Vulnerability of the 19 Limerick sites with source protection reports. 150
Figure 5.20 Vulnerability of all Fergus groundwater sites. 151
Figure 5.21 Vulnerability of Robe groundwater sites. 151
Figure 6.1 Monthly rainfall and 30 year average for Claremorris, Co. Mayo. 156
Figure 6.2 Monthly rainfall and 30 year average for Corofin, Co. Clare. 157
Figure 6.3 Monthly rainfall and 30 year average for Shannon Airport, Co. Clare 157
Figure 6.4 Rainfall and effective rainfall at Claremorris, Corofin and Shannon.. 158
Figure 6.5 Seasonal changes in median TP in groundwater of the Fergus catchment. 160
Figure 6.6 Seasonal changes in median TP in groundwater of the Robe catchment. 160
Figure 6.7 Seasonal changes in median TP in Limerick groundwater. 161
Figure 6.8 Fergus boreholes with gross TP levels. 162
Figure 6.9 Robe boreholes with gross TP levels. 163
Figure 6.10 Limerick boreholes with gross TP levels. 164
Figure 6.11 P fractions and rainfall events at Robe springs. 166
Figure 6.12 P fractions and rainfall events at the Fergus springs. 168
Figure 6.13 Autosampler TP data and daily rainfall for RS06 spring, Robe catchment. 171
Figure 6.14 RS06 Daily TP: reduced TP scale, 8 hourly samples averaged. 172
Figure 6.15 Autosampler TP data and daily rainfall for FS13 Spring. Clear diamond represents possible erroneous TP value. 173

Figure 6.16 Autosampler TP data and daily rainfall for FS05 Spring. 174
Figure 7.1 Major Great Soil Groups at groundwater sampling locations in the Maigue and Deel catchments (soil data from Finch and Ryan, 1966). 181
Figure 7.2 General soils of Co. Limerick. 182
Figure 7.3 Groundwater total P (A) and log total P (B) for the major Great Soil Groups in Limerick. The two outliers (starbursts) are LB05 and LB25. 185
Figure 7.4 Groundwater total P (A) and log total P (B) for the major Great Soil Groups in Limerick after removing the two outliers in Figure 7.3. 186
Figure 7.5 Groundwater total P (A) and log total P (B) for the soil drainage classes in Limerick. The two outliers are LB05 and LB25. WtE = well to excessive. 187
Figure 7.6 Groundwater total P (A) and log total P (B) for the soil drainage classes in Limerick after removing the two outliers in Figure 7.5. WtE = well to excessive. 187
Figure 7.7 presents a general soils map for the Fergus catchment. Examination of the influence of soils in a highly karstic catchment such as the Fergus is fraught with difficulties. Figure 7.7 General soils map for the Fergus catchment. 187
Figure 7.8 Frequency histogram of Great Soil Groups at the Fergus catchment groundwater sampling locations. 189
Figure 7.9 Groundwater log TP for the Great Soil Groups in the Fergus catchment. Outlier in the Brown Earth Group is FB03 (circle). 192
Figure 7.10 Log total P for the major Soil Series in the Fergus Catchment. Outlier in Kinvarra Series is FB03 (circle) (soil series data from Finch, 1971, see Table 7.8). 193
Figure 7.11 (A) Groundwater log TP and soil drainage classification in the Fergus catchment. Outlier is FB03 (starburst). (B) excluding Feale and Drombanny Series. 194
Figure 7.12 Robe catchment soils 195
Figure 7.13 Limerick CORINE land cover classes and groundwater sampling locations. 200
Figure 7.14 CORINE land cover classes for Limerick Groundwater sites. See Table 7.14 for explanation of class codes. 201
Figure 7.15 Groundwater log total P ($\mu g\ l^{-1}$) CORINE land cover classes for Fergus catchment groundwater sites. 202
Figure 7.16 Fergus catchment CORINE land cover classes and groundwater sampling locations. 203
Figure 7.17 CORINE land cover classes for Robe catchment groundwater sites. The starburst is borehole RB07. 204
Figure 7.18 Robe catchment CORINE land cover classes and groundwater sampling locations 205
Figure 7.19 Scatterplots between Limerick groundwater log TP and DED agricultural characteristics. O = Maigue catchment sites, X = Deel catchment sites, and | = other catchments. (F) examines the Deel sites excluding LB12. 209
Figure 7.20 Scatterplots of between Fergus groundwater Log TP and DED agricultural characteristics. (F) Log TP versus sheep/ha with Kilfenora DED (one site) removed. 210
Figure 7.21 Scatterplots of between Robe mean groundwater TP and DED agricultural characteristics. 212
Figure 8.1 Velocity area method for measuring flow in rivers and springs. 215
Figure 8.2 Overall site type boxplots of all major sampling runs in the Fergus. (A) Log TP (B) TP ($\mu g\ l^{-1}$). 218
Figure 8.3 Site type Boxplots of TP ($\mu g\ l^{-1}$) from the six major sampling runs in the Fergus catchment. 219
Figure 8.4 Median TP levels at each site type during the major sampling runs. 220
Figure 8.5 September 1998 high stage conditions: Total P Loadings and P concentrations along the River Fergus. 221
Figure 8.6 July 1999 Low stage conditions. Total P Loadings and P concentrations along the River Fergus. 223
Figure 8.7 September 1999 Medium stage conditions. Total P Loadings and P concentrations along the River Fergus. (*) Poplar Br. Loading (FR03). 224

**Figure 8.8 Total phosphorus loadings in the Upper Fergus catchment before Lough Inchquin. 226**
**Figure 8.9 Temporal variations in TP at Robe River sites. 229**
**Figure 8.10 Overall site type boxplots of all major sampling runs. 229**
**Figure 8.11 Median TP comparison between River Robe and groundwater sites. 230**
**Figure 8.12 Site type boxplots of TP ($\mu g\ l^{-1}$) from the six major sampling runs in the Robe catchment. 230**
**Figure 8.13 P fractions and loadings from the major springs of the Robe catchment. 232**
**Figure 8.14 Flow duration curves for the Maigue and Deel catchments. 236**
**Figure 9.1 Conceptual diagram to identify the risk posed by groundwater phosphorus to surface water. 248**

# LIST OF TABLES


Table 1.1 Suggested methodologically defined classification of P forms in water (From Haygarth and Sharpley, 2000). Terms in bold are used in this research. 5
Table 1.2 Phosphorus summary data from GEMS/Water 1994-96 groundwater sites 8
Table 1.3 Dissociation equations of phosphoric acid (after Andrews *et al.*, 1996). 11
Table 2.1 Ownership and abstraction rate of national groundwater monitoring dataset.20
Table 2.2 Source type and abstraction rate of national groundwater monitoring dataset.20
Table 2.3 Characteristics of coverages incorporated in GIS analysis of EPA P dataset. 24
Table 2.4 Classification of predicted MRP values from the soil P desorption model (Daly *et al.*, 2000). 34
Table 2.5 CORINE land cover classes for the EPA groundwater MRP (unf.) data. 39
Table 2.6 Geological strata and median MRP (unf.) $\mu g\ l^{-1}$. 40
Table 2.7 Pearson Product-Moment correlations between mean unf. MRP and percentage of river length for each water quality class. 45
Table 2.8 Comparison between NGQMP Limerick sites derived geologies using GIS and their actual geologies. 51
Table 3.1 Characteristics of Springs in Upper Fergus Catchment. Trace data from Drew (1988). 60
Table 3.2 Characteristics of springs south of Lough Inchquin. Trace data from Coxon (1995). 60
Table 3.3 Trophic status and size of lakes relevant to Fergus catchment. 64
Table 3.4 Characteristics of springs sampled in Robe catchment 68
Table 3.5 Trophic status and size Lough Mask (after Lucey *et al.*, 1999). 69
Table 4.1 Quality control parameter for the measured P fractions. 81
Table 4.2 Limerick catchments field water chemistry and total P. 85
Table 4.3 Fergus catchment field water chemistry and total P. 85
Table 4.4 Robe catchment field water chemistry and total P. 86
Table 4.5 TDP and DRP as a percentage of TP for each catchment 88
Table 4.6 Generic geologies for Limerick trilinear diagram. 93
Table 4.7 Pearson Product-Moment correlations for TP and major ions in the Fergus catchment in February 1999. (Bold = $p<0.05$; Bold+underline = $p<0.01$). 112
Table 4.8 Pearson Product-Moment correlations for P fractions and major ions in the Fergus in June 1999. (Bold = $p<0.05$; Bold+underline = $p<0.01$). 112
Table 4.9 Pearson Product-Moment correlations for P fractions and major ions in the Fergus in September 1999. (Bold = $p<0.05$; Bold+underline = $p<0.01$). 113
Table 4.10 Calcite and hydroxyapatite saturation indices for Fergus and Robe sites. 117
Table 5.1 Aquifer classification used by the Geological Survery of Ireland (Daly and Warren, 1998). 139
Table 5.2 Lithological descriptions for site locations in Co. Limerick. 142
Table 5.3 Lithological descriptions for site locations in the Fergus catchment derived from the Clare groundwater protection scheme bedrock map. 144
Table 5.4 Sites on the Namurian Gull Island Formation, potentially intercepting groundwater from the apatite layer. 147
Table 5.5 Vulnerability mapping guidelines for Irish groundwaters. 149
Table 6.1 Meteorological Stations used in this study 156
Table 7.1 Soil Series and Great Soil Group for each groundwater site in County Limerick (soil data from Finch and Ryan, 1966). 183
Table 7.2 Parent Material of each soil series derived for each groundwater site in County Limerick (after Finch and Ryan, 1966). 184
Table 7.3 Typical parent material of Limerick groundwater sites and associated soil classification (after Deakin, 1994). 185
Table 7.4 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.3. 185
Table 7.5 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.4. 186
Table 7.6 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.5. 187

Table 7.7 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.6. 187
Table 7.8 Soil classification for Fergus catchment groundwater locations (soil data from Finch, 1971). 190
Table 7.9 Description of soil parent material at the Fergus groundwater sites (soil data from Finch, 1971). 191
Table 7.10 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.9. 192
Table 7.11 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.10. 193
Table 7.12 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.11. 194
Table 7.13 Summary characteristics of the Robe catchment soils (after Walsh and Burke, 1980). 194
Table 7.14 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Limerick CORINE data (see Figure 7.14). 201
Table 7.15 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Fergus catchment CORINE data (see Figure 7.15). 204
Table 7.16 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Robe catchment CORINE data (see Figure 7.17). 206
Table 7.17 Definition of CSO statistics used in the analysis of groundwater P. 207
Table 7.18 Pearson-product moment correlation matrix of Limerick groundwater log TP and DED statistics. 5% significance limit = 0.344, 1% significance limit = 0.442. 208
Table 7.19 Summary statistics of Fergus DEDs. 210
Table 7.20 Summary statistics of Robe DEDs. 211
Table 8.1 Summary statistics of TP at Fergus surface water sampling locations. 217
Table 8.2 Summary statistics of total P for all combined major sampling runs in the Fergus catchment. 218
Table 8.3 Summary statistics of total P ($\mu g\ l^{-1}$) for each major sampling run in the Fergus catchment. 220
Table 8.4 Summary flow data from Lough Dromore springs FS13 and FS14. 225
Table 8.5 Summary statistics of total P ($\mu g\ l^{-1}$) River Robe sampling locations. 228
Table 8.6 Summary statistics of major sampling runs in Robe (Figure 8.10). 229
Table 8.7 Summary statistics for TP ($\mu g\ l^{-1}$) for each major sampling run in the Robe catchment. 231
Table 8.8 Estimated total P loading at each of the Robe surface water sites. 233
Table 8.9 Baseflow estimate for the Maigue and Deel Rivers. 235
Table 8.10 Summary phosphorus data (Doris *et al.*, 1999) along the River Deel in 1996. 237
Table 8.11 Summary total P statistics for groundwater sites in the Deel catchment. 237
Table 8.12 Summary phosphorus data (Doris *et al.*, 1999) in the River Maigue 1996. 238
Table 8.13 Summary total P statistics for groundwater sites in the Maigue catchment. 239

## ABBREVIATIONS

Chemical

| | |
|---|---|
| DRP | dissolved reactive phosphorus |
| MRP (unf.) | molybdate reactive phosphorus (unfiltered) |
| Ortho-P | orthophosphate |
| P | phosphorus |
| PP | particulate phosphorus |
| TDP | total dissolved phosphorus |
| TP | total phosphorus |

Statistical/Analytical

| | |
|---|---|
| ANOVA | analysis of variance |
| QA | quality assurance |
| QC | quality control |

Organisations

| | |
|---|---|
| CSO | Central Statistics Office |
| GSI | Geological Survey of Ireland |
| EPA | Environmental Protection Agency |

Hydrological

| | |
|---|---|
| PE | potential evapotranspiration |
| ER | effective rainfall |
| RF | rainfall |
| DSW | depth to standing water |

Miscellaneous

| | |
|---|---|
| NGQMP | national groundwater quality monitoring programmme |
| DED | district electoral division |
| REPS | Rural Environmental Protection Scheme |
| GIS | Geographical Information System |

# CHAPTER 1. CONTEXT OF RESEARCH

## *1.1 General introduction*

Phosphorus (P) is generally considered the key nutrient in freshwater, the lack of which limits plant growth. Eutrophication, the enrichment of waters by nutrients, results in a deterioration in water quality and amenity value through excessive growth of algae and higher plants. This proliferation of blue-green algae in the water column and growth of rooting plants can decrease the in-water oxygen levels to such an extent that many fish species cannot survive. Water abstraction for domestic and industrial supply, salmonid fisheries and water contact sports are among the beneficial uses of surface waters which can be negatively impacted by the process of eutrophication.

Loss of P from land to surface waters is receiving considerable attention both internationally and within Ireland. In 1995 and 1998 two international workshops on P loss to water (Tunney *et al.*, 1997 and Foy & Dils, 1998, respectively), both which took place in Ireland, provide a comprehensive summary of on-going research in this area. In the second workshop, sponsored by the OECD, Sharpley *et al.* (2000) identify the need to establish the relative importance of different pathways of P transport within catchments. The third and most recent workshop, which took place in Plymouth, U.K., emphasised the need to better understand the hydrochemical connectivity involving P transfer from source to impact (Haygarth *et al.*, 2001). Many investigations have examined phosphorus losses from land through overland flow and drainage waters. However, the least known and often neglected route of P transfer is via groundwater discharge.

This project aims to examine P levels in a range of Irish hydrogeological situations, both to fill this gap in basic scientific knowledge, and to determine the circumstances in which concentrations likely to trigger eutrophication are likely to arise. The main focus will be on determining the hydrogeological factors which allow P from anthropogenic sources to enter the saturated zone and pass through the aquifer, discharging at springs and as river baseflow.

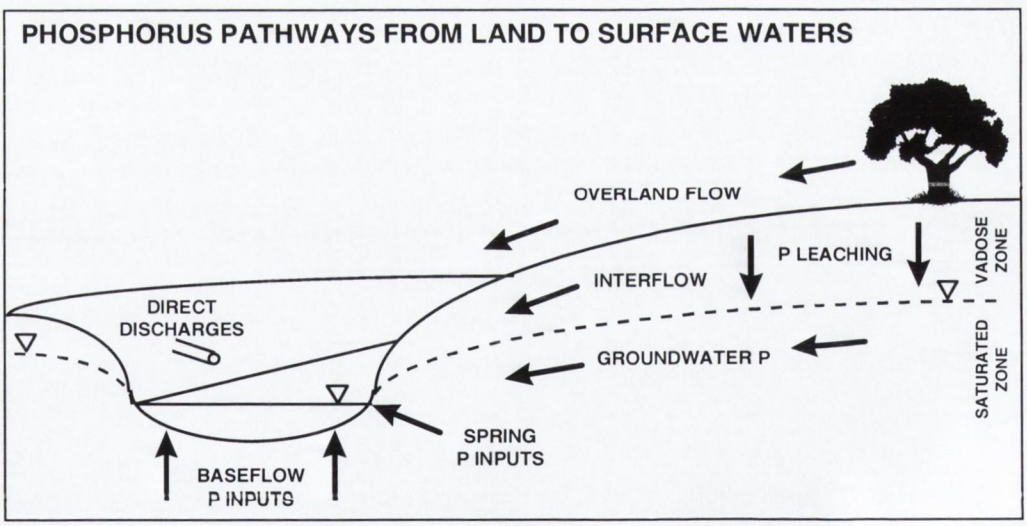
This chapter will provide the context of this thesis by describing the associated problems of surface water quality in Ireland, examining the reasons why P has been neglected from

groundwater studies and outlining the key background relevant to this research. Finally, this chapter explains the aims and objectives of this research, and describes the structure of the thesis.

### *1.2 Surface water quality in Ireland*

Phosphorus is the key nutrient which generally limits the growth of plants in freshwater (Vollenweider, 1968). Whilst P is essential to all forms of life and has no direct toxic effects to humans or animals - indeed, P has been added to drinking water supply systems in order to reduce plumbosolvency - it is the effect P has on biological productivity that is of environmental concern. This is because P is generally the nutrient in shortest supply in freshwater and thus changes in P will have a direct effect on plant biomass. Therefore, an understanding of P loadings from all sources is crucial. Figure 1.1 indicates various pathways of P movement from land to water, including groundwater inputs via springs and as river baseflow

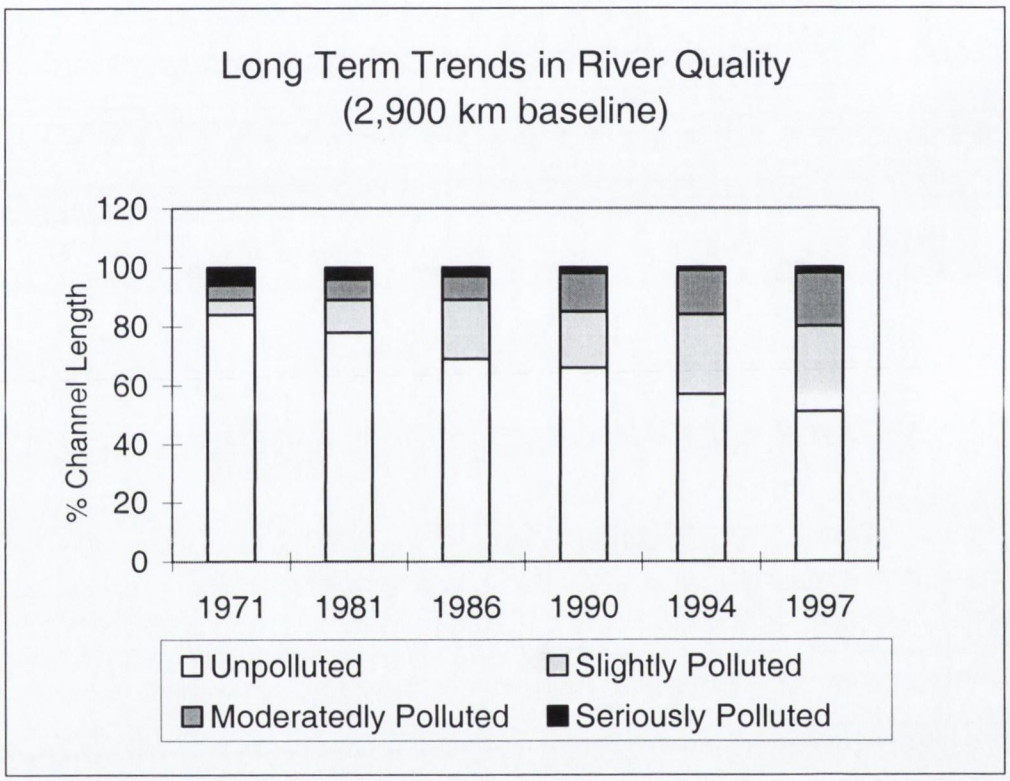
**Figure 1.1 Phosphorus pathways from land to surface waters including groundwater inputs at springs and as river baseflow.**




Economic development creates many stresses and pressures on the environment. Ireland's current unprecedented economic growth has created major challenges for environmental protection. In the Environmental Protection Agency's (EPA) millennium report on the state of the environment the eutrophication of rivers and lakes was identified as the most serious environmental pollution problem affecting the Republic of Ireland (Stapleton *et al.*, 2000). The most recent assessment of river and lake water quality in Ireland (Lucey *et al.*,

1999) indicated that whilst the bulk (67%) of surveyed baseline channel was in a satisfactory condition, a considerable proportion was polluted to some degree. Moreover, examination of long-term available data for 2,900 km of stream length (see Figure 1.2) indicates a consistent trend of increasing slight and moderate pollution, and a recent reversal of the trend of decreasing serious pollution which had been falling off gradually.

**Figure 1.2 Percentage of channel length in four Biological Quality Classes (Adapted from Lucey *et al.*, 1999).**




Of the 120 lakes examined during 1995 -1997, 97 or 81% were reported as having either oligotrophic or mesotrophic status, which is indicative of satisfactory water quality conditions. The remaining 23 lakes were in unsatisfactory condition, 18 being reported with moderately to highly eutrophic status, and 5 were designated as hypertrophic. Examining the same data by surface area: 65.5% (582.5 $km^2$) were classified as oligotrophic/mesotrophic; 31.8% (283 $km^2$) were classified as eutrophic; and 2.7% (24 $km^2$) were classified as hypertrophic. Thus, the water quality status of rivers and lakes represents a serious threat to environmental protection in Ireland.

### 1.3 Sources of phosphorus in Irish surface waters

Phosphorus in surface waters may arise from diffuse (non-point source), chiefly agricultural activities, and from point sources, chiefly waste discharges from municipal and industrial waste treatment plants. For the period 1995 to 1997, Lucey *et al.* (1999) indicate that most incidents of serious pollution in rivers were suspected to be due to sewage discharges. In respect of the incidents of slight and moderate pollution most incidents can be attributed to agriculture. Due to both easier identification and control, considerable progress has been made to eliminate point source inputs of phosphorus. Legislation such as the Urban Wastewater Directive (CEC, 1991) is continuing to increase the degree of P removal from urban discharges through the upgrading of existing treatment plants and the provision of new plants. In a recent assessment of upgraded sewage treatment plants, Lucey *et al.* (1999) report a significant decrease in the amount of serious pollution in receiving waters subsequent to additional pollution abatement measures. As a result, diffuse sources of P may be expected to be responsible for a larger share of water quality problems in the future.

Agricultural sources of P include the landspreading of slurries and dirty water, application of inorganic fertilisers and manures, and farmyard runoff. Tunney (1990) estimated the P balance in Irish agriculture to be 77,296 tonnes of inputs and 31,255 tonnes of outputs. The surplus P either accumulates in the soil or is lost through transfers to aquatic ecosystems (Sharpley *et al.*, 1995).

### 1.4 Nomenclature in phosphorus analysis of freshwaters

There are a wide variety of terms used to describe various forms of phosphorus in waters. This is largely due to the multitude of disciplines involved in phosphorus research. Limnologists, soil scientists and hydrologists are among these varied disciplines and each has historically adopted phosphorus terminologies based on their own experiences and norms. However, as elucidated by Haygarth and Sharpley (2000), this has led to misinterpretations which can impair scientific communication. They suggest a revised nomenclature which is presented in Table 1.1 and includes equivalent established terms. Terms marked in bold are those used in this research.

**Table 1.1 Suggested methodologically defined classification of P forms in water (From Haygarth and Sharpley, 2000). Terms in bold are used in this research.**

| *New Classification* | *Equivalent established terms* |
|---|---|
| RP (<0.45) | Molydate reactive P (MRP), **dissolved reactive P (DRP)**, soluble reactive P (SRP), dissolved molydate reactive P, orthophosphate, iorganic P, phosphate |
| RP (unf) | Total reactive P (TRP), raw unfiltered sample, **MRP (unf.)*** |
| TP (<0.45) | **Total dissolved P (TDP)** |
| TP (unf) | **Total P on a raw unfiltered sample (TP)** |
| UP (<0.45) | **Dissolved organic P (DOP)**, soluble organic P (SOP), dissolved non reactive P (DNRP) |
| TP (>0.45) | **Particulate P (PP)** |
| RP (>0.45) | Molydate reactive particulate P (MRPP), particulate reactive P |

(*) This form of P is used in the EPA NGQMP groundwater P data.

This table attempts to address issues associated with filtration and the molybdate blue reaction used in P analysis. Commonly filtration using a 0.45 $\mu$m pore filter is used to distinguish between dissolved or particulate forms of P. However, it has been shown that this does not clearly determine soluble P (Haygarth *et al.*, 1997); colloidal P, for example can pass through this pore size. Inorganic and organic P forms are generally distinguished using some form digestion procedure. However, it has been shown that the molybdate blue procedure can also determine loosely bound inorganic and organic forms of P (e.g. Stevens, 1979 cited in Haygarth and Sharpley, 2000). Therefore, *sensu stricto*, the terms used in this study, DRP, DOP, PP, TDP and TP are potential misnomers or at least do not fully describe the P form analysed. Nonetheless, they are used here on the basis that their derivation and limitations have been clearly stated.

In Ireland, the most common term used by state organisations involved in surface water and groundwater monitoring is unfiltered MRP or orthophosphate (Doris *et al.*, 1999). This form of phosphorus is equivalent to RP (unf) in Table 1.1 and involves analysing an unfiltered raw water sample directly for DRP using the method described in Chapter Four, Section 4.2.4. During this study the terms presented in Figure 4.1 are used to describe all analysis carried out in this study. Where P forms from other studies are quoted the original terminology is used except in situations where the methods adopted by the authors can be clearly associated with those outlined in Figure 4.1.

## *1.5 Why groundwater phosphorus has been neglected*

### 1.5.1 Regulatory requirements

Phosphorus has been a frequently neglected parameter in studies of groundwater chemistry. Except in very large quantities P does not pose a human health risk, and eutrophic conditions will not occur in groundwater because light is essential for algal growth. In Irish groundwater studies, P has been overlooked primarily because the maximum admissible concentration for drinking waters under the Directive on water intended for human consumption CEC (1980) (5000 $\mu g\ l^{-1}$ $P_2O_5$; Flanagan, 1992) is rarely approached except in areas of gross localised contamination. The recently revised Directive on water intended for human consumption (CEC, 1998) due to be implemented in 2003, does not contain any limit for P.

Phosphorus is generally considered innocuous because of its typically low mobility in groundwater (Fetter, 1999). Concern for P in groundwater has focused on its impacts on fouling water treatment plants and indeed P has sometimes been added to prevent plumbosolvency (Gray, 1994). The main focus of water quality programs has been on P levels in surface waters due to the threat of eutrophication. Since the levels of P in groundwater are not a perceived threat to its quality in terms of drinking water, it has largely been ignored in groundwater monitoring programs. The most recent assessment of groundwater quality and quantity in Europe (EEA, 1999) contains no data on groundwater P levels. EUROWATERNET, a recent EU initiative to monitor Europe's inland waters (EEA, 2000), omits P as a data requirement for groundwater monitoring sites.

However, in surface waters the concern with P is at much lower concentrations. Annual mean total P concentrations in excess of only 20 $\mu g\ l^{-1}$ may trigger eutrophication in some lakes (Champ, 1998). The flushing effect in rivers may provide them with greater protection to P loadings; however McGarrigle's (1998) study on national river data for the period 1991-1994 suggests that adverse impacts become apparent once unfiltered molybdate reactive phosphate levels exceed 30 $\mu g\ l^{-1}$ (see Section 1.4 for a description of various P fractions). The recent regulations on water quality standards for P (DELG, 1998) set out a similar suite of target levels for rivers and lakes of varying trophic status in a national strategy to tackle surface water eutrophication. Therefore, a dichotomy exists

between regulatory levels required for groundwater P in terms of drinking water quality and the level of P required to induce eutrophic conditions in surface waters.

### 1.5.2 International studies of phosphorus in groundwater

Water quality monitoring is required for the effective management of water resources. National and regional scale monitoring programmes generally tend to concentrate on a range of objectives and due to their size have inherent limitations. In a regional assessment of groundwater quality in the U.S. Hamilton and Helsel (1995) report inconsistent analytical techniques, incomplete analyses, and limited ancillary information such as site characteristics and land-use as among the key limitations. Nonetheless, the authors conclude that these monitoring programs were useful for identifying similarities in groundwater quality and in developing hypotheses about major factors that affect regional groundwater quality.

There are few groundwater-monitoring programs that cover entire countries. Loftis (1996) cites only two truly national programs: the U.S. Geological Survey National Water Quality Assessment Program (Leahy *et al.*, 1993) and the Australian Groundwater Quality Assessment Program (Evans and Bauld, 1993). More common are regional groundwater assessments which generally focus on either large river basins or areas within administrative boundaries. However, there are few national or regional studies which include the analysis of P in groundwater.

*GEMS/Water database*

The Global Environmental Monitoring System (GEMS) was initiated in 1974 as a means of promoting and coordinating the collection of environmental data. The global water quality monitoring (GEMS/Water), was established in 1976 jointly by WHO, UNESCO, WMO and UNEP (Chapman, 1996). The objectives of the project are:

- To collaborate with Member States in the establishment of new water monitoring systems and to strengthen existing ones;
- To improve the validity and comparability of water quality data within and between Member States, and;
- To assess the incidence and long-term trends of water pollution by selected persistent and hazardous substances.

By 1998 a total of 538 water quality monitoring stations were included in the network, of which groundwater sites comprised 92 stations. The Global Data Centre, located at the Canada Centre for Inland Waters, Burlington, Canada, processed all water quality data received, for the latest monitoring period 1994-96. A statistical summary of the data is available on the Internet at the GEMS/Water website http://www.cciw.ca/gems/. Data from the 92 groundwater stations were examined for P analyses. Table 1.2 presents the findings of this examination.

**Table 1.2 Phosphorus summary data from GEMS/Water 1994-96 groundwater sites**

| *Country* | *GEMS/Water Station No.* | *P fraction analysed* | *Mean ($\mu g\ l^{-1}$)* | *Depth (m)* | *Number of Samples.* |
|---|---|---|---|---|---|
| India | 031016 | Total Phosphate | 41 | NA | 11 |
| | 031026 | | 655 | 0.6 | 13 |
| | 031027 | | 76 | 1.2 | 13 |
| | 031015 | | 16 | NA | 4 |
| | 031006 | | 48 | NA | 5 |
| | 031003 | | 55 | NA | 24 |
| Lithuania | 170001 | Total Phosphorus | 14 | 164 | 3 |
| | 170002 | | 53 | 120 | 3 |
| | 170003 | | 222 | 15.5 | 2 |
| Mali | 099005 | Total Phosphorus | 60 | 0 | 1 |
| | 099003 | | 110 | 0 | 2 |
| Mexico | 037011 | Dissolved Reactive | 16 | NA | 4 |
| | 037012 | P | 20 | 120 | 9 |
| Pakistan | 056007 | Total Phosphorus | 25 | 0 | 2 |
| Poland | 021008 | Total Dissolved P | 300 | 6.3 | 2 |

Of the 92 groundwater sites only 15 reported any fraction of P, only six countries are represented, and four different P fractions were analysed.

The U.S. Geological Survey National Water Quality Assessment (NAWQA) program is designed to assess historical, current, and future water-quality conditions in representative river basins and aquifers nationwide (http://water.usgs.gov/nawqa/). One of the primary objectives of the program is to describe relations between natural factors, human activities, and water-quality conditions and to define those factors that most affect water quality in different parts of the Nation. A recent examination of NAWQA, focused on nutrients in groundwater. From a dataset of 2,130 wells collected since 1991 (no springs) Nolan and Stoner (2000) report median levels of orthophosphate levels of 10 and 20 $\mu g\ l^{-1}$ for agricultural and urban groundwater studies. The authors suggest P from leaky municipal sewer systems and residential septic tank systems may be the cause for higher P levels in

urban areas. The authors also note that groundwater quality criteria have not been established in the U.S.

The Irish EPA's National Water Quality Monitoring Programme (NWQMP) is discussed in details Chapter 2. This programme has included P analysis since 1995. For the 1995-97 monitoring period median unfiltered molybdate reactive phosphate levels of 17 $\mu g\ l^{-1}$ were reported.

More frequent, but still under represented in terms of P analysis, are regional groundwater assessments. These generally focus on large river basins or areas within administrative boundaries. Rao and Prasad (1997) sampled 113 wells in April 1993 from the 817 $km^2$ lower Vamasadhara river basin in northern Andhra Pradesh, India. They report groundwater phosphate levels of between 720 and 7007 $\mu g\ l^{-1}$. The authors attribute these high values to weathered apatite mineral releases. However, it should be noted that the detection limit for the method they employed (vanadomolybdophosphoric acid colorimetric method; APHA, 1989) is 200 $\mu g\ l^{-1}$, and it is unclear whether the sample was filtered. In addition, most of the sampling locations were from open dug wells. Therefore, it is not clear whether these phosphate levels reflect actual aquifer concentrations. They may represent shallow groundwater impacted by surface run off from agricultural land, and if unfiltered, reflect particulate matter inputs.

Muldoon *et al.* (1990) examined the hydrogeological influences on lake water in northwestern Wisconsin, U.S., which included an assessment of groundwater P levels. Samples from 109 domestic wells had total dissolved P (TDP) concentrations ranging from <4 to 298 $\mu g\ l^{-1}$, with a median of 32 $\mu g\ l^{-1}$. They also found a correlation between lake P and groundwater P in upgradient wells. Of the geological units which constituted the aquifers, lowest median TDP levels were found in the basalt and dolomite sites (20 and 24 $\mu g\ l^{-1}$) and highest in the sandstone and sand and gravel sites (30 and 34 $\mu g\ l^{-1}$).

Kilroy *et al.* (1997) carried out a water quality assessment of the Las Vegas Valley area and the Carson and Trukee river basins, Nevada and California during the monitoring period 1969 to 1990. Nutrients were included in this assessment of 363 wells in this study. The authors reported orthophosphate levels in the shallow aquifers (well depth less than 50 ft) were significantly higher in basin areas than in headwater areas (medians, 290 and 34 $\mu g\ l^{-1}$

P), but no such difference was reported for the deep aquifers (well depth greater than 50 ft). Shallow and deeper aquifers both reported higher orthophosphate in agricultural areas than in urban and range areas. In agricultural areas, they also found significantly higher concentrations of orthophosphate in shallow aquifers (median, 220 $\mu g\ l^{-1}$ P) than in samples from deep aquifers (median, 50 $\mu g\ l^{-1}$ P).

Spruill *et al.* (1998) report on the water quality in the Albemarle-Pamlico drainage basin in North Carolina and Virginia between 1992 and 1995. Whilst the shallow groundwater in the basin had median orthophosphate levels of 35 $\mu g\ l^{-1}$ P, the authors report that several of the streams in the catchment receive significant phosphorus loads from deep groundwater. They attribute high groundwater orthophosphate levels in these areas (median, 200 $\mu g\ l^{-1}$ P) to natural deposits of phosphate in Miocene and Cretaceous sediments.

Webber and Wadsworth (1976) examined phosphorus in wells, springs and boreholes in the East and West Midlands of the UK. 124 of the 163 samples were below 20 $\mu g\ l^{-1}$ P, and only 16 were greater than 100 $\mu g\ l^{-1}$ P.

These previous assessments highlight the infrequency of P analysis in national groundwater studies and the difficulty of making inter-country comparison due to the differing form of P used. There is a need for monitoring programmes to analyse consistent forms of P to provide comparison of groundwater P levels within a country and between countries.

### *1.6 Movement of phosphorus to groundwater*

Freshwater will, to varying degrees, contain amounts of dissolved gases and solids. The composition of any aqueous solution will be a function of several factors including the initial composition of water, the partial pressure of the gas phase, the type of mineral matter the water contacts, and the pH and oxidation potential of the solution (Fetter, 2001).

Phosphorus is transported in dissolved and particulate forms. In natural waters dissolved P exists predominantly as various dissociation products of phosphoric acid ($H_3PO_4$), see Table 1.3.

**Table 1.3 Dissociation equations of phosphoric acid (after Andrews *et al.*, 1996).**

| $H_3PO_4$ Dissociation Products | Equations |
|---|---|
| $H_3PO_4 \rightarrow H_2PO_4^- + H^+$ | Eq. 1 |
| $H_2PO_4 + H^+ \rightarrow HPO_4^{2-} + 2H^+$ | Eq. 2 |
| $HPO_4^{2-} + 2H^+ \rightarrow PO_4^{3-} + 3H^+$ | Eq. 3 |

Phosphorus is usually in sediments as insoluble iron (III) phosphate ($FePO_4$), therefore under reducing conditions P can be returned to the water column in association with iron (III) reduction to iron (II) (Andrews *et al.*, 1996). In groundwater it is expected that such reducing conditions should prevail and thus may be a key control on P movement in the saturated zone.

Phosphorus is usually retained in soils by the precipitation of relatively insoluble calcium and iron phosphates, by adsorption on iron hydroxide or by adsorption on to soil particles (Andrews *et al.*, 1996). Thus, commonly P is thought to have low mobility in groundwater (Fetter, 1999). It is also expected that DRP would be the dominant fraction given that typically groundwaters have lower particulate loads than surface waters. However, Dils (1997) found that PP was the dominant fraction in a Caroniferous shale aquifer in Leicestershire, UK. Although the wells sampled were very shallow (<2m) and may also have been impacted by the dispersion of P-rich clay particles originating from the parent material.

Most studies of P mobility in groundwater have focused on plumes from septic systems (e.g. Robertson, 1995; Ptacek, 1998). In these studies the concentration of P present in groundwater appears largely controlled by the constraints of phosphate mineral solubility. Processes of sorption have been reported important controls on P migration velocity. In these situations there is a definite point source provided a continuous load to groundwater and therefore to some degree geochemical equilibrium will be established. In situations where the P source is diffuse it is less clear whether such steady-state systems can be established. In such circumstances hydrological factors may exert greater control.

Research into P losses from soil to water has concentrated on the overland flow pathway. This focus is not without legitimate reason. Phosphate ions ($PO_4^{3-}$) are strongly adsorbed

onto positively charged particles and can react with many cations, particularly calcium, aluminium and iron to produce relatively insoluble minerals (e.g. hydroxyapatite). Nonetheless, though strongly adsorbed onto soil, P can show enhanced leaching to groundwater because in some circumstances the sorption capacity of the soil can be exceeded. The degree of saturation will be dependent on land use, soil type and P inputs (Breeuwsma & Reijerink, 1992). Groenenberg *et al.* (1996) examined P leaching to groundwater in phosphate-saturated soils in the Netherlands. They conclude that P leaching is strongly influenced by the occurrence of periods of high groundwater levels in which the groundwater table enters the phosphate saturated topsoil. Other authors (e.g. Isenbeck-Schröter *et al.*, 1993) have suggested precipitation of P minerals (e.g. hydroxyapatite) as an important mechanism for limiting vertical distribution of P. Leaching of P from soils has been identified in areas which have characteristics such as coarse textured soils (Eghball *et al.*, 1996), sandy soils with high permeability (e.g. Chen *et al.*, 1996), soils with low P sorption capacity (Breeuwsma *et al.*, 1995) and areas with shallow water tables (e.g. Grant *et al.*, 1996).

Increasing attention has been given to preferential flow as a mechanism for agricultural contaminants to reach groundwater. Movement through cracks in the soil, worm burrows and other macropores reduces the contact time between percolating water and soil and thus decreases the natural attenuation capability of the soil (Ryan, 1998). Several authors (e.g. Dils & Heathwaite, 1996) have suggested preferential flow as a mechanism for P to bypass the soil's natural sorbing capacity.

Septic tank systems, whilst more indicative of point rather than diffuse sources, have provided some information on P migration rates. Robertson *et al.* (1998), in a review of phosphate mobility in septic tank plumes, report plume concentrations of 500-5000 $\mu g\ l^{-1}$ P and migration rates of one metre per annum in calcareous sand aquifers. Given the long-term use of septic tank systems and the minimum recommended set-back distance from surface water bodies of 10 metres (NSAI, 1991), even this highly retarded phosphate migration velocity may be of concern under certain circumstances.

### *1.7 Groundwater phosphorus derived from geological materials*

There few examples in the literature which examine geological influences on groundwater P levels. Grobler and Silberbauer (1985) found that spatial variance in P export coefficients could be accounted for if catchments were grouped by their geological characteristics. Catchments located in highly erodable sedimentary geology had higher SRP export rates than in catchments of igneous geology. Muldoon *et al.* (1990) examined the hydrogeological influences on lake water in northwestern Wisconsin, U.S., which included an assessment of groundwater P levels. Of the geological units which constituted the aquifers, lowest median TDP levels were found in the basalt and dolomite sites (20 and 24 $\mu g\ l^{-1}$) and highest in the sandstone and sand and gravel sites (30 and 34 $\mu g\ l^{-1}$). The authors, suggest that hydroxyapatite is present in the sandstones may be the source, but acknowledge that anthropogenic factors may also be significantly contributing to P levels in groundwater. Overall, there is an apparent paucity of information on hydrogeological controls on groundwater P. Where available, emphasis has been on water table levels.

Geological phosphorus may also be an important source of groundwater P under certain circumstances. The only new source of phosphorus to global ecosystems is the result of weathering of continental material (Filippelli and Souch, 1999). More than 90% of all phosphorus eroded from continental rock is carried to the sea or deep lakes in an inert form (Horne and Goldman, 1994). Apatite, $Ca_5(PO_4)_3(F,Cl,OH)$, is the primary mineral sought for fertilizer production. Some countries such as Morocco, USA, Tunisia and Togo are major exporters of phosphate rock (Cook and Shergold, 1983). However, the uneven supply of phosphate rock is one of the limiting factors restricting agricultural development in many parts of the world.

In Ireland, sedimentary phosphate rock of Namurian age occurs in north-west County Clare. The known deposits are of low grade but up to 105,000 tonnes were mined, particularly during the Second World War when overseas supplies were restricted (Notholt and Highley, 1979). Since 1947 Irish inorganic P fertilizer requirements are met entirely by imports, especially from Morocco. The main phosphate occurrences lie in the area to the south west and south east of Lisdoonvarna from Fisherstreet in the west to Noughaval in the east. They occur as lenses and thin discontinuous layers in the basal portion of a dark shale facies resting upon an erosion surface of the Visean Upper Carboniferous Limestone (O'Brien, 1953). Three key areas were mined during the 1940s: Lismoher,

located 1.5km north east of Kilfenora; Noughaval, located 4km north east of Kilfenora and immediately west south west of Noughaval village; and Teergonean; located at the Aille River, 1km east of Doolin village (O'Raghallaigh *et al.*, 1997).

Concern has been raised over the threat to surface waters by the mining of such apatite deposits. In Florida for example, where there is a large phosphate mining industry, large volumes of rock are excavated and waste tailings are disposed in an area with a very high water table (Horne and Goldman, 1994). However, apatite is a very insoluble mineral. Lloyd and Heathcote (1985) cite a solubility for hydroxyapatite, $Ca_5OH(PO_4)_3$, of 30 mg $l^{-1}$ (at pH 7). Dissolved P is readily sorbed onto soil and is thought to have a very low mobility in groundwater (Fetter, 1999). In acidic, quartz-sand aquifers P may be mobile, but in carbonate aquifers it will be quickly precipitate as apatite or some other phosphate mineral (Sam Upchurch, Pers. Comm.).

Some authors have cited geological P as possible source of elevated groundwater P levels. Rao & Prasad (1997) report on the groundwater quality of the Vamsadhara river basin, India, and conclude that the high phosphorus levels in the groundwater were not attributed to chemical fertiliser application but to weathered apatite mineral releases in the parent material. Spatial variation of phosphorus in the groundwater correlated with soil leachate characteristics to indicate the dominance of geological sources over fertiliser sources. As discussed in Section 1.5.2, the use of dug wells and the detection limit of the adopted method in this study may preclude any direct relationships to groundwater P. Dils (1997) reported a logarithmic decline in total phosphorus in piezometers between surface and 100cm, then a linear increase in total P between 1 and 2 metres (up to 800 $\mu g\ l^{-1}$ TP). Dils concluded that the increased concentration of total P was attributable to the weathering of naturally P rich parent material rather than P accumulation due to leaching. In this case the source material was phosphorus rich marine clay bands embedded within the Coal Measures of Carboniferous Shales. Spruill *et al.* (1998) report on the water quality in the Albemarle-Pamlico drainage basin in North Carolina and Virginia between 1992 and 1995. Whilst the shallow groundwater in the basin had median orthophosphate levels of 35 $\mu g\ l^{-1}$ P, the authors report that several of the streams in the catchment receive significant phosphorus loads from deep groundwater. They attribute high groundwater orthophosphate levels in these areas (median, 200 $\mu g\ l^{-1}$ P) to natural deposits of phosphate in Miocene and Cretaceous sediments. Therefore, whilst some conventional wisdom

indicates that geological P is unlikely to contribute to the groundwater P load, there are published examples of elevated groundwater P levels that may be attributed to naturally occurring geological P.

### *1.8 National strategies to deal with eutrophication*

Strategies to deal with the eutrophication issue in Ireland have derived from legislative initiatives at European and national level. The Department of Environment (DoE, 1997) issued a strategy document in 1997 outlining several initiatives to tackle eutrophication. The apotheosis of this strategy, which emphasised a catchment based approach to managing this problem, was the development of the Lough Derg/Lough Ree catchment monitoring and management system . This has been followed by a similar system for the catchments of Lough Leane, and the Boyne, Liffey and Suir (The Three Rivers Project). The Water Quality Standards for Phosphorus Regulations (DELG, 1998) have been introduced under the requirements of the Dangerous Substances Directive (CEC, 1976). These regulations set out environmental quality standards for rivers and lakes with the objective of maintaining or improving water quality by reference to biological quality rating/trophic status or phosphate concentrations.

A joint initiative between the Department of Environment and Local Government, the EPA and the Geological Survey of Ireland, was recently launched to provide a methodology for the preparation of groundwater protection schemes (DELG *et al.*, 1999). These schemes essentially comprise two components: groundwater protection or land zones; and groundwater protection responses for potentially polluting activities. A groundwater protection scheme enables authorities to take account of the potential risk to groundwater resources and sources, and geological and hydrogeological factors when considering the control and location of potentially polluting activities. Regarding the activity of landspreading of organic wastes, phosphorus has been identified as a contaminant of concern, particularly where it acts as a pathway for P movement to lakes, streams and wetlands.

Section 66(3) of the Waste Management Act, 1996 allows a local authority to request a nutrient management plan in circumstances where it considers this to be necessary to prevent nutrient losses to water arising from the use of chemical fertilisers and organic fertilisers such as animal slurries and farmyard manures. In order to help to reduce the P

load from sewage the Department of the Environment and Local Government in conjunction with the Irish Detergents and Allied Products Association (IDAPA) have agreed to eliminate phosphate-based laundry products by the end of 2002 (DELG, 1999).

At a European level the Water Framework Directive will adopt a basin management approach to maintaining and improving the quality of both surface waters groundwaters and surface waters (EU Water Framework Directive, 2000). All these initiatives aim wholly or partly to assist in maintaining and improving Ireland's surface water quality, and provide the legislative context for this research.

### *1.9 Aims and Objectives*

The introduction of this chapter highlights the need for developing better understanding of all P movement pathways from soil to water, including the least known: groundwater. This research aims to further existing knowledge of the contribution of groundwater P to surface water eutrophication by examining P in a range of Irish hydrogeological situations to determine the circumstances in which P concentrations likely to trigger eutrophication are liable to occur.

To achieve these aims the following objectives were developed:

- Assess the national distribution patterns of groundwater P in Ireland, both in terms of geographic regions and land use categories;
- Identify suitable catchments for detailed monitoring to examine temporal (time series and precipitation), spatial (including hydrogeology and land use) and intrinsic conditions (water chemistry and site typology) which result in elevated groundwater P concentrations;
- Hydrograph analysis of catchments during low flows to assess P loading to surface waters via baseflow discharge in rivers.

From these approaches the chief controls of P levels in Irish aquifers will be determined, and areas where groundwater P is a potential source of eutrophication will be identified.

### *1.10 Thesis Structure*

A theme-based approach has been adopted in the presentation of this research. Each chapter presents an introductory literature review with a summary of the main aims, followed by relevant information on materials and methods. Thereafter, results and

discussions are presented. Several appendices are included and contain more detailed information on methods and analytical results and are referenced when appropriate.

This research is based on work carried out on two distinct datasets. Firstly, a national dataset comprising P data from the EPA's National Groundwater Quality Monitoring Program (NGQMP) was assessed and is presented in Chapter Two. This chapter examines this national dataset spatially using a range of land characteristic coverage. A second, dataset based on data from catchments in Cos. Mayo, Clare and Limerick collected in this study, provides the basis for all subsequent chapters.

Chapter Three provides detailed descriptions of the characteristics of the study catchment areas and includes information on climate, soils, hydrology, geology and hydrogeology. Maps illustrating the sampling locations of each area are also presented.

The first major results chapter is presented in Chapter Four, where the hydrochemistry of the studied catchments is examined. The influence of field parameters and major anions and cations on groundwater P levels are assessed. The distribution and concentration of different P fractions in groundwater is also presented.

Chapter Five is concerned with the identifying the hydrogeological factors that may determine groundwater P concentrations. Bedrock geology, Quaternary deposits, unsaturated zone thickness and aquifer type are examined for each of the catchment areas.

The temporal patterns of P in groundwater are examined at several scales in Chapter Six. Seasonal and more short-term changes of groundwater P concentrations are presented in this chapter. The effects of temporal changes on P levels in karstic springs are particularly examined here.

Land use and management is assessed in Chapter Seven using both interpreted satellite data from the CORINE land cover database and agricultural statistics at the district electoral division level from the Central Statistics Office of Ireland. Soil types in each catchment are also examined here with a particular emphasis on soil hydrology characteristics.

Chapter Eight draws together the findings of the previous chapters on groundwater P in the context of the surface waters in each catchment area. Phosphorus loadings from flow measurements at springs are presented and compared to receiving water P loads.

Finally, Chapter Nine provides a summary of the research and brings together the conclusions of each chapter. Recommendations and scope for future research are also put forward.

# CHAPTER 2. PHOSPHORUS IN IRISH GROUNDWATERS

## *2.1 Introduction*

This chapter examines the only national groundwater phosphorus dataset available for the Republic of Ireland. The dataset is examined spatially using inherent site characteristics and several land-use coverages. In this way, general P levels in Irish aquifers are assessed and a platform is created for the detailed study of the selected catchment areas. This dataset forms part of the EPA's National Water Quality Monitoring Program (NWQMP) and first included groundwater during the 1995-97 period (Lucey *et al.*, 1999). The EPA's groundwater quality monitoring program focuses on seven key objectives (EPA, 2001):

1. To establish that groundwater quality reflects the geological characteristics of the aquifers, and check whether it is impaired by anthropogenic influences;
2. To define the state of groundwater quality and to detect changes and trends of quality on a national basis;
3. To comply with National and EU legislation, especially the Nitrates Directive;
4. To identify any groundwater affected by pollution;
5. To repeat monitoring for nitrates every four years in aquifers where nitrate concentrations greater than 25 mg $l^{-1}$ $NO_3$ have been found;
6. To identify vulnerable zones;
7. To identify user requirements and activities that affects the quantity and quality of groundwater.

To achieve these aims the EPA have established three monitoring networks: a representative network; a user-related network; and a pollutant-related network (EPA, 1994). The P dataset is derived from the representative monitoring network. This network is operated on a national basis in order to define the state of the groundwater quality, to detect changes in groundwater quality and to assess causes of such changes. Sampling is carried out twice yearly to coincide with groundwater levels being at their lowest and highest.

## 2.2 Materials and methods

### 2.2.1 Structure of the monitoring network for groundwater phosphorus

During the 1995-97 monitoring period not every site was visited twice yearly. Therefore, for the purposes of obtaining representative water quality data, the EPA only used sites with a minimum of four sampling runs during this period (Lucey, *et al.*, 1999). Unfiltered samples taken at these sites were analysed for molybdate reactive P (MRP), and are here referred to MRP (unf.). A detailed explanation of phosphorus fractions and the analytical techniques involved is presented in Section 1.4. For MRP (unf.) data a total of 833 samples were analysed at 189 stations. Mean MRP (unf.) data for the 189 sites was provided by Micheál Mac Cárthaigh of the EPA. Table 2.1 and Table 2.2 summarise the ownership, source type and abstraction rates of these sites. The ownership divisions are based on whether the groundwater supply are maintained by local authorities (public), small rural communities (group schemes) or individual (private). Of the 189 sites the majority of sites are public water schemes, which also have the largest daily abstraction rates. Boreholes were the most common source type closely followed by springs. Largest abstraction rates were recorded at the spring sites.

**Table 2.1 Ownership and abstraction rate of national groundwater monitoring dataset.**

| *Ownership* | *Number of Sites* | *Mean Abstraction Rate ($m^3$ $day^{-1}$)* | *Median Abstraction Rate ($m^3$ $day^{-1}$)* |
|---|---|---|---|
| Total EPA dataset | 189 | 630 | 182 |
| Public Schemes | 113 | 849 | 436 |
| Private Schemes | 35 | 180 | 66 |
| Group Schemes | 34 | 139 | 76 |
| Unknown | 5 | | |

**Table 2.2 Source type and abstraction rate of national groundwater monitoring dataset.**

| *Source Type* | *Number of Sites* | *Mean Abstraction Rate ($m^3$ $day^{-1}$)* | *Median Abstraction Rate ($m^3$ $day^{-1}$)* |
|---|---|---|---|
| Bore | 97 | 433 | 175 |
| Springs | 69 | 886 | 425 |
| Dug Wells | 13 | 293 | 300 |
| Mixed Source | 5 | 688 | 684 |
| Gallery | 1 | | |
| Unknown Source | 4 | | |

Figure 2.1 indicates the location of each of the 189 sites by source and ownership. County boundaries are also shown (see Figure 2.2 for county names). It can be seen that whilst there is a good general coverage, there are some large areas devoid of sites. Counties Tipperary, Waterford and Wexford have no sites, and counties Dublin and Kilkenny only have one. Lucey *et al.* (1999) identified this lack of coverage.

Notwithstanding these limitations there are some spatial trends in the available sites. Public supplies are evenly distributed across the country. Springs sources are concentrated in a central and mid-west portion of the country, with a propensity of boreholes in other areas. This trend could reflect more surficial expression of groundwater in the central and mid-western regions and deeper groundwater in other regions. Springs are more common in limestone areas, particularly where there is some degree of karstification. This latter point could explain the large number of springs in the Cos. Galway, Mayo and Roscommon.

Figure 2.3 illustrates the profile of source type for public, private and group groundwater supplies. Both the public and group schemes have near equal numbers of bores and springs. In contrast, the majority of the private schemes are boreholes. This may be due to limited options on private land holdings, whereas, public and group schemes can also target suitable springs and wells in a larger area.

Figure 2.1 Location map of public, group and private groundwater supply schemes used in the EPA's national groundwater quality monitoring programme.

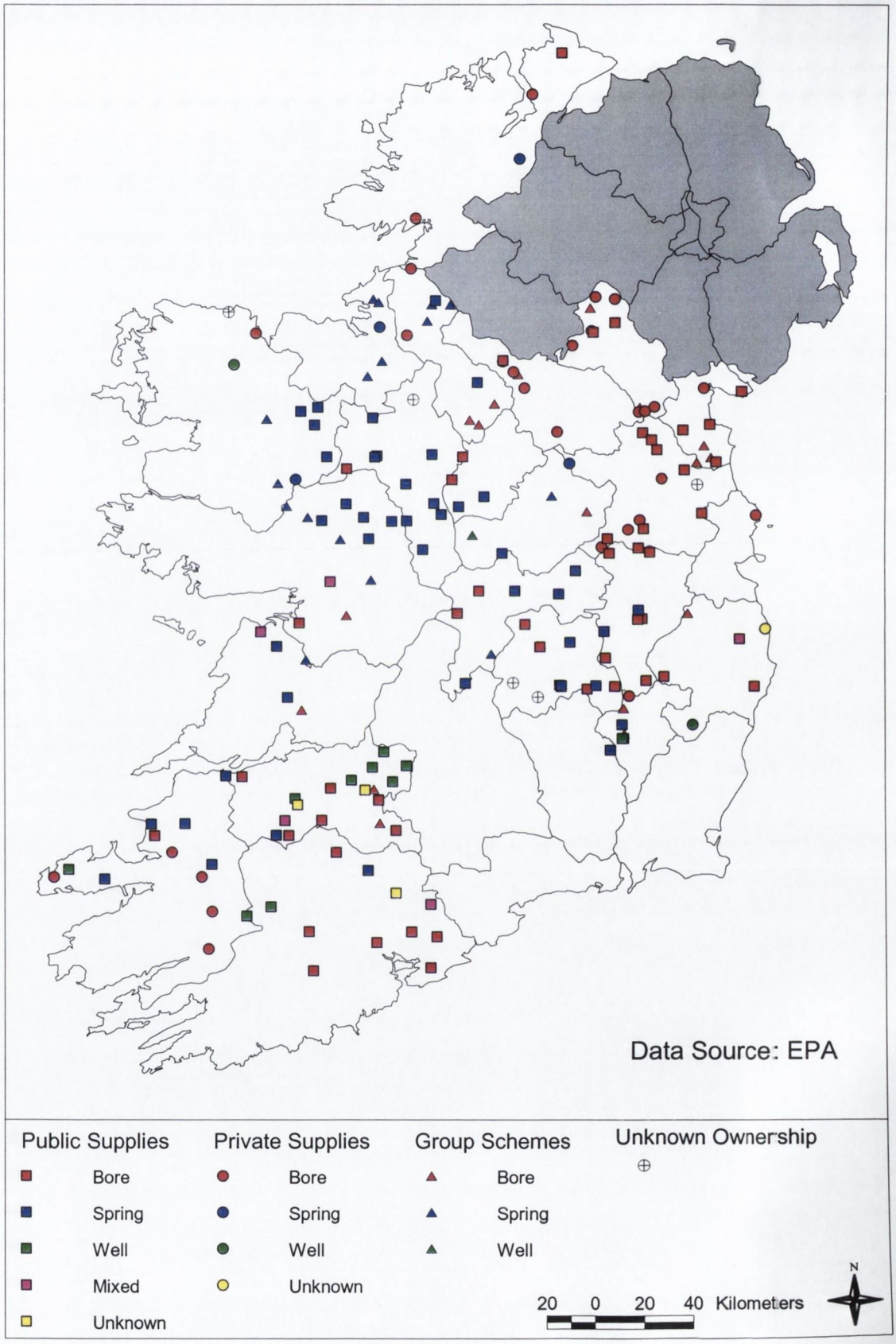
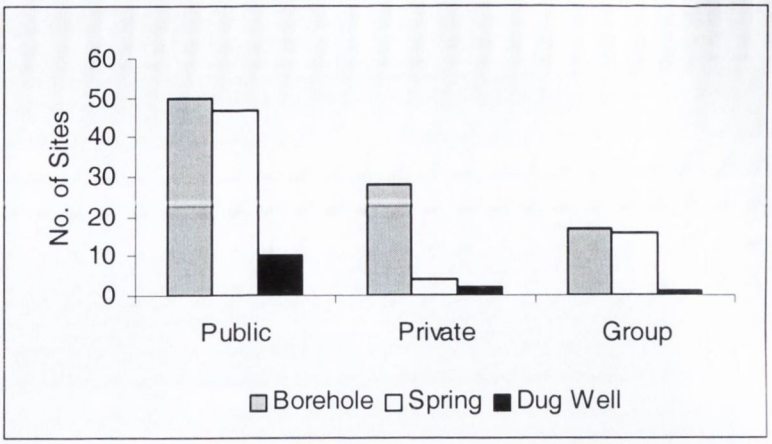


Figure 2.2 County boundaries of the Republic of Ireland.

**Figure 2.3 Source type of public, private and group groundwater supplies.**




### 2.2.2 Available datasets

One of the key limitations of any assessment involving geographical information is lack of suitable or compatible datasets (Burrough and McDonnell, 1998). Table 2.3 lists the datasets used in this project and their characteristics. A brief explanation of each is given here with more detail in the results sections of this chapter. The general problem with some of these coverages is that effectively point data of springs and boreholes are being compared with large polygons of several square kilometres. In addition, some of the datasets are quite dated. Maps like the geology and hydrometric regions are satisfactory since these are quite permanent features of the landscape. The CORINE land cover data was provided by Paul Mills of Compass Informatics Ltd. The resolution of CORINE is 100m but the age of the data is about 10 years old. The stocking density data are both quite old, being derived from the last census (CSO, 1991), and at a large scale. The soil P maps from Teagasc have poor resolution (10 km grid) but the age of the dataset is reasonably contemporaneous with the groundwater P data. The soil P desorption model (Daly *et al.*, 2000) is based on a slightly better 5 km grid.

**Table 2.3 Characteristics of coverages incorporated in GIS analysis of EPA P dataset.**

| *Dataset* | *Type (units)* | *Source* | *Resolution* | *Age* |
|---|---|---|---|---|
| Soil Phosphorus | Morgans P (mg $kg^{-1}$) | Teagasc | 10X10 km grid | 1995-97 |
| P desorption model | Desorption Class | EPA | 5X5 km grid | 1999 |
| Stocking Density | Livestock Units per ha. | CSO | County scale | 1991 |
| CORINE | Land Cover | Compass | 100m | 1990 |
| Geology | Geological strata | GSI | ca. 375m | 1962 |
| Hydrometric Regions | River basin boundaries | EPA | | |

### 2.2.3 Factors affecting the quality of spatial data

There are several factors that affect the quality of spatial data. These include (Burrough and McDonnell, 1998):

- Age of the dataset;
- Areal coverage;
- Map scale and resolution;
- Density of observations.

Goodchild *et al.* (1993) point out that scale maps of 1:500,000 and 1:1,000,000 have an effective resolution of 250 m and 500 m, and a minimum resolving area of 6.25 ha and 25 ha respectively. Therefore, for example, the Geological Map of Ireland used in Section 2.3.9, with a scale of 1:750,000, lies somewhere intermediate (ca. 375 m). This can lead to margin of error when trying to establish whether a bore, some centimetres in diameter is within a cartographic boundary. Zhang *et al.* (1996) found that a 1:100,000 mapping scale will omit small parcels of agricultural land, and non-agricultural lands can be included. Burrough (1994) also points out how errors can arise out of processing spatial data. For example, the accurate representation of curved shapes will depend on the number of vertices used during the digitising process. In a similar way, when rasterizing a vector map, grid cells can sometimes be too large to resolve spatial details. Thus, errors associated with spatial data can limit its degree of usefulness.

### 2.2.4 Summary of GIS methods used in assessment of the national dataset

Geographical information systems (GIS) are a powerful mapping and interrogation tool. There are a range of GIS methods that can be adopted to map and analyse spatial data. This project focused on a point-in-polygon assessment of the available datasets. This is probably the simplest of GIS methods, but suitable given the incomplete coverage of the groundwater sampling locations and scale of the coverages. Point-in-polygon assessment essentially involves querying the GIS to identify what category of the studied coverage each groundwater site lies within. In this way a table is derived which lists each groundwater location with attribute data including the polygon name of the studied coverage. Hydrometric region 26 (see Section 2.3.10), which represents the Upper Shannon river basin, has the largest number of groundwater sites (25) evenly spread across the basin. These facts facilitated examination of this region with more complex GIS techniques.

### 2.2.5 Boxplots for graphical presentation

Boxplots present the data in terms of medians and the components of the type used here are explained in the Figure 2.4 below (Velleman, 1993). They graphically present the medians of the data from the minimum to the median and of the data from the median to the maximum. The shaded portion of the boxplots used in the figures that follow represents the 95% confidence intervals around the median.

**Figure 2.4 Explanation of the components of boxplots.**

Starburst represents a very extreme outlier

Circle represents extreme values.

Horizontal bar of "T" (whiskers) is 75%$^{ile}$ + 1.5 x interquartile range (IQR)

Top of box is the 75$^{th}$ percentile.

The horizontal bar in the box is the median.

Base of box is the 25$^{th}$ percentile.

Horizontal bar of inverted "T" (whiskers) is 25%$^{ile}$ – 1.5 x IQR

Extreme values (circles) represent values which exceed the upper or lower whiskers of the boxplot, i.e. greater than 75%$^{ile}$ + 1.5, or lower than 25%$^{ile}$ – 1.5 x IQR. Extreme outliers (starbursts) represent values greater than 75%$^{ile}$ + 3 x IQR, or lower than 25%$^{ile}$ – 3 x IQR.

## *2.3 Results*

### 2.3.1 Introduction

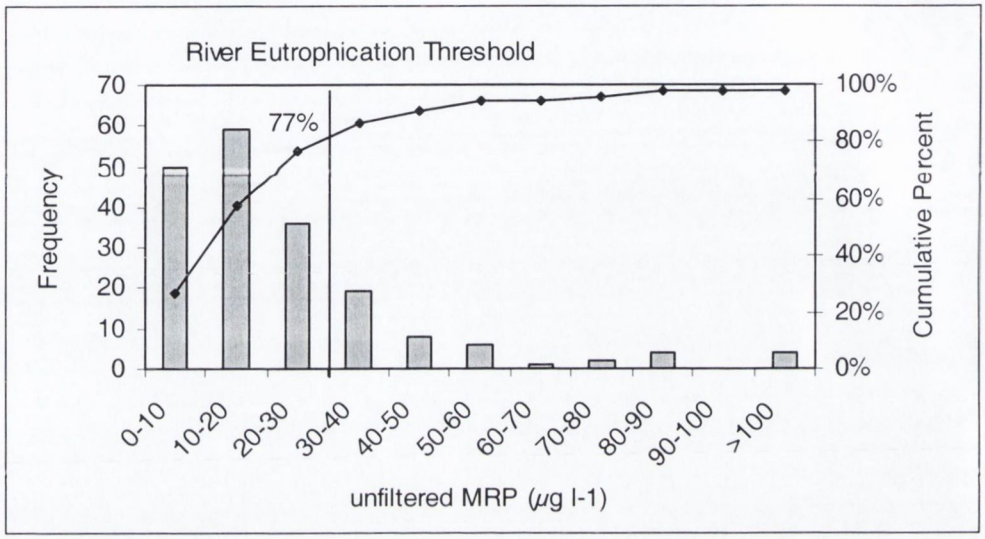
A summary of the P data found in the NGQMP is given here followed by the GIS assessment of the available coverages using a combination of maps and graphs. The maps all take up one page and are each presented on the page immediately subsequent to their reference in the text.

### 2.3.2 Phosphorus concentrations in the NGQMP

Samples collected by the EPA were analysed for MRP (unf.), i.e., colorimetric analysis on the raw water sample using the molybdate-ascorbic acid method (see Section 1.4). Figure 2.5 presents a frequency histogram of the data. The data range from 3 to 548 $\mu g\ l^{-1}$ and are highly skewed, with 95% of the data located below 60 $\mu g\ l^{-1}$. The mean and median off the

data are 26 and 17 $\mu g\ l^{-1}$ of MRP (unf.) respectively. McGarrigle's (1998) study on national river data for the period 1991-1994 suggests that adverse impacts become apparent once MRP (unf.) levels exceed 30 $\mu g\ l^{-1}$. As can be seen from Figure 2.5, 77% of the data are below this threshold. However, 23% of the data exceed this threshold.

**Figure 2.5 Frequency distribution histogram of mean MRP (unf.) data from the EPA NGQMP. The line plots the cumulative percent for each column.**




To allow the use of parametric statistics in the sections that follow the data was log-transformed. This converted the skewed distribution to a normal distribution which is one of the base assumptions for parametric statistics (Daly *et al.*, 1995). This effect can be clearly seen in Figure 2.6.

**Figure 2.6 EPA groundwater MRP (unf.) (A) and log-transformed MRP (unf.) (B).**

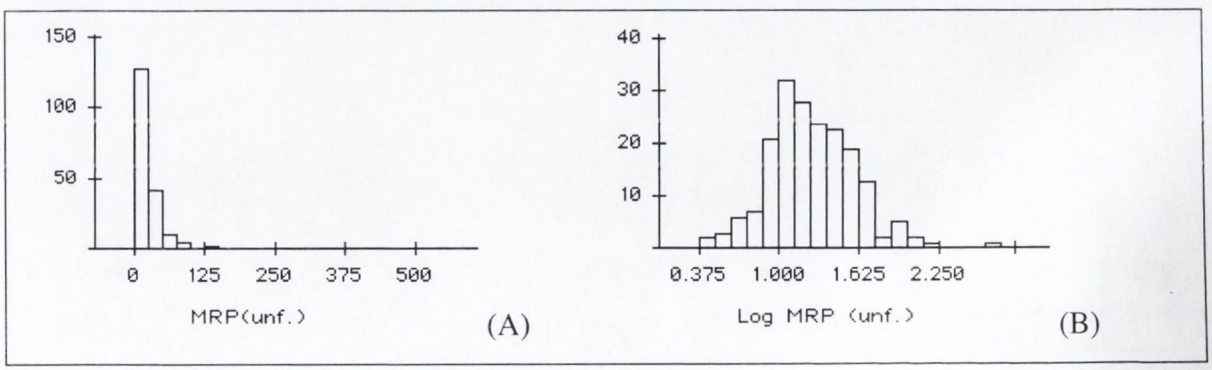
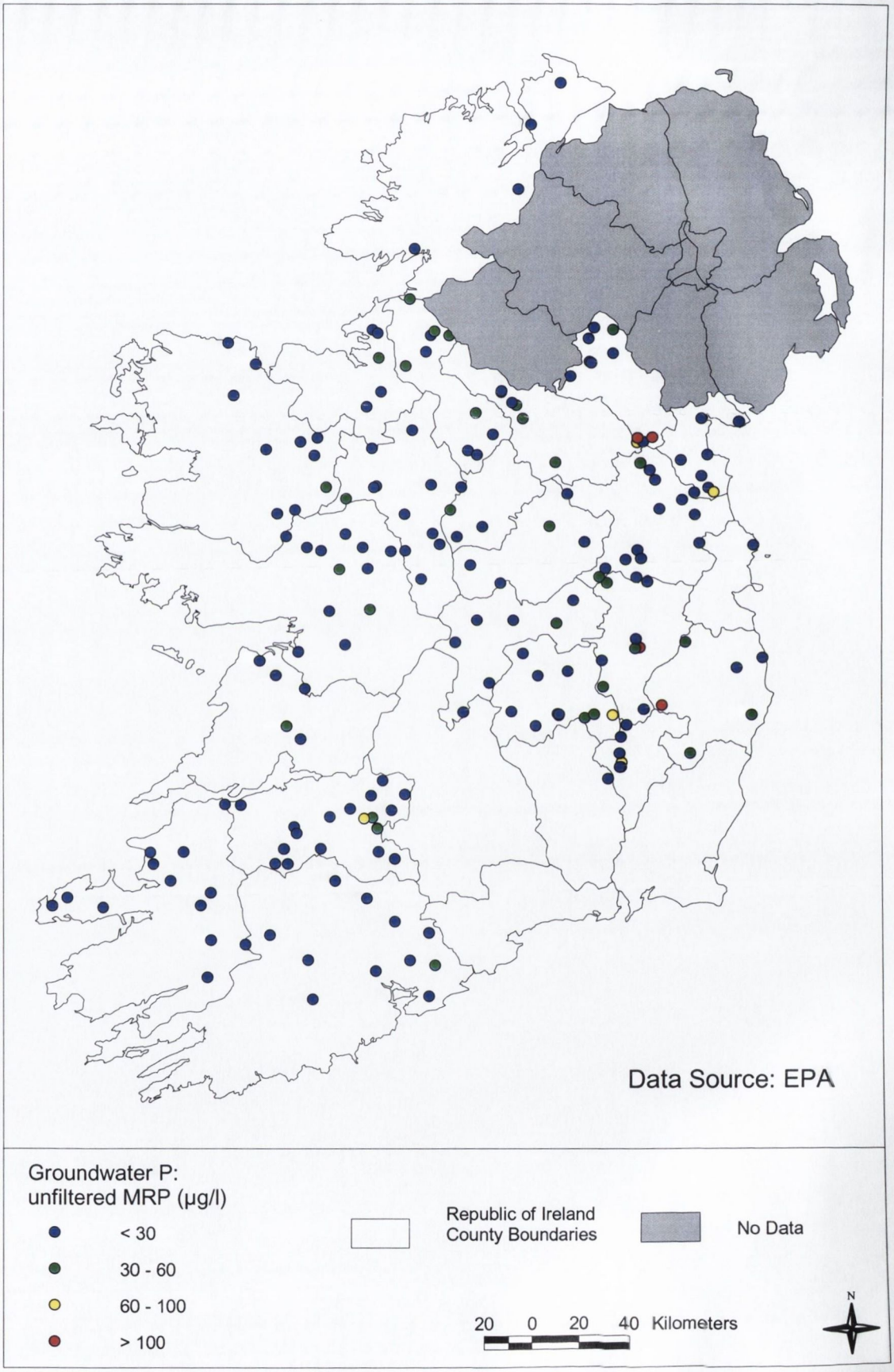


Figure 2.7 Spatial distribution of groundwater phosphorus levels in Irish aquifers from the EPA's NGQMP.



### 2.3.3 Spatial distribution of phosphorus levels in Irish aquifers.

The spatial distribution of groundwater P levels at sites in the EPA NGQMP are presented in Figure 2.7. Spatially all sites with < 60 $\mu g\ l^{-1}$ of MRP (unf.) are evenly distributed across the country. Sites with elevated P levels (> 60 $\mu g\ l^{-1}$ of MRP (unf.)) are located in the eastern half of the country except for one site in Co. Limerick.

### 2.3.4 Groundwater site location characteristics

Three primary source types exist in the dataset, bores, springs and wells, with a smaller number of mixed and unknown sources. Figure 2.8 presents mean MRP (unf.) values for each source type. The data were log transformed to normalize data and allow the use of parametric statistics. An ANOVA of the transformed data indicated that boreholes are significantly more vulnerable to elevated P levels than from the other three source types ($p < 0.01$).

As pointed out in Table 2.1, public water supply schemes dominate the EPA NGQMP. Figure 2.9 presents mean MRP (unf.) values for private supplies, group schemes and public supplies n the NGQMP. Whilst the private schemes have a slightly higher mean than the group and public supplies, this difference is not statistically significant. An extreme outlier of 548 $\mu g\ l^{-1}$ MRP (unf) in the Group schemes was omitted from this analysis.

**Figure 2.8 Mean MRP (unf.) levels at different source types of the EPA NGQMP (error bars denote plus and minus one standard error).**

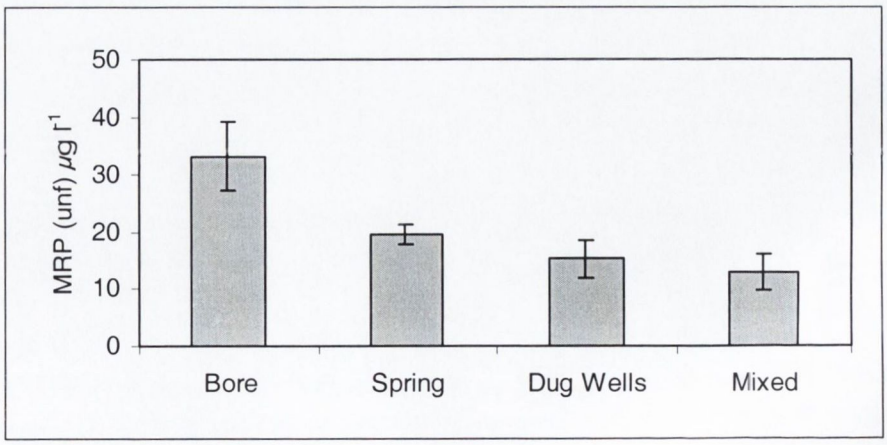
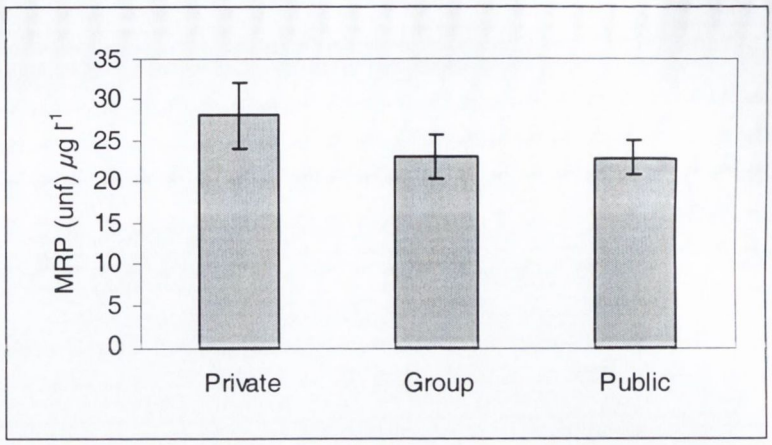
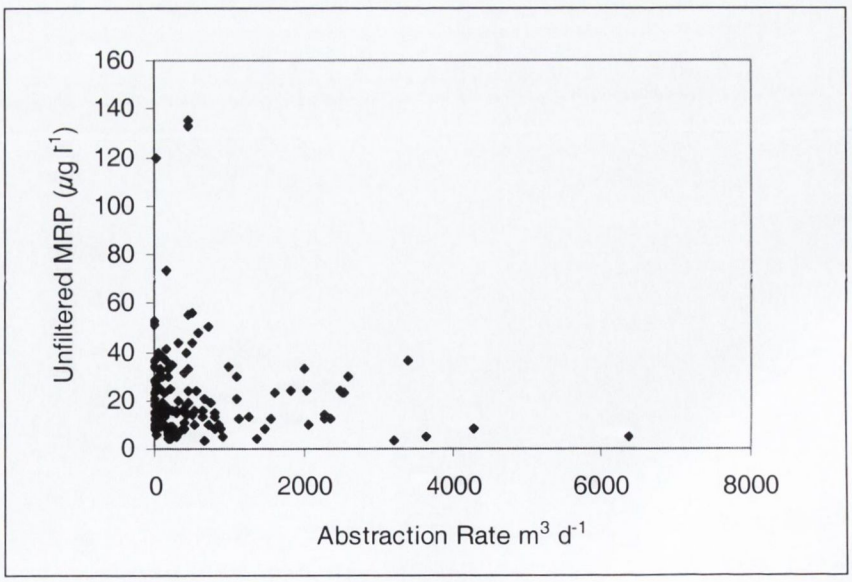


**Figure 2.9 Mean MRP (unf.) levels at different ownership types of the EPA NGQMP (error bars denote plus and minus one standard error).**




Average daily abstraction rates were examined for 132 of the NGQMP sites. No abstraction rates were available for the remaining sites. Figures 1.4 presents a scattergram of MRP (unf.) and mean daily abstraction rates of the NGQMP sites. One outlier (Group scheme borehole with 548 $\mu$g $l^{-1}$ MRP unf.) was removed from this graph. There is a general logarithmic decline in P as abstraction rate increase. This may represent a dilution effect where greater abstraction rates result in a dilution of phosphorus in the supply. However, this relationship was not statistically significant.

**Figure 2.10 MRP (unf.) and daily abstraction rates of NGQMP sites**

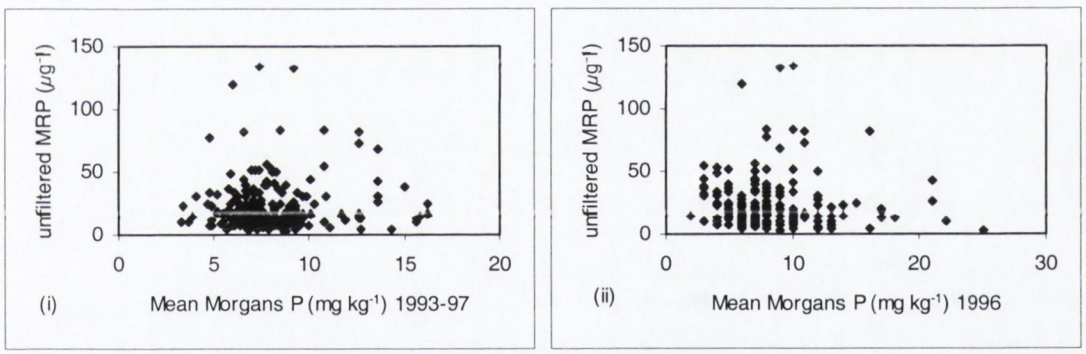



## 2.3.5 Soil phosphorus

Soil phosphorus data are collected by Teagasc, the Irish Government's agricultural research advisory organisation. Public access to national P soil levels is limited to a 10 km grid

basis. Figure 2.12 (i) presents mean Morgan's P (agronomic soil test used by Teagasc to measure plant available P) levels for the years 1993 to 1997 in a 10 km grid. This dataset was provided by Dr. Brian Coulter of Teagasc, Johnstown Castle, Co. Wexford. Daly *et al.* (2000) attempted to improve the resolution of this 10 km grid by using a geocoding procedure which tried to link addresses of soil samples from the 1996 Teagasc Soil P database with an existing GIS database of some 1200 townland names. They achieved a 66% success rate in linking farm addresses with the town and villages database. The new locations were then interpolated to create polygons of varying soil P levels. Figure 2.12 (ii) is the product of this analysis. Included in Figure C is the NGQMP MRP (unf.) data. There is no clear spatial pattern in either map. A point-in-polygon assessment of both maps was carried out. The derived attribute tables were exported to MS EXCEL and examined in the statistical package DATADESK. Figure 2.11 shows scatterplots for both maps. No significant relationship was found in either dataset.

**Figure 2.11 Groundwater MRP (unf.) and (i) mean Morgans P (1993-97) from 10 km grid and (ii) mean Morgans P (1996) from interpolated polygons.**




### 2.3.6 Soil phosphorus desorption model

Daly *et al.* (2002) developed a model to predict P loss to surface waters in river catchments nationally using input parameters from a landcover database, soil P data and soil P desorption data. A key outcome of this research identified a clustering effect controlled by soil hydrology. The two groups to emerge were identified as wet and dry soils. Separate prediction models were constructed for each group. Figure 2.13 presents a map of the predicted surface water MRP levels in a 5 km grid for the wet and dry catchments, with the NGQMP MRP (unf.) levels superimposed.

Figure 2.12 (i) Mean Soil Morgans P levels for years 1993 - 1997 10km grid (Coulter et al., 1999).
(ii) Mean Soil Morgans P levels for 1996 interpolated polygons (Daly et al., 2000).

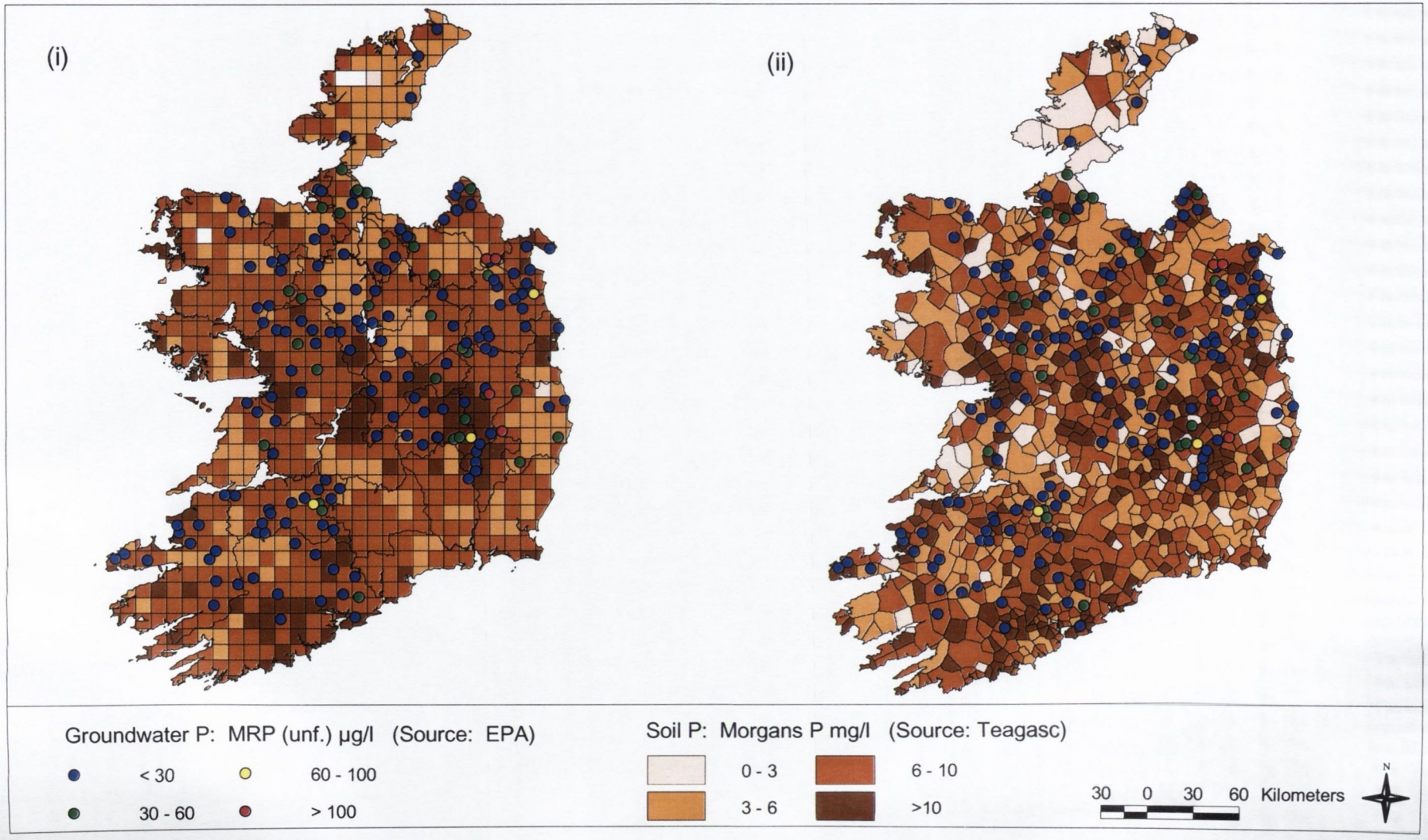
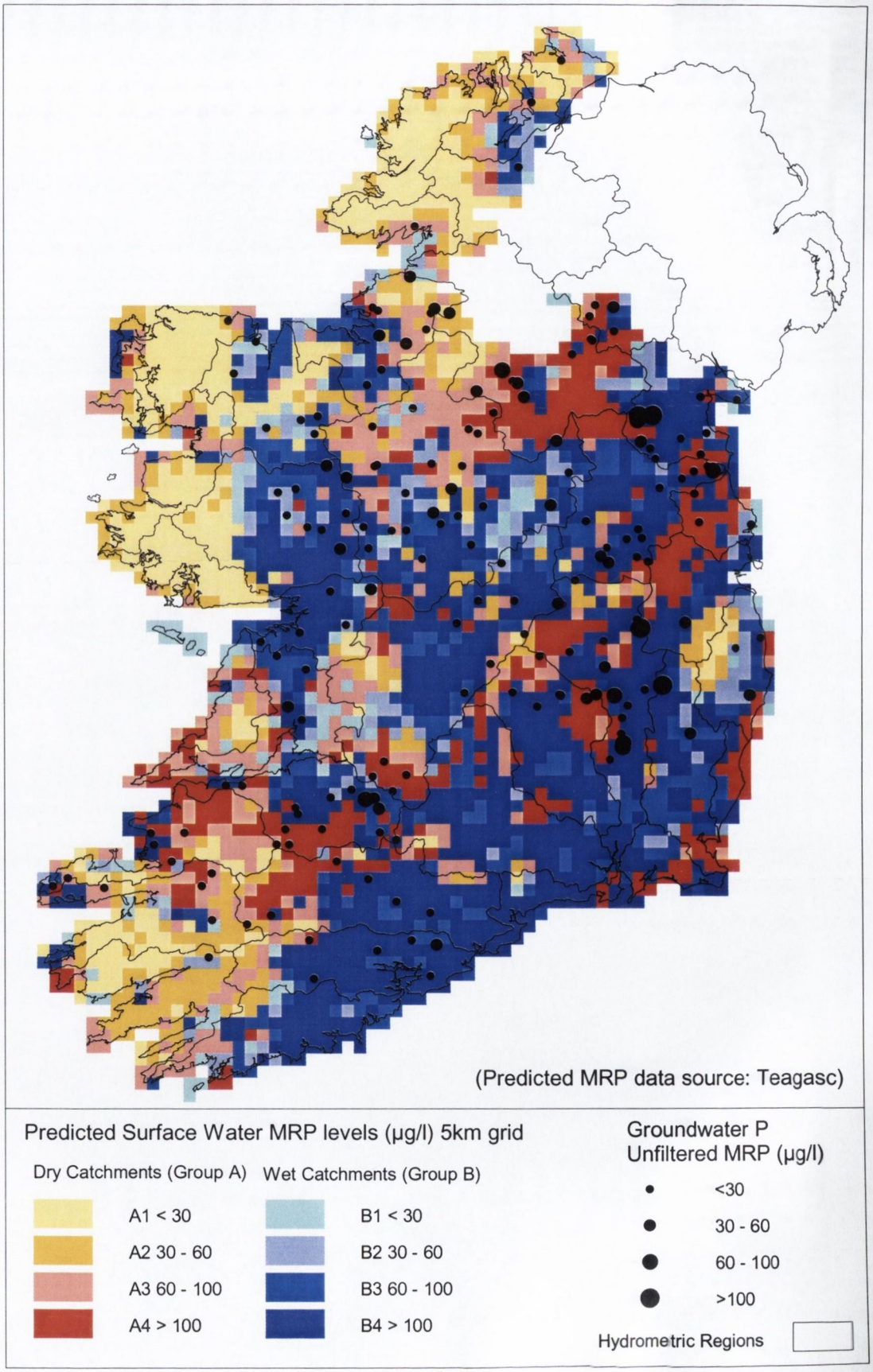


Figure 2.13 Predicted surface water MRP levels in dry & wet catchments (Daly et al., 2002). The EPA NGQMP groundwater MRP (unf.) data are superimposed.



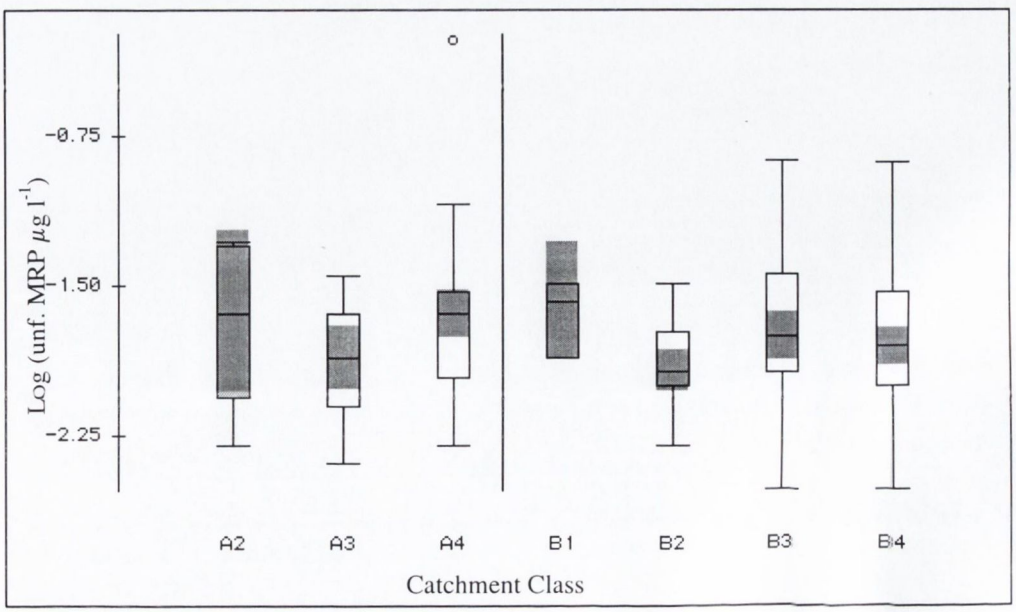
Group A (dry) and group B (wet) catchments are subdivided into four classes based on predicted MRP levels. Table 2.4 summarises these classifications.

**Table 2.4 Classification of predicted MRP values from the soil P desorption model (Daly *et al.*, 2000).**

| *MRP Class* | *MRP Range* $\mu g\ l^{-1}$ | *EPA Pollution Class* |
|---|---|---|
| A1/B1 | 0-30 | Unpolluted |
| A2/B2 | 31-60 | Slightly polluted |
| A3/B3 | 61-100 | Moderately polluted |
| A4/A4 | >100 | Seriously polluted |

A point-in-polygon assessment was carried out for the groundwater P data using the predicted MRP coverage. The derived attributed table was exported from Arcview and examined in Datadesk. An ANOVA was carried out after removing four major outliers in the data (groundwater P values >100 $\mu g\ l^{-1}$). Figure 2.14 presents boxplots of the data analysed by ANOVA; again the groundwater data were log-transformed to allow for parametric statistics. The ANOVA results indicated no significant differences between the means of groundwater P in each MRP prediction class. It should be noted that the groundwater P mean for the lowest MRP prediction class in both groups is higher than all other classes. Therefore, highest groundwater MRP (unf.) is located in catchments where lowest MRP levels are predicted in surface water. However, these means are not statistically different.

**Figure 2.14 Boxplots for the natural log of NGQMP MRP (unf.) and for group A (dry) and group B (wet) predicted MRP classes.**



### 2.3.7 Stocking densities

The agricultural division of the Central Statistics Office (CSO) collects detailed information on livestock density in Ireland every ten years. The last census occurred in 1991. This information is available at different geographical scales: province, county, rural district and district electoral division (DED). Given the point nature of groundwater sampling locations, the smallest scale, DED, is the most desirable. Unfortunately, it is difficult to obtain the boundaries of DEDs in for such a large number of sites spread across the country. This was achieved for the three catchment study areas, but not for each of the 189 sites in the NGQMP.

In order to examine stocking densities at national level, county scale census information was obtained from Coulter *et al.* (1999). This information is also freely available from CSO (1991). Coulter *et al.* (1999) present stocking density tables for each county for cows and replacements, other cattle, sheep and overall stocking density.

Figure 2.15 presents a map with overall stocking density and the NGQMP groundwater P levels. Greatest overall stocking density occurs in a southern region stretching from Cork to Wexford and a north eastern corner of Cos. Meath, Cavan, Louth and Monaghan. The location of high groundwater P data does not appear to clearly coincide with areas of high stocking density. Figure 2.16 plots each of the components of the overall stocking density against mean groundwater P. No significant relationships were apparent for any of the stocking density components.

Figure 2.15 Total stocking density by county (after Coulter et al., 1999) and EPA groundwater P data from the NGQMP.

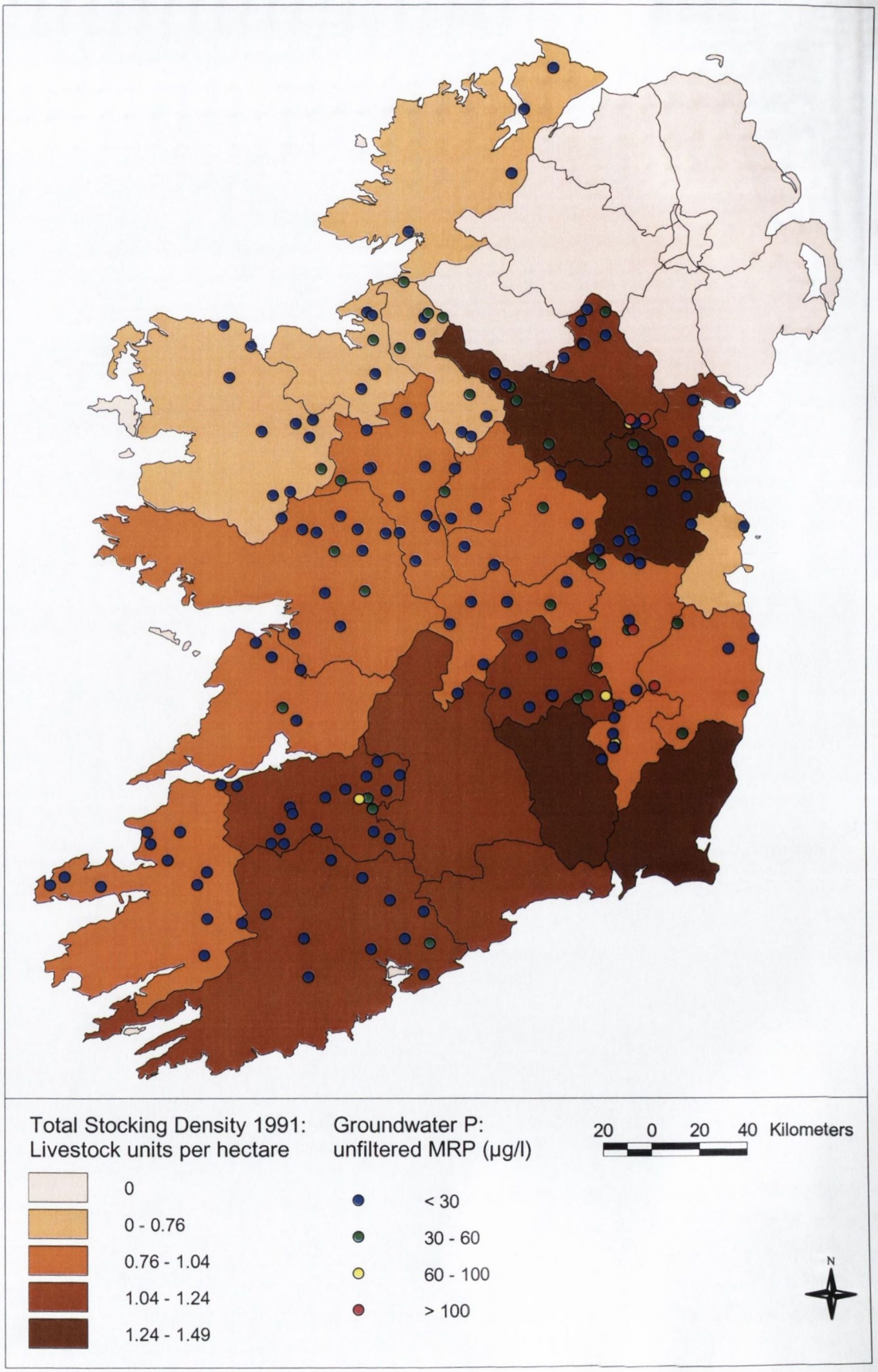
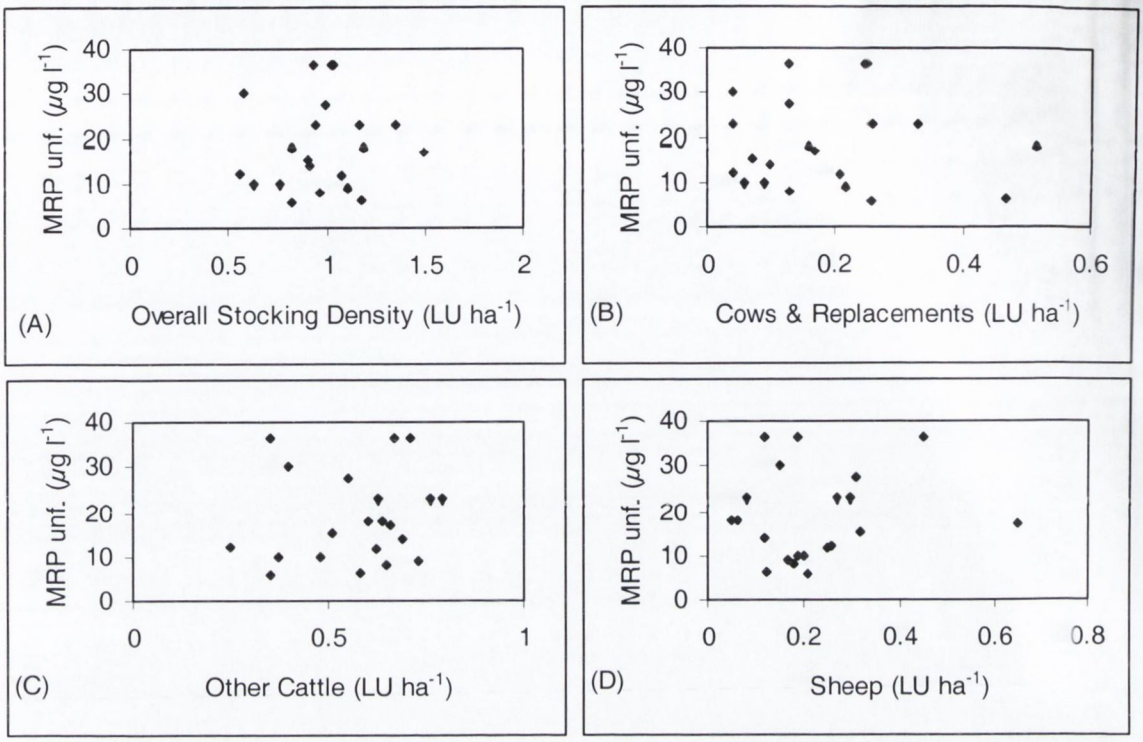


**Figure 2.16 Median county groundwater P levels and (A) overall stocking density (B) cows & replacement density (C) other cattle density and (D) sheep density.**




## 2.3.8 CORINE land use classification

The CORINE landcover data is from a project carried out by the European Space Agency (O'Sullivan, 1994). The landcover classifications are derived from satellite images which attribute different classes depending on measured absorbances which are compared with ground-truth assessments. Figure 2.17 presents the CORINE landcover classes for Co. Limerick as an example. The dataset is so large to preclude presentation of the complete national dataset. A point-in-polygon assessment was carried out using the NGQMP groundwater P data. Figure 2.18 presents the boxplots of land cover classes using log-transformed MRP (unf.) data. Summary statistics of this assessment and explanations for the codes used in Figure 2.18 are presented in Table 2.5. The majority of the sites, 74%, are located in the three pasture classes. This is not surprising considering that Allot *et al.* (1998) report that the CORINE project classifies 68% of the Republic of Ireland's land area as agricultural, and Lafferty *et al.* (1999) report that in 1991 89% of all farms were pasture. With only 26% of the remaining sites spread in the other recorded classifications comparison between classifications is difficult. From Table 2.5 sites it can be seen that with the three pasture classes mean MRP (unf.) levels followed degree of intensity.

Figure 2.17 CORINE land cover classes for Co. Limerick, with groundwater P levels from the EPA NGQMP.

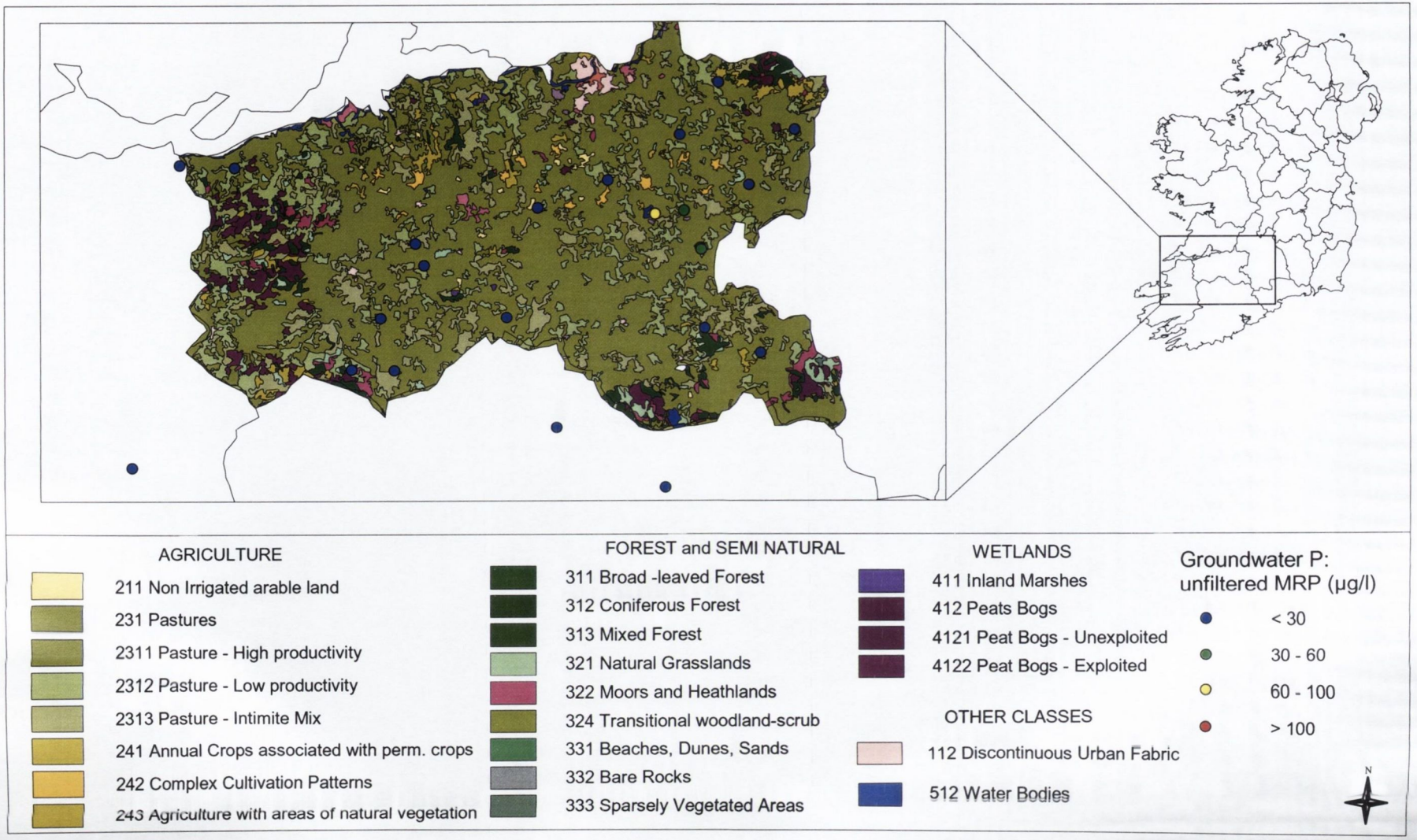


**Figure 2.18 CORINE land cover classes for EPA groundwater MRP (unf.) data.**

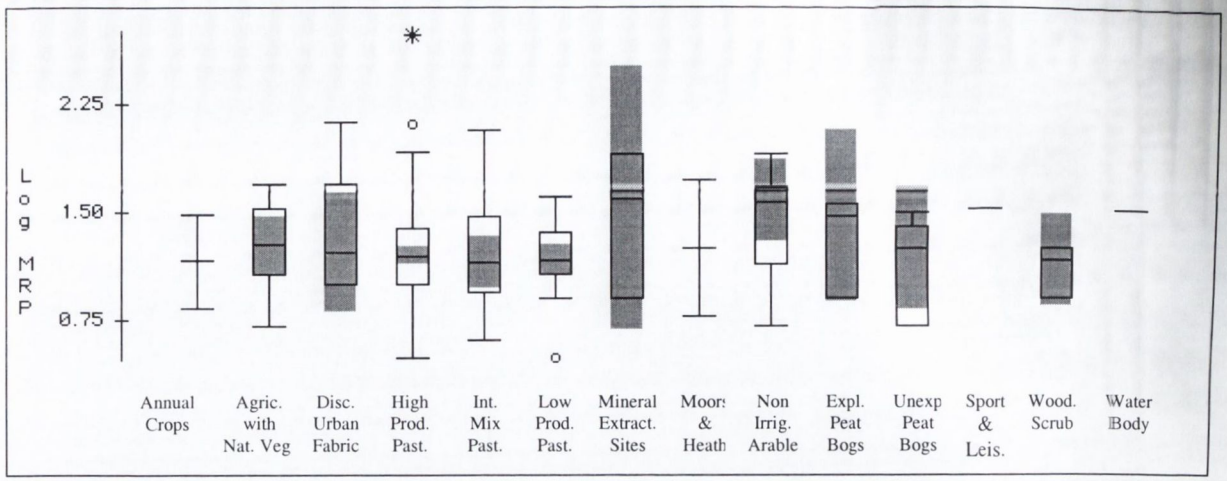



**Table 2.5 CORINE land cover classes for the EPA groundwater MRP (unf.) data.**

| *Group* | *Count* | *Mean* | *Median* ($\mu g\ l^{-1}$) | *StdErr* |
|---|---|---|---|---|
| Agricultural Classes | | | | |
| Low Productivity Pasture | 18 | 18 | 15 | 2 |
| Intimate Mix Pasture | 22 | 25 | 15 | 6 |
| High Productivity Pasture | 99 | 28 | 16 | 6 |
| Agriculture with Natural Vegetation | 12 | 22 | 19 | 4 |
| Annual Crops assoc. with perm. crops | 2 | 19 | 19 | 12 |
| Non Irrigated Arable Land | 9 | 35 | 38 | 9 |
| Artificial Surfaces | | | | |
| Discontinuous Urban Fabric | 7 | 39 | 17 | 17 |
| Sport & Leisure Sites | 1 | 34 | 34 | na |
| Mineral Extraction Sites | 3 | 43 | 40 | 21 |
| Forest and Semi-natural | | | | |
| Woodland-Scrub | 3 | 14 | 15 | 3 |
| Moors and Heathlands | 2 | 30 | 30 | 24 |
| Wetlands | | | | |
| Peat Bogs - Unexploited | 7 | 17 | 18 | 4 |
| Peat Bogs - Exploited | 3 | 25 | 30 | 9 |
| Water Bodies | 1 | 33 | 33 | na |

Non irrigated arable land yielded highest mean P levels in the agricultural group. However, an ANOVA (using log-transformed data) between the means of each classification reported no statistically significant difference. Small sample number within the other classes makes precludes any useful comparisons. One of the sites was classified as been located in a

water body, highlighting the potential for misclassification of sites which are close to class polygon boundaries.

### 2.3.9 Geology

The most recent national geological map of Ireland is a 1984 Mineral Deposits Map of Ireland (scale 1:750,000; ERA maptec/GSI, 1984). However, this map is not available in digital form. An earlier map, Geological Map of Ireland (scale 1:1,000,000; GSI, 1962), was obtained from the GSI in digital format and so was used for GIS interrogation. Figure 2.19 presents this earlier geological map with the NGQMP groundwater P data.

The map shows the dominance of Carboniferous Limestone in the central region. This is borne out by the number of sites located in these strata. Table 2.6 lists median MRP (unf.) levels for each rock type which contains one or more sites. The left hand side lists geological strata containing 3 or less sites, and the right hand side lists strata with 5 or more sites. Both groups are sorted by their MRP (unf.) levels. It can be seen that 65% (122 of the 189 sites) are located in Carboniferous Limestones. The sites located in Ordovician rocks have the highest groundwater P levels.

**Table 2.6 Geological strata and median MRP (unf.) $\mu g\ l^{-1}$.**

| *Geology (Where n ≤3)* | *Median MRP (unf.)* | *Count (n)* | *Geology (Where n ≥5)* | *Median MRP (unf.)* | *Count (n)* |
|---|---|---|---|---|---|
| Dingle Beds | 6 | 3 | Lower Avonian/Carb. | 8 | 9 |
| Cambrian Quartzite | 10 | 1 | Old Red Sandstone | 12 | 12 |
| Schist & Gneiss | 10 | 2 | Upper Avonian | 12 | 11 |
| Quartzite | 12 | 1 | Coal Measures | 13 | 6 |
| Triassic | 15 | 1 | Silurian Quartzite | 14 | 10 |
| Kiltorcan Beds | 15 | 2 | Middle Carb. L/stone | 17 | 26 |
| Millstone Grit & Sands | 40 | 1 | Lower Carb. L/stone | 19 | 78 |
| Ryolites | 44 | 1 | Upper Carb. L/stone | 21 | 18 |
| Granite | 74 | 2 | Ordovician | 40 | 5 |

An ANOVA (using log-transformed data) was carried out on strata with five or more sites, i.e., the right hand side. The ANOVA indicates that the data have significantly different means. Figure 2.20 shows the boxplots of the geological strata containing five or more sites. Sites in Ordovician rocks have MRP (unf.) levels significantly higher than several categories.

Figure 2.19 The geology of Ireland with groundwater P levels from the EPA NGQMP.

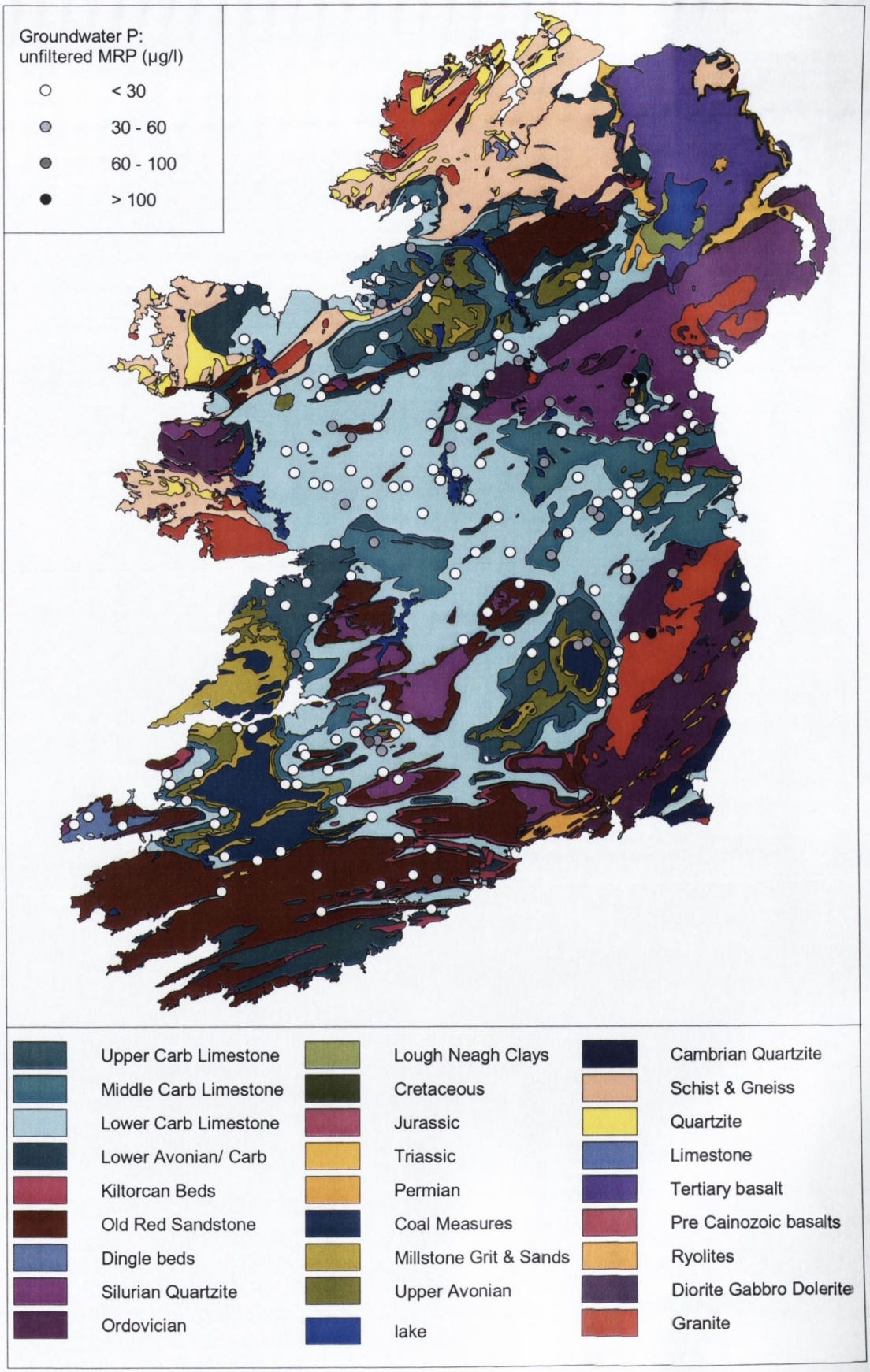
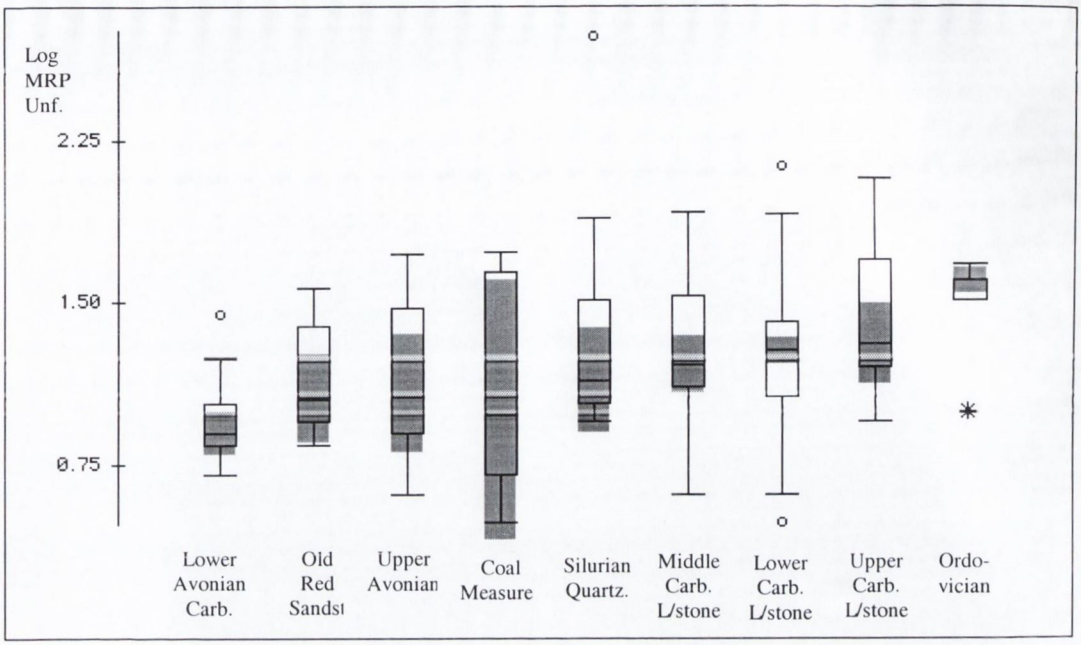


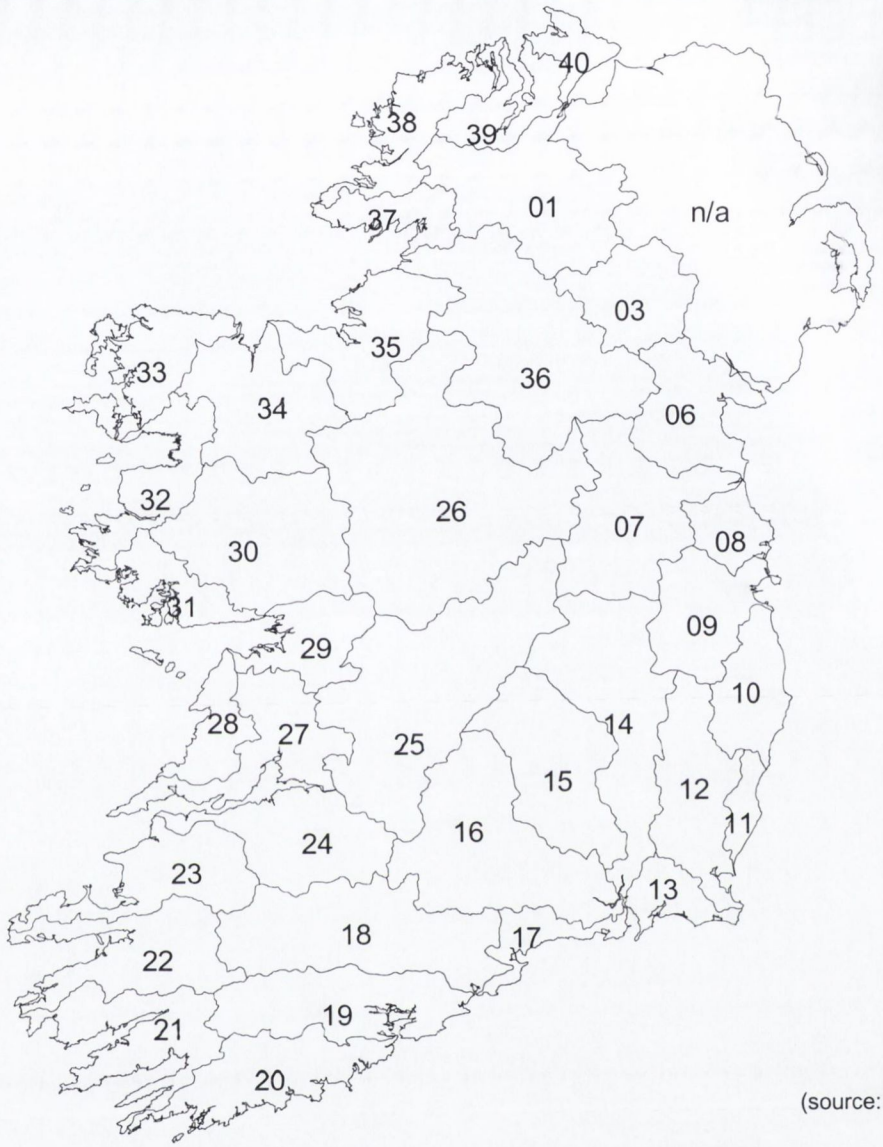
**Figure 2.20 Boxplots of Log transformed MRP (unf.) data for each geological Strata with five or more sites.**




## 2.3.10 Hydrometric regions

For the purposes of data collection and processing Ireland is divided into 40 hydrometric regions, see Figure 2.21. Each hydrometric region comprises a single river catchment or a group of smaller ones (MacCarthàigh, 1996). The EPA uses these regions as units of study to publish reports on water quality nationally. As discussed in chapter one, the EPA use a classification system for rivers based on physical, chemical and biological criteria. River lengths are thus classified as having waters that are unpolluted (Class A), slightly polluted (Class B), moderately polluted (Class C) or seriously polluted (Class D) (Lucey *et al.*, 1999). Figure 2.22 presents a map of the hydrometric regions shaded according to the percentage of river length classified as unpolluted (Class A). The NGQMP groundwater P data are also presented in this map. A point-in-polygon assessment was carried out and the derived attribute table exported for analysis. The data were examined for relationships. The extreme outlier of 548 $\mu g\ l^{-1}$, and regions with 3 or fewer sites were excluded from analysis. Ten regions contained only one site, and two contained only 3 sites. Ten regions contained no sites from the NGQMP. This left 18 hydrometric regions with more than three sites each. Scatterplots of % Class A, B, C and D river length from the 18 hydrometric regions and mean MRP (unf.) are presented in Figure 2.23.

Figure 2.21 Hydrometric regions of the Republic of Ireland.




(source: EPA)

| | | |
|---|---|---|
| 01 - Foyle | 17 - Colligan-Mahon | 30 - Corrib |
| 03 - Bann | 18 - Blackwater (Munster) | 31 - Galway Bay North |
| 06 - Newry, Fane, Glyde & Dee | 19 - Lee, Cork Harbour & Youghal Bay | 32 - Erriff-Clew Bay |
| 07 - Boyne | 20 - Bandon-Ilen | 33 - Blacksod-Broadhaven |
| 08 - Nanny-Delvin | 21 - Dunmanus-Bantry-Kenmare | 34 - Moy & Killala Bay |
| 09 - Liffey and Dublin Bay | 22 - Laune-Maine-Dingle Bay | 35 - Sligo Bay & Drowse |
| 10 - Ovoca-Vartry | 23 - Tralee Bay-Feale | 36 - Erne |
| 11 - Owenavorragh | 24 - Shannon Estuary South | 37 - Donegal Bay North |
| 12 - Slaney & Wexford Harbour | 25 - Lower Shannon | 38 - Gweebarra-Sheephaven |
| 13 - Ballyteigue-Bannow | 26 - Upper Shannon | 39 - Lough Swilly |
| 14 - Barrow | 27 - Shannon Estuary North | 40 - Donagh-Moville |
| 15 - Nore | 28 - Mal Bay | n/a - No Data |
| 16 - Suir | 29 - Galway Bay South East | |

Figure 2.22 Percentage of river length with class A water quality (unpolluted) in each hydrometric region and groundwater P data from the EPA NGQMP.

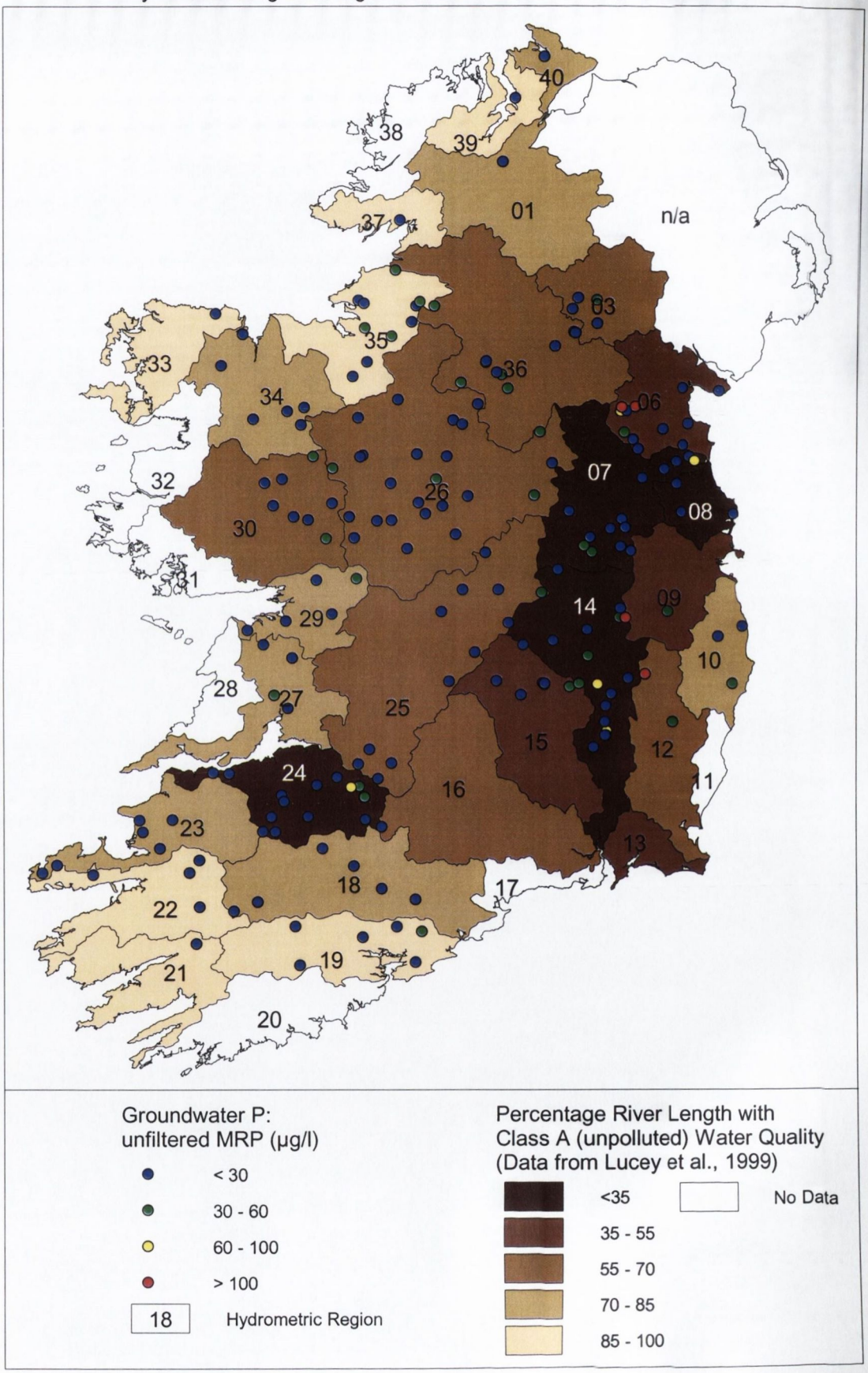


**Figure 2.23 Scatterplots of percentage river length with water quality class A, B, C, and D, and mean unf. MRP for each hydrometric region.**

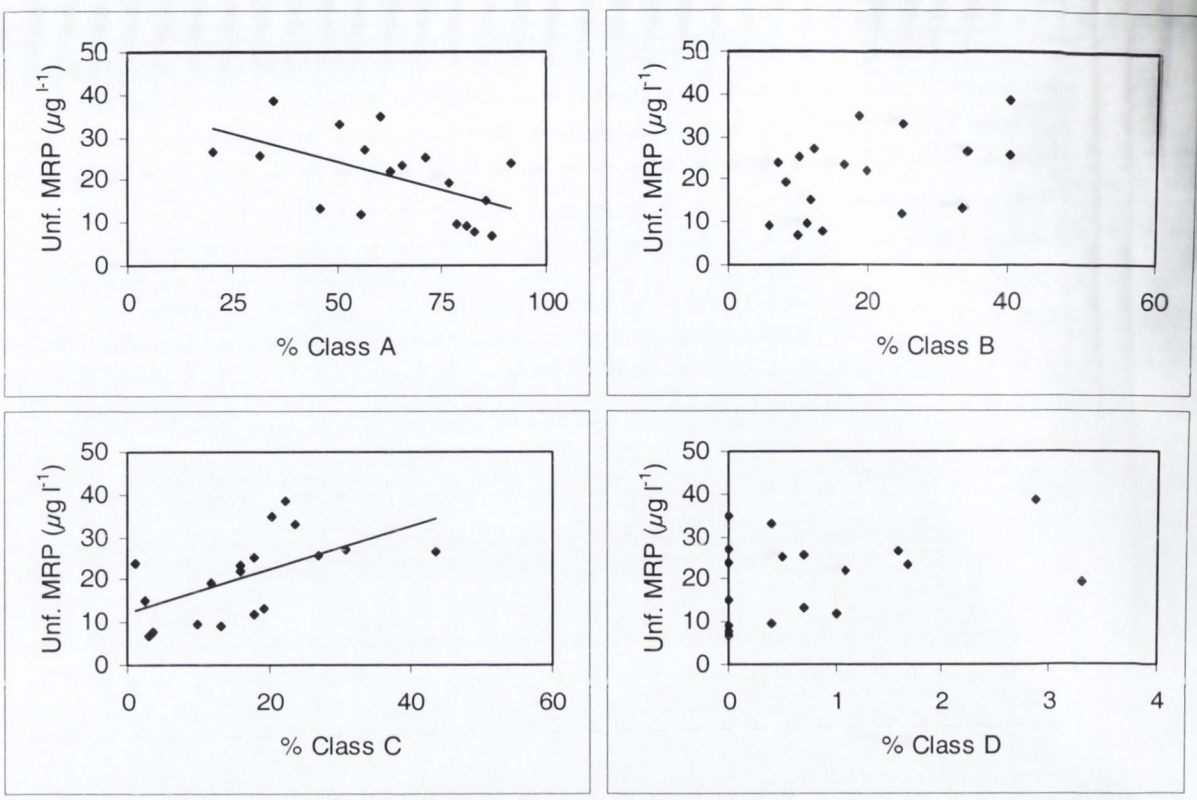



Table 2.7 presents results from Pearson Product-Moment correlations between mean unf. MRP and percentage of river length for each water quality class. A significant negative correlation was found in percentage of river length with class A water, i.e. the lower the percentage of unpolluted river water, the higher the groundwater P. A significant positive correlation was found in percentage of river length with class C water, i.e. the higher the percentage of moderately polluted river water, the higher the groundwater P. Both these relationships indicate that poor river water quality coincides with poor groundwater quality (higher P) in a hydrometric region. No significant correlations were found in class B or D.

**Table 2.7 Pearson Product-Moment correlations between mean unf. MRP and percentage of river length for each water quality class.**

| *Water Quality Class* | *Correlation Coefficient* | *Significance* |
|---|---|---|
| A (unpolluted) | -0.58 | $p<0.05$ |
| B (slightly polluted) | 0.46 | Not Significant |
| C (moderately polluted) | 0.58 | $p<0.05$ |
| D (seriously polluted) | 0.33 | Not Significant |

*Hydrometric Region 26: Upper Shannon River Basin*

For this region the 25 groundwater P data points where interpolated using the Inverse Distance Weighting (IDW) method (Burrough, and McDonnell, 1998). The boundary of region 26 was used as a mask for the interpolation, so whilst there are several groundwater site locations close to the outside of this boundary, they were not included in the interpolations. The interpolation results in a new surface with groundwater P levels mapped in a 100 m grid across the region. This new grid coverage can then be compared with other grid coverages using cross tabulation and summarisation tools in Arcview. Figure 2.24 (ii) presents the interpolated groundwater P grid and allows visual comparison with other coverages.

Figure 2.24 (i), presents the interpolated Morgans Soil P coverage for region 26 (derived from Figure 2.12 (ii)). When visually compared the two maps display some concurrencies, e.g., the dark blue patch (high groundwater P) in the east of the region coincides with a dark brown (high soil P) areas in the soil map. In contrast, the predominantly high soil P area in the south of region 26 coincides with a low P zone in the interpolated groundwater map. It is this latter observation which emerges after both maps are examined spatially.

Using the Spatial Analyst Extension in Arcview, the soil P map was converted to a grid and, using the summarisation command, summarised with respect to the interpolated groundwater P grid. This analysis produces summary statistics on the range of soil P values (2 – 19 mg $l^{-1}$ Morgans P). Mean data of the interpolated MRP (unf.) values for each soil P level in region 26 is plotted in Figure 2.25.

The regression is significant to the probability $p<0.01$. The data also yielded a pearson product-moment correlation coefficient of –0.64, again significant to the probability $p<0.01$. Thus there appears a negative relationship between soil P and groundwater P.

Figure 2.24 Hydrometric region 26: (i) Soil phosphorus levels (ii) Interpolated groundwater P data.

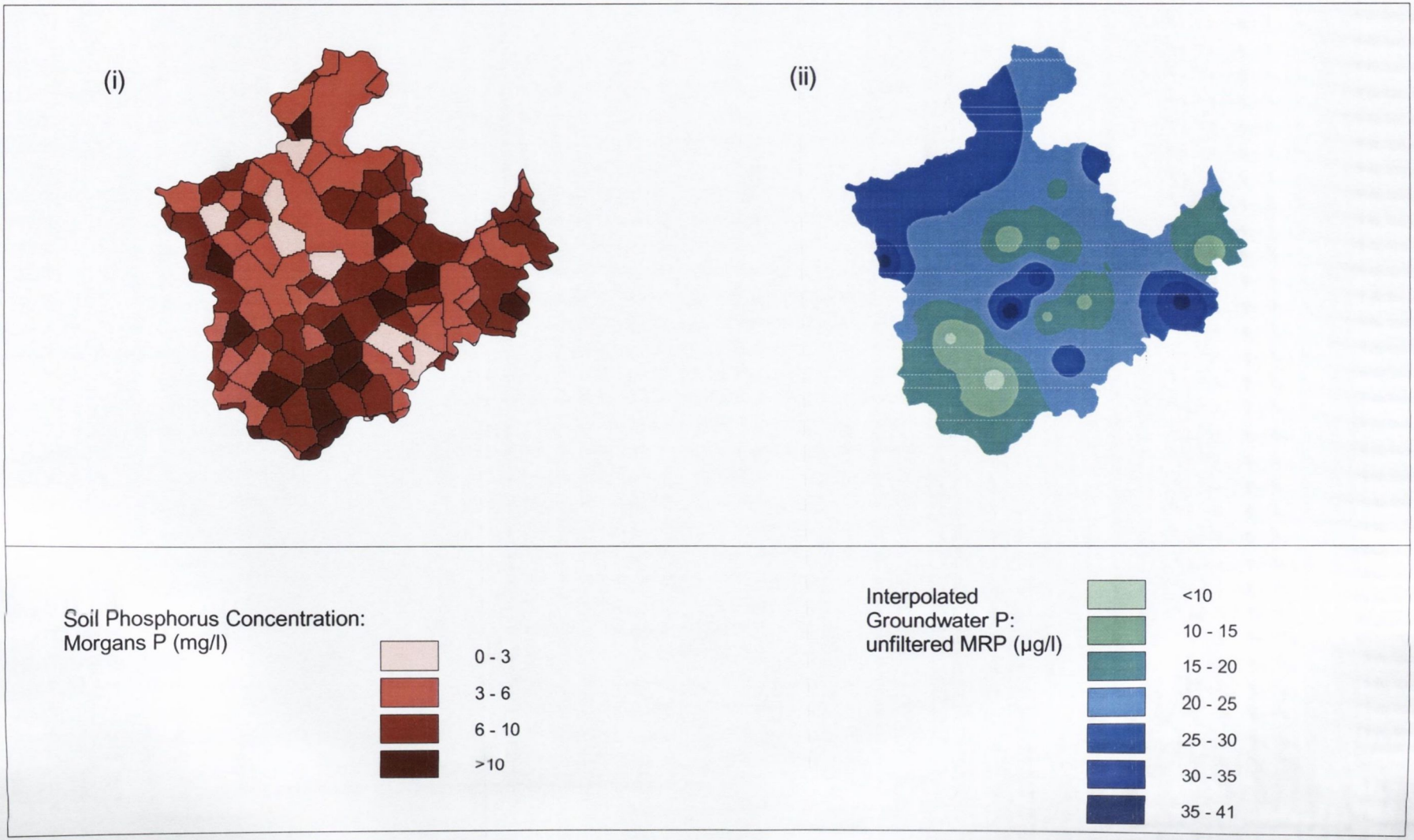
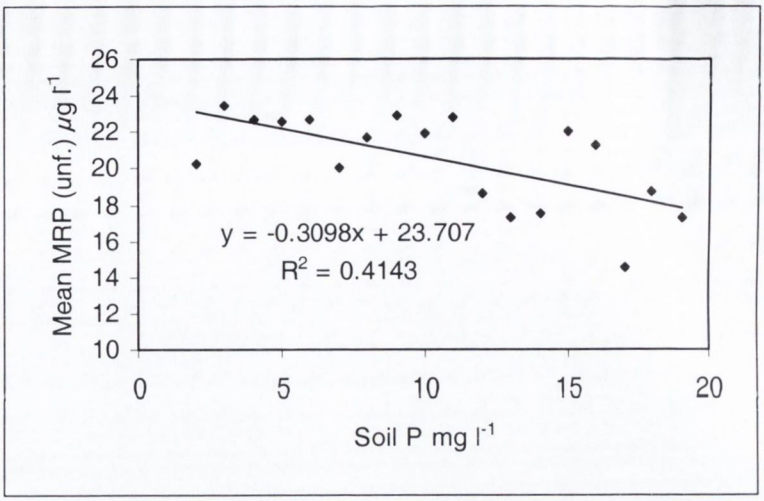


**Figure 2.25 Mean interpolated MRP (unf.) for soil P levels hydrometric region 26.**




## *2.4 Discussion*

### 2.4.1 Relationships.

The NGQMP groundwater P sites comprise a wide variety of scheme and source types. Nonetheless, there was no statistical difference between either the three main scheme types (Public, Group and Private). Therefore, use of the dataset for comparison with national spatial coverages is valid. While there are large areas without sites, it is by far the best available national groundwater P dataset. Groundwater from boreholes had highest P concentrations. This may reflect the poor construction and protection of some bores from contamination at the surface (Daly, 1985; 2000). The zone of contribution (ZOC) of actively pumping bores may be more limited spatially than that of springs, therefore any P source within the ZOC will be diluted to a lesser extent.

There was a weak negative relationship between unfiltered MRP concentration and daily abstraction rates. This variation with abstraction rate may be related to a dilution effect. In the Chapter Five the Limerick sites indicated stronger, significant negative relationship, and the possible causes are discussed further there.

No relationships were identified between soil P levels and groundwater P. Given that 90% of annual P loss can come from less than 10% of land area (Heathwaite *et al.*, 1998) the importance of identifying critical source areas has been highlighted (Gburek *et al.* 2000). Thus correlations between P concentrations at point data (bores, springs and wells) and 10

km square soil P grids are unlikely to be of significant value if at all present. Several authors have identified strong relationships between soil P levels and P losses to water at field scale (Brookes *et al.*, 1997; Pote *et al.* 1996) and at catchment scale (Sharpley *et al.*, 1994). Therefore, examination of the effect soil P levels has on groundwater P is probably best served at scales of greater resolution.

Use of the soil P desorption model developed by Daly *et al.* (2000) again suffered through issues of scale (5 km grid). This model is primarily driven by soil hydrology, therefore, highest predicted P levels in rivers are expected in the catchments with more impermeable soils. The corollary being, lowest predicted P levels are expected in more permeable soils, exactly the soils where higher groundwater P levels are likely (Eghball *et al.*, 1996; Chen *et al.* 1996). Therefore, whilst no significant correlations were identified, it is interesting that for both dry and wet catchments, areas predicted with low P (unpolluted) surface water had the highest median groundwater P concentrations.

The stocking density coverage was the smallest scale coverage, being at county level, thus good relationships with groundwater P were not expected and not found. Allott *et al.* (1998) did find positive correlations between cattle stocking density and lake total P for 31 lake catchments using statistics at the smaller district electoral division (DED) level. Obviously larger scale coverage is required for meaningful analysis. Stocking densities will be examined in more detail at DED level for the three catchment areas (see Section 7.4).

The CORINE land use classification database has been used in many studies examining P loss to water. Allott *et al.* (1998) and Daly *et al.* (2000) both report significant correlations between the high productivity pasture class and P concentration in surface waters. Unfortunately 74% of the sites were located in a pasture class, thus interclass comparison is difficult. Of the sites located under high, low and intermediate productivity grasslands, the high productivity grasslands had highest groundwater P levels, but these difference were not significant. Sites located in non-irrigated arable land had the highest P levels.

The geological map used had problems of scale and the use of generic geological terms such as the subdivision of the Lower Carboniferous Limestone (into Upper, Lower and Middle Carboniferous Limestone) which has been superseded by more recent geological

work. Carboniferous Limestone accounted for 65% of the sites. Despite this several of the means of the various geological categories were significantly different. In particular, five sites located in Ordovician rocks had highest median MRP (unf.). Four of these sites were located in Co. Wicklow. No clear reason can be attributed to this trend. The next highest P median P levels were located in the "Upper Carboniferous Limestone" which correlates loosely to purer limestone which is susceptible to karstification.

The hydrometric region coverage was again of a small scale. However, the hydrometric boundaries yielded some useful analysis. The percentage of river length classified as Class A (unpolluted river length) was negatively correlated with mean groundwater MRP (unf.). In addition, percentage of river length classified as Class C (moderately polluted) was positively correlated with mean groundwater MRP (unf.). These correlations highlight the intrinsic relationship between surface water and groundwater in river catchments. Thus, even at this national scale, higher P concentrations in groundwater were identified in catchments experiencing poorer water quality. This relationship supports the approach adopted by the EU Water Framework Directive which incorporates both surface water and groundwater issues in the management of basins. The high sample number in hydrometric region 26 offered some further possibilities to using catchment-type boundaries as units of studies. The inverse relationship between soil P and groundwater P is unexpected, because many authors cite high soil P status as a characteristic which facilitates P leaching (e.g., Breeuwsma *et al.*, 1995). The low range of mean MRP (unf.) (14 – 23 $\mu g\ l^{-1}$) in this analysis may disguise actual positive relationships that are only visible over larger ranges on groundwater P.

### 2.4.2 Sources of error

As mentioned in Section 2.2.3, several factors can contribute to errors when using spatial data. Probably the most important one for this chapter is that of map scale and resolution. The key GIS tool used was that of point-in-polygon to identify what coverage characteristic each site lies within. The accuracy of the grid location of each site and that of each coverage is essential to avoid incorrect classifications. An example of such a misclassification was given in Table 2.5 of Section 2.3.8, where one of the groundwater sites was incorrectly classified as been located in a water body. This issue is examined further in Table 2.8 below, which gives a comparison between the geologies derived using

the GIS national map for the Limerick's NGQMP sites and their actual known geologies. Six of the eighteen geologies were incorrect, giving only a 67% success rate. The dated nature of the geological map will also be an issue. Together these points highlight the potential pitfall when using GIS and the necessity for obtaining up to date and accurate coverages at a suitable scale.

**Table 2.8 Comparison between NGQMP Limerick sites derived geologies using GIS and their actual geologies.**

| *Site Name* | *National Geological Map* | *Actual Geology* | *Correct* |
|---|---|---|---|
| Herbertstown | Ryolites | Volcanics | Y |
| Martinstown - Ballinvreena | Lower Carb Limestone | Old Red Sandstone | N |
| Broadford WS | Middle Carb Limestone | Muddy Shelf Limestone | Y |
| Ballyagran-Castletown WS | Old Red Sandstone | (ORS) Kiltorcan | Y |
| Croom WS | Lower Carb Limestone | Waulsortian Limestone | Y |
| Hospital WS | Lower Carb Limestone | Ballysteen Limestone | Y |
| Ballylanders | Silurian Quartzite | Silurian | Y |
| Glin WS | Coal Measures | Namurian | Y |
| Hospital WS | Lower Carb Limestone | Ballysteen Limestone | Y |
| Fedamore WSS | Lower Carb Limestone | Waulsortian Limestone | Y |
| Pallasgreen WS | Middle Carb Limestone | Volcanics | N |
| Caherconlish WSS | Lower Carb Limestone | Old Red Sandstone | N |
| Murroe WS | Old Red Sandstone | Old Red Sandstone | Y |
| Doon WS + Aug.ex Foileen WS | Lower Avonian/Carb | Ballysteen Limestone | N |
| Rathkeale (Kilcolman) WS | Lower Carb Limestone | (ORS) Kiltorcan | N |
| South West RWSS | Lower Carb Limestone | Waulsortian Limestone | Y |
| Clonagh | Old Red Sandstone | Lower Ballysteen | N |
| Lough Gur | Lower Carb Limestone | Waulsortian Limestone | Y |

### 2.4.3 National versus catchment scale assessment

Integrating research scale has been identified as a key issue for research into phosphorus loss from non-point sources (Heathwaite and Sharpley, 1999). Whilst much research focuses on soil column up to field level, it is at larger scales that nutrient management strategies are applied. This chapter in many ways highlights the limits of the corollary approach, i.e. attempting to derive causative factors at national level. Merot and Durand (1995) examined the effect of catchment size on water quality observations, and concluded that process-orientated investigations and deterministic model testing are best served by smaller catchments because observations will reflect specific characteristics of the site. It is this specificity, that is inherent of the EPA NGQMP dataset, which is often absent in the examined national GIS coverages. It is not surprising therefore that the key benefits of this assessment were achieved in examining the site specific characteristics of the dataset.

The main overall findings of this assessment include:

- 23% of groundwater P nationally is at levels which induce adverse impacts in rivers;
- High groundwater P concentrations were generally located in the eastern half of the country;
- Groundwater P levels are highest in bores compared to springs and dug wells, possibly due to poor protection and construction;
- Higher groundwater P was found in hydrometric regions with poor river water quality;
- Whilst, the highest reported value was derived from a group scheme, overall ownership of sites was not a deterministic factor for high groundwater P;
- Higher abstraction rates may induce a dilution effect on P.

Therefore, several valuable observations are made. Examination of this dataset against various coverages, whose characteristics have been reported to impact on P loss from soil to water only yielded some tentative conclusions. The correlation between surface water quality and groundwater P at hydrometric region level highlights this strong inter-relationship. The NGQMP will be even more valuable when its coverage includes the large gaps in the south eastern portion of the country and there are plans to measure parameters such as pH and dissolved oxygen in-situ (Micheal MacCarthaigh, pers. comm.).

In conclusion, national scale assessments are an essential aspect of water quality management. They provide valuable information regarding environmental thresholds and geographical distribution. However, since the key controls of many pollutants are at local scale, catchment level or smaller scale assessments are best applicable to determining processes and trends. It is for these reasons that three catchment areas were selected for detailed investigation of groundwater P.

# CHAPTER 3. CATCHMENT DESCRIPTIONS

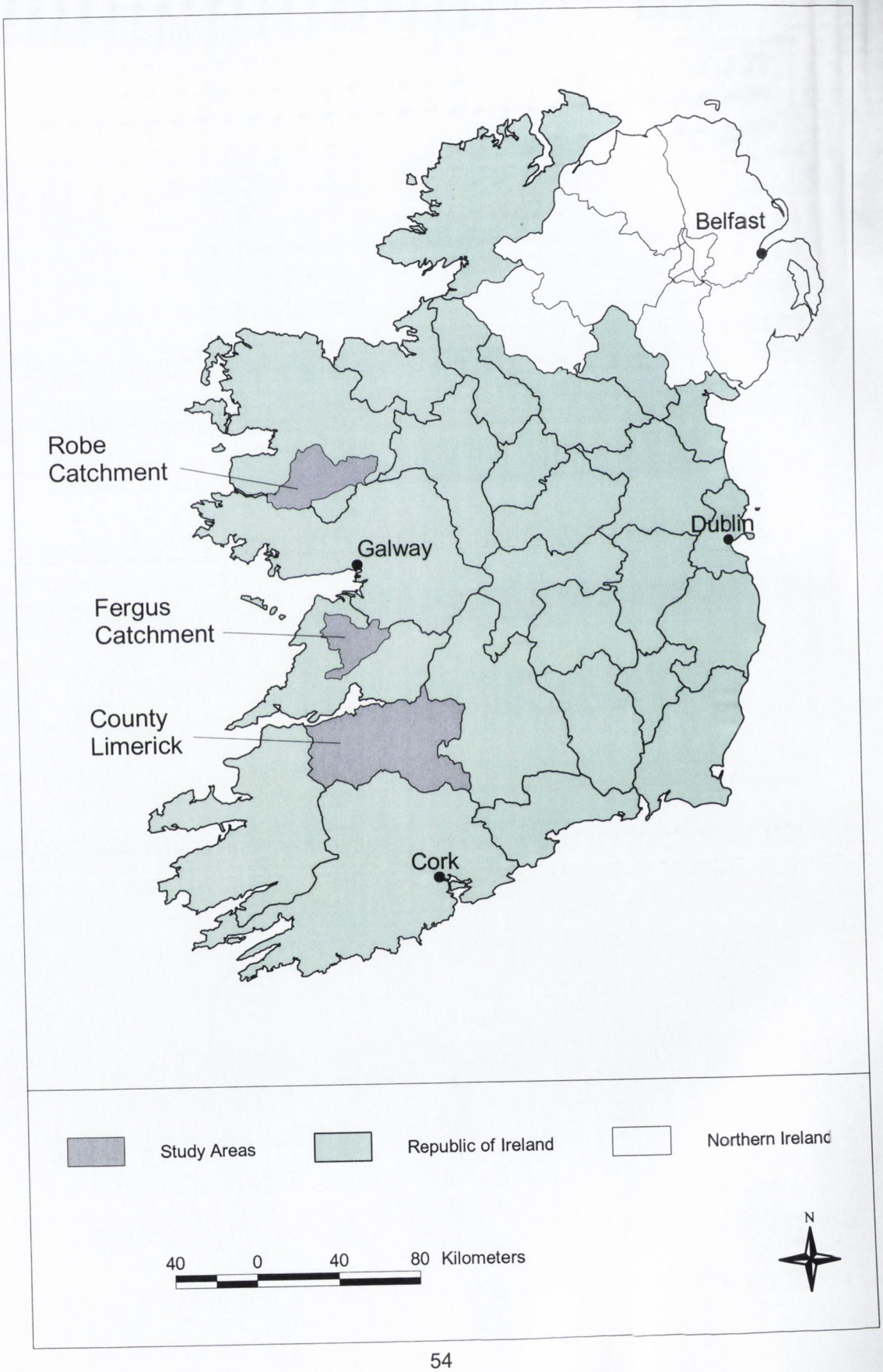
## 3.1 Introduction

The primary objectives of the fieldwork were to identify areas with a significant groundwater phosphorus component that impacts on surface water quality and to characterise these situations where they exist. A catchment-based approach was adopted. Preference was given to catchments that had phosphorus surface water problems and for which basic hydrogeological information was already available in order to build on existing knowledge. The catchments chosen were the Robe in Co. Mayo, the Fergus in Co. Clare, and the Deel and Maigue in Co. Limerick (although sites were included outside these catchments in Co. Limerick to allow for an assessment of more diverse hydrogeological conditions). Figure 3.1 shows the location of these catchment areas.

The most comprehensive hydrogeological studies available in the Republic of Ireland at county scale are in the form of groundwater protection schemes by the Geological Survey of Ireland (GSI). These schemes comprise a main report and several county-wide maps including: bedrock geology; Quaternary deposits (subsoils); depth to bedrock; hydrogeological data; aquifer type; groundwater vulnerability; and groundwater resource protection.

At the beginning of this project (December 1997) Co. Limerick had been subject to detailed hydrogeological investigation by the GSI in the form of a protection scheme (Deakin *et al.*, 1998). The poor surface water quality of the county's largest catchments, Deel and Maigue made Co. Limerick ideal for field studies. Stapleton *et al.* (2000) report that for the 1995-97 water quality monitoring period all sampling stations at the Deel or Maigue had median MRP levels greater than the 30 $\mu g\ l^{-1}$, the eutrophication threshold for Irish rivers. Towards the end of this project a similar scheme was almost completed for Co. Clare (Deakin and Daly, 2001). The Fergus catchment has also been subject to several hydrological and hydrogeological studies (Coxon, 1995; Drew, 1988; Drew, 1990). The highly karstified nature of this catchment and thus strong interaction between groundwater and the River Fergus and the many lakes provided a solid basis for field studies.

Figure 3.1 Location map of the groundwater phosphorus study areas.



The Robe catchment in Co. Mayo has not been thus far subject to a groundwater protection scheme. However, a STRIDE European Union research project which included the production of aquifer protection plans for Cos. Galway, Mayo and Roscommon (Thorn, 1995) assembles much of the available hydrogeological data for the Robe Catchment. Additional relevant hydrogeological studies include: Coxon (1986); Coxon and Drew (1986); Drew and Daly, (1993). The River Robe is the largest of all the catchments contributing to Lough Mask, a nationally important brown trout fishery. Hydrogeologically, the Robe catchment is also an interesting study area since it is an aquifer which is described as intermediate between a karstic, conduit flow aquifer (like the Fergus catchment) and a non-karstic, diffuse flow aquifer (like most of the Limerick aquifers) (Coxon and Drew, 1986).

In summary, whilst the level of basic hydrogeological knowledge is constantly improving throughout Ireland, the aforementioned studies provided a strong case for choosing these catchments. Furthermore, each of these areas is experiencing varying degrees of deteriorating surface water quality issues associated with elevated P levels.

This chapter provides introductory descriptions of the three catchment areas in terms of bedrock geology, Quaternary deposits, hydrogeology, hydrology and surface water quality. The surface water quality data is derived from the EPA's latest report on water quality in Ireland (Lucey *et al.*, 1999). This report, summarising water quality in Ireland between 1995-97, is the latest in the triennial series published by the EPA. The two previous reports in the series were for the monitoring periods 1987-90 and 1991-1994. These reports divide Ireland into 40 hydrometric regions. Figure 2.21 presents the boundaries of each of these regions. Surface water quality is reviewed only insofar as it pertains to P. The general groundwater quality of these catchments is not presented here, however, further details on the general groundwater chemistry of these catchments is presented in the Section 4.4.

## *3.2 Fergus Catchment*

### 3.2.1 Introduction

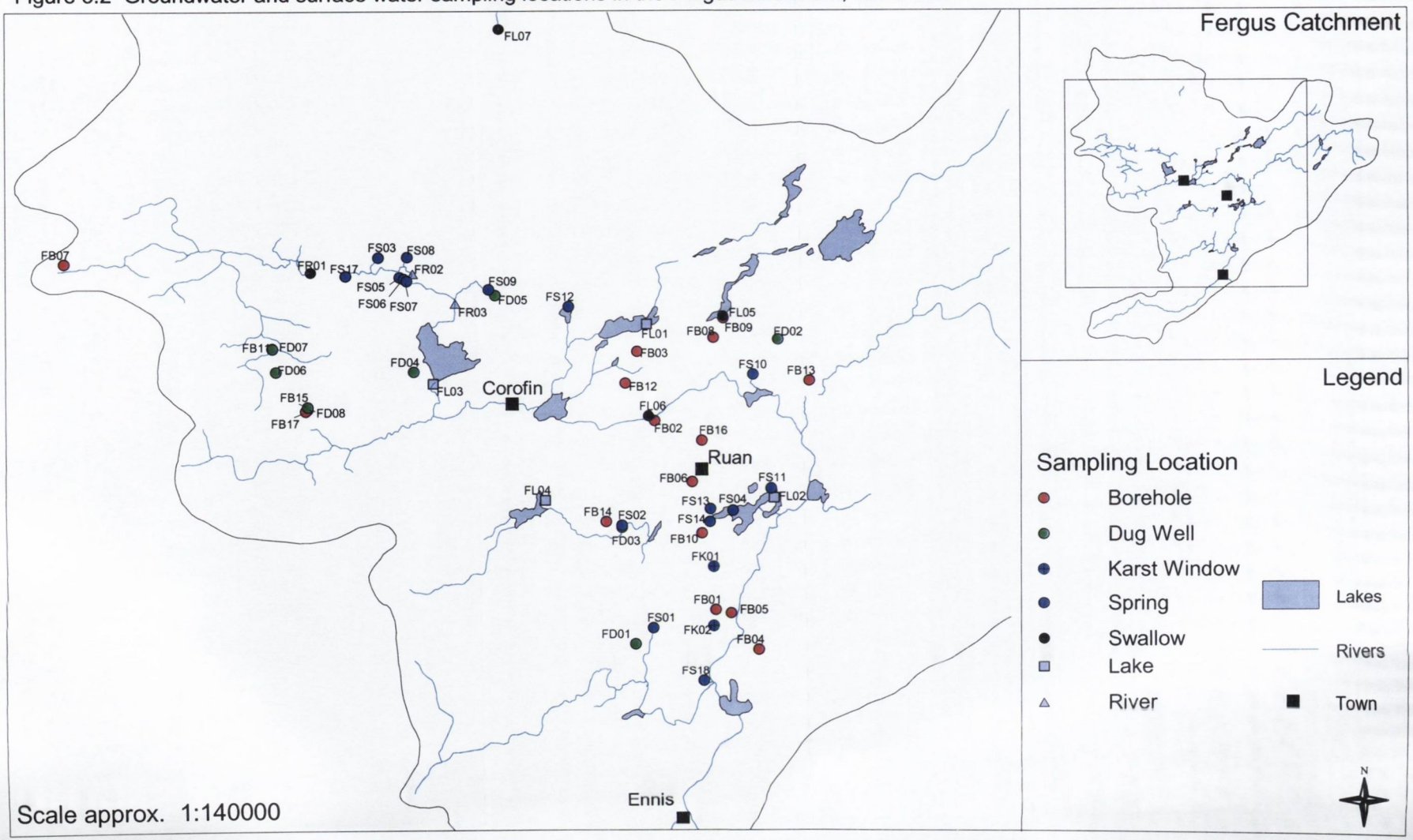
The Fergus catchment lies in the centre of Co. Clare. The northern part of the catchment incorporates the southern limit of the Burren limestone plateau which is 200-300m above sea level. The topography steadily drops to 100m at Carron Turlough and to 30m at Lough Inchquin. The majority of the Fergus River flows in a lowland corridor between Upper Carboniferous shales and sandstones to the west and Devonian sandstones of the Slieve Aughty mountains in the east. The long-term mean rainfall (1961-1990) for the Irish Meteorological Service station at Corofin is 1217 mm.

Figure 3.2 presents the 59 sampling locations of all sites in the Fergus catchment. Included in this map are a group of four sites located outside the catchment near the town of Lisdoonvarna. These sites were sampled due to their location near areas where phosphate rock was once mined. This is discussed in more detail in the Section 5.4.4. The grid references of all sampling locations and their basic characteristics are presented in Appendix A, Table A.1.

### 3.2.2 Bedrock geology

The Fergus catchment is situated in Co. Clare and for ease of description can be divided into two areas. The northern section comprising the upper reaches of the Fergus River (upstream of Lough Inchquin) drains both the shales to the west and via underground drainage a large part of the Burren plateau which is composed of almost horizontal, very pure Visean limestones (Drew, 1995). The southern section (downstream of Lough Inchquin) consists of a Carboniferous limestone lowland corridor lying between Upper Carboniferous shales and sandtones to the west and the Devonian sandstone of the Slieve Aughty Mountains to the east (Coxon, 1995). Fifty nine groundwater and surface water sites were sampled in the Fergus catchment making it the most comprehensively sampled of the three catchment areas.

Figure 3.2 Groundwater and surface water sampling locations in the Fergus catchment, Co. Clare.



The individual bedrock geology of each site was obtained from the Clare groundwater protection scheme bedrock maps (Deakin and Daly, 2001) which is based on the GSI 1:100,000 bedrock map sheet 17 (Sleeman *et al.* 1999) and unpublished field mapping and compilation carried out by Conor MacDermot, Bedrock Section, GSI. These are described in more details in Section 5.4 and in Appendix A, Table A.4.

### 3.2.3 Quaternary deposits (subsoils)

In Co. Clare, till or boulder clay is the most widespread Quaternary deposit. Tills are classified according to the dominant clast lithology and are described in detail in the Clare groundwater protection report (Deakin and Daly, 2001). In the northern section of the catchment the Burren plateau is often completely devoid of any soil or subsoil except thin patches of rendzina soils (Finch, 1971).

Namurian tills dominate in the western areas overlying Namurian rocks. In general these tills are greater than 10m thick and are clay rich with low permeability. These thicker areas are expressed morphologically as drumlins. In the inter-drumlin areas the tills are 1.5 to 10 m thick and the permeability varies significantly.

A patchy cover of glacial deposits, mostly limestone till, overlies the southern lowland section of the catchment. In places this forms drumlin ridges, rising 15-30 metres above the flat lowland, while elsewhere it is generally less than three metres thick, and in places absent (Coxon, 1995). The limestone tills are mainly derived from three limestone formations (Slievenagasha, Burren and Tubber; see Section 5.3.3). These tills have a high proportion of silt relative to clay and generally have moderate permeability. Some of the sites located near the River Fergus or lakes overlie some alluvial deposits which are generally thin. The Quaternary deposit classification of all the Fergus sites is presented in Appendix A, Table A.4.

### 3.2.4 Hydrogeology

The Slievenagasha Formation underlies the majority of the upper Fergus. Drew (1988) identified the importance of chert-rich beds in this Formation in influencing underground water routes. Drew (1988) also indicates that the stratal dips are very low and variable, however, the regional dip is to the south and, most of the underground flow is down-dip in

the bedding planes. The limestone of the lowland, southern area, the Burren Formation, is a pure bioclastic calcarenite (Coxon, 1995). It contains no primary permeability, but is well bedded and jointed thus having extensive secondary permeability.

The limestone areas of the catchment are generally classified as being a regionally important aquifer (Deakin and Daly, 2001). The sites located on the Namurian shales to the west are classified as locally important aquifers, i.e. moderately productive only in local zones possibly where the Namurian strata is thinner. Further west, as the shales thicken, the area is classified as been a poor aquifer, generally unproductive.

The Geological Survey of Ireland (GSI) primarily carries out groundwater vulnerability mapping in Ireland. The GSI has developed a vulnerability mapping approach which is underpinned by three key natural and hydrogeological factors: subsoil type and thickness above the water table; recharge type (whether diffuse or point); and in sand/gravels, the thickness of the unsaturated zone (Daly and Warren, 1998). Using these criteria, groundwater is classified into one of four types of vulnerability (extreme, high, moderate and low). Given the karstic nature of the limestone in the Fergus catchment and minimal subsoil cover most of this portion is designated with extreme vulnerability, with pockets of high and low vulnerability. The more impermeable shale and increased subsoil thickness and clayey nature result in most of the sites on the Namurian shale being classified with low vulnerability, with pockets of high vulnerability. Groundwater vulnerability is discussed in more detail in Section 5.5.3.

### 3.2.5 Hydrology

The hydrology of the Fergus catchment has been assessed in detail in the northern section by Drew (1988, 1990) and the southern section by Coxon (1995). Drew (1988) estimates the rainfall in the Burren to be 1500 mm of which 520 mm is lost through evapotranspiration. In the north recharge is rapid, either via concentrated inputs from sinking streams at the shale/limestone interface, or via diffuse inputs over the limestone plateau. Several of these sinking streams which feed the River Fergus have been traced using fluorescent dyes (Drew, 1988). The source of the Fergus River is on the Namurian shales to the west. The river then travels east, sinking at An Clab (FR01) where it reaches the shale/limestone interface. The Fergus River re-appears at one or more risings (dependent on stage) at Poulnaboe (FS17) 900 m east of An Clab. Downstream of these

risings the River is augmented by a series of springs until in reaches Lough Inchquin. Table 3.1 summarises the characteristics of the springs for which flow data or tracing data are available. Figure 3.3 presents the springs, sink holes and underground connections in the upper Fergus catchment.

**Table 3.1 Characteristics of Springs in Upper Fergus Catchment. Trace data from Drew (1988).**

| *Spring Name* | *Low flow Discharge ($m^3 s^{-1}$)* | *Positive trace from sink* | *Source of Trace* | *Travel Times metres/hr* |
|---|---|---|---|---|
| FS17 | 0.007 | FR01 | Ecock, 1981 | 21 |
| FS08 | 0.020 | FL07 | Drew, 1988 | 110 |
| FS03 | 0.007* | Seven Streams | Drew, 1988 | 58 |
| FS09 | 0.005 | None traced | | |
| FS05, FS06, FS07 | 0.265* | FL07 | Drew 1988 | 110 |

Asterix (*) denotes flows measured by the author

The largest spring is the Elmvale group (FS05, FS06, FS07) that, under low stage conditions, becomes the headwater of the Fergus River. Positive traces from sinks to these springs are also indicated. Drew (1988) indicates that whilst the Elmvale springs have a positive trace from Carran Turlough (FL07), the abundance of shale debris at the springs may indicate a direct connection with the shale/limestone interface. The river then travels southwards through a series of lakes until it becomes tidal below the town of Ennis. This length of the river course includes some artificial stretches created by drainage engineers in the nineteenth century, and a significant proportion of the river flow does not follow the whole above-ground course, but takes a series of short-cuts from swallow holes in the river bed and lake shores to springs which feed the river further south. Figure 3.4 presents the springs, sink holes and underground connections in the lower Fergus catchment. The characteristics of these springs where available are listed in Table 3.2.

**Table 3.2 Characteristics of springs south of Lough Inchquin. Trace data from Coxon (1995).**

| *Spring name* | *Low flow discharge $m^3$/sec* | *Positive trace from* | *Travel times m/hr* |
|---|---|---|---|
| FS13, FS14 | 0.087 and 0.062* | FL06 | 89 – 124 |
| FS18 | 0.116 | FL06 | 163 – 244 |
| FS18 | 0.116 | Sink after FK02 | 91 –130 |
| FS10 | NA | FL05 | 71 – 142 |

Asterix (*) denotes flows taken in this study. FS18 flow data by K.T. Cullen & Co., 1996.

Figure 3.3 Springs, swallow holes and underground connections of the upper Fergus catchment (after Drew 1988).

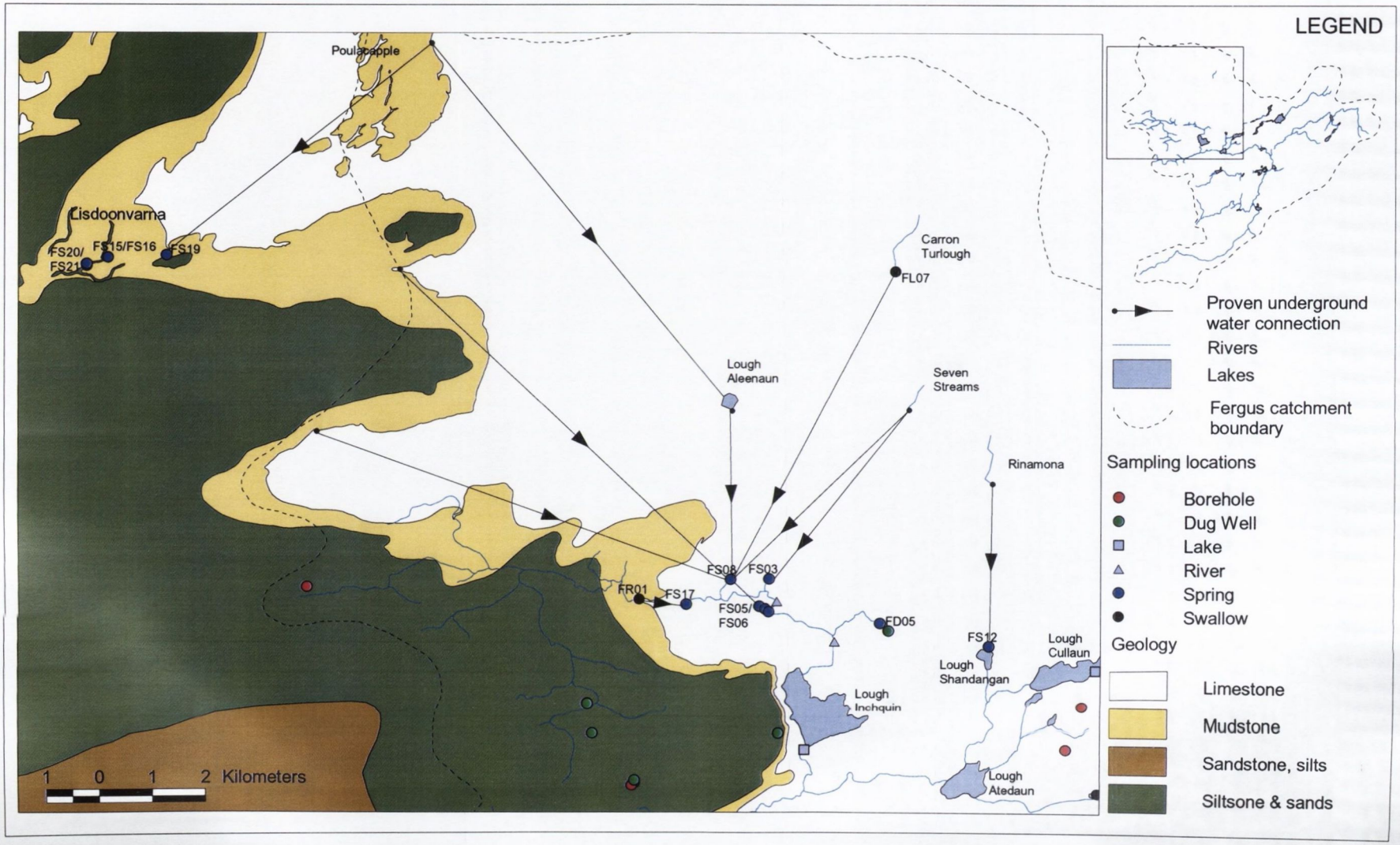
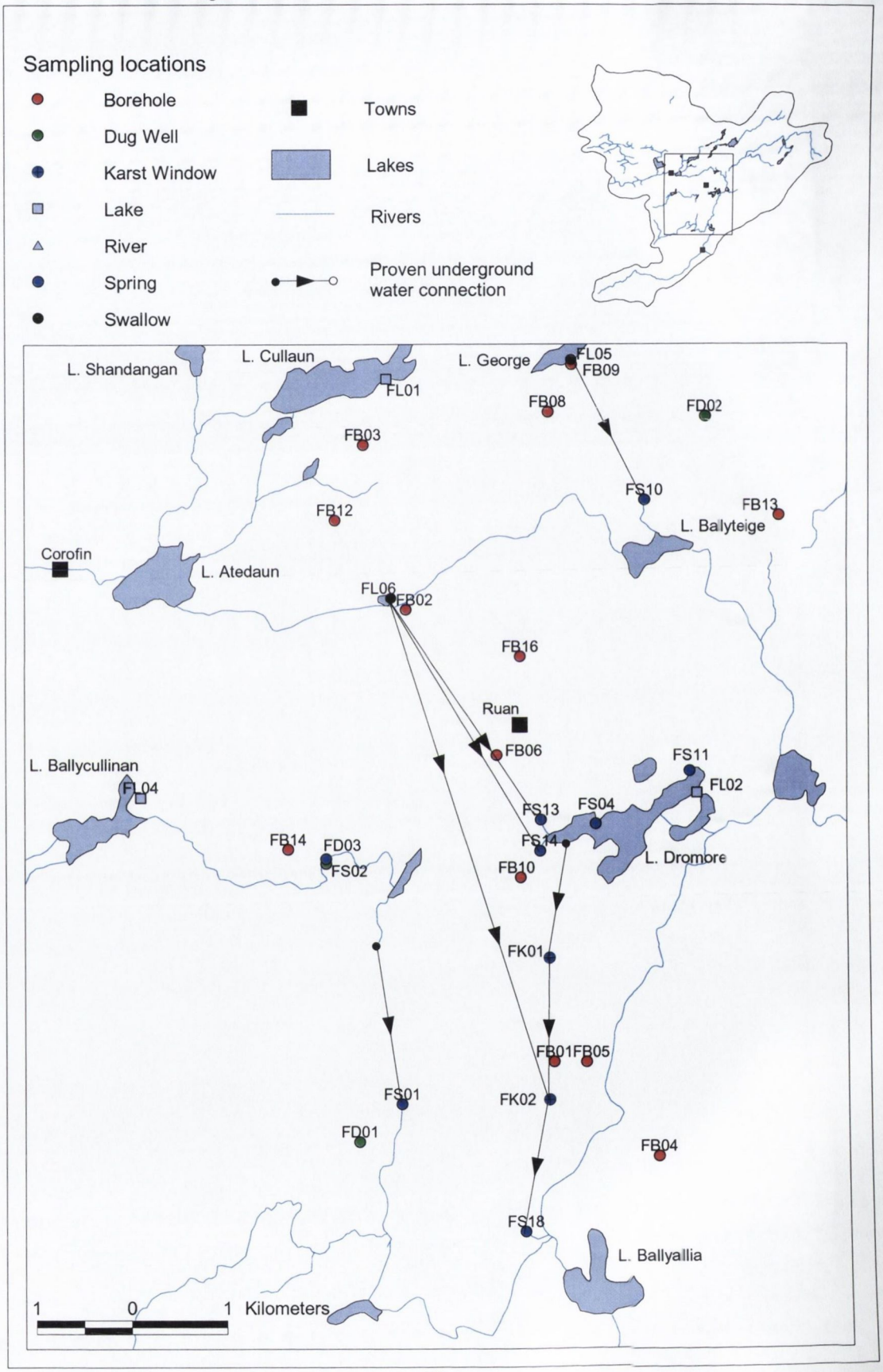


Figure 3.4 Springs, swallow holes and underground connections in the lower Fergus catchment.



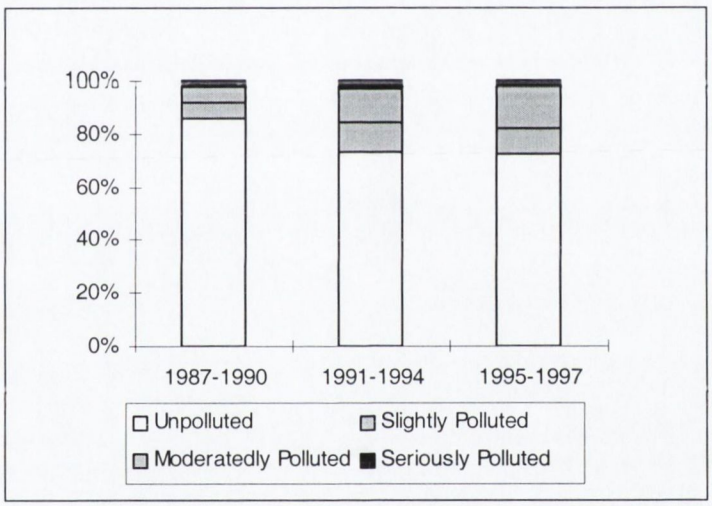
This interdependence of groundwater and surfacewater creates difficulties in managing spring drinking water sources because, while the catchment area will be quite large, the spring may only account for part of the flow from this area (Coxon and Drew, 2000).

### 3.2.6 Surface water quality

#### Rivers

Hydrometric Region 27 (see Figure 2.21) predominantly comprises the River Fergus and its tributaries. Figure 3.5 illustrates the trends in river quality experienced in Region 27 during the monitoring periods 1987-90, 1991-94 and 1995-97.

**Figure 3.5 River quality trends in Hydrometric Region 27 (Lucey *et al.*, 1999).**




The general trend is similar to that discussed in Chapter 1 regarding the national river quality status. The percentage of river length classified as unpolluted has dropped steadily from 85.5% in 1987-90 to 72.8% in 1995-97. In addition the percentage of river length classified as slightly or moderately polluted has generally increased since 1987-90. There was a slight increase in the percentage of seriously polluted channel length in 1991-94, but this trend seems to have been arrested by the latest monitoring period. The percentage of slightly polluted channel length also decreased during the latest monitoring period.

#### Lakes

Table 3.3 lists the trophic status and size of four lakes from this study that are located within the Fergus catchment (see Figure 3.3 and Figure 3.4 for locations of these lakes).

**Table 3.3 Trophic status and size of lakes relevant to Fergus catchment.**

| *Lake* | *Size ($km^2$)* | *Overall Trophic Status* |
|---|---|---|
| Inchquin | 1.1 | Mesotrophic |
| Cullaun | 0.63 | Oligotrophic |
| Ballycullinan | 0.04 | Strongly Eutrophic |
| Dromore | 0.53 | Moderately Eutrophic |

After Lucey *et al.* (1999)

## *3.3 Robe Catchment*

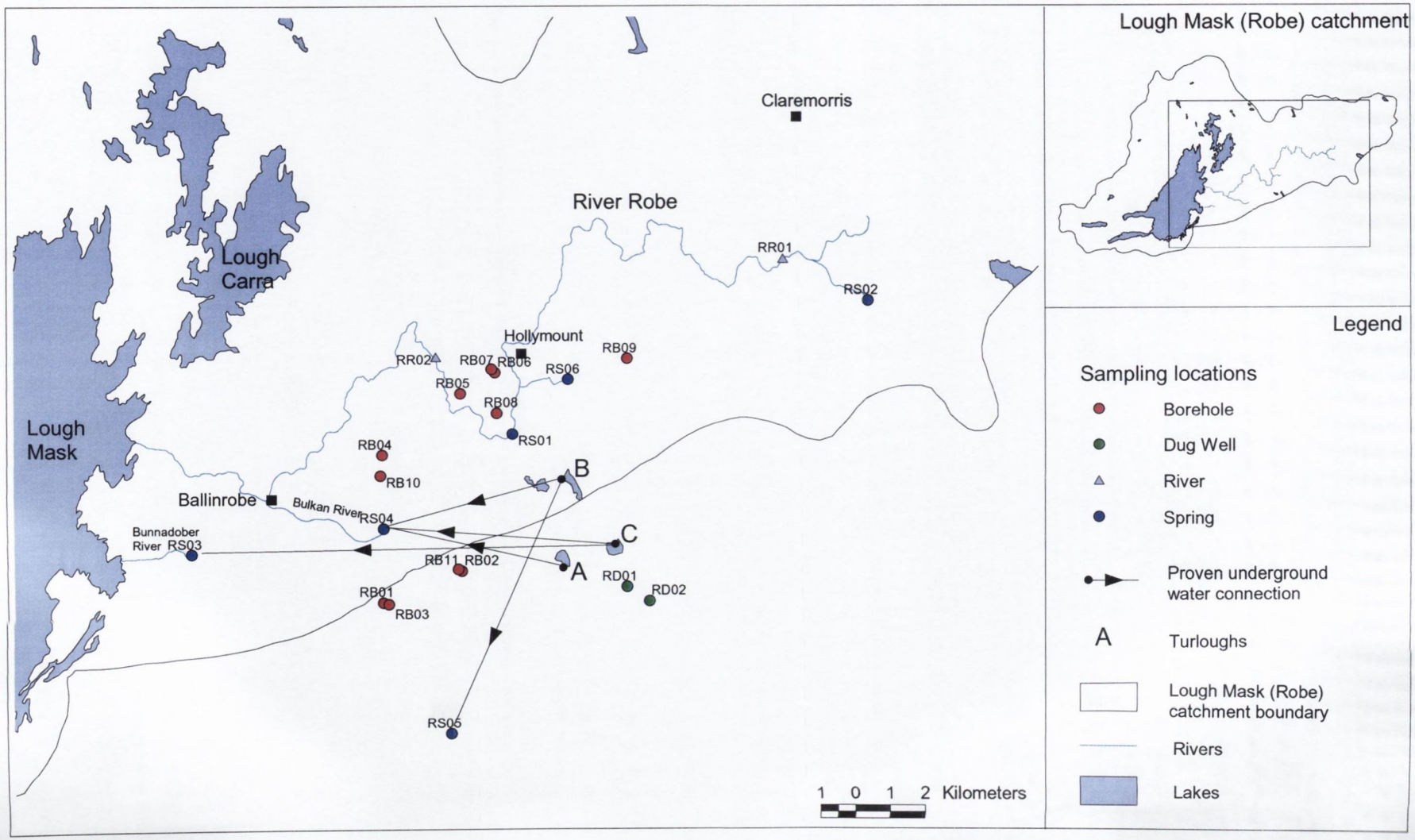
### 3.3.1 Introduction

The Robe catchment is situated in Co. Mayo. It eventually drains into Lough Mask in the west. It is the largest of the tributaries in the Lough Mask catchment, an important brown trout fishery. Between 1983 and 1999 the annual catch per angler steadily decreased in Lough Mask (Rodgers and de Barra, 2000). The River Robe and its tributaries contribute over 50% of the brown trout habitat for the Lough Mask fishery. The general sampling area near Ballinrobe is between 30 and 50 m above sea level and up to 90 m near Claremorris. The long term mean annual rainfall (1961-1990) for the Irish Meteorological Service station at Claremorris is 1143 mm. Figure 3.6 presents the 21 sampling locations in the Robe catchment and proven underground traces. The grid references of all sampling locations and their basic characteristics are presented in Appendix A, Table A.2.

### 3.3.2 Bedrock geology

Highly fractured sub-horizontal Carboniferous limestones underlie the Robe catchment. To the east the limetones become less pure and the degree of karstification decreases (Coxon and Drew, 1986). Pure limestones dominate the catchment with Muddy limestones prevalent east of Ballindine. The geology of the Robe catchment is discussed in more detail in the Section 5.4.5.

Figure 3.6 Robe catchment sampling locations, and undergound water connections (after Coxon, 1986).



### 3.3.3 Quaternary deposits (subsoils)

Most of the catchment lies between 15 and 60 m above OD. The dominant landforms are due to glacial and fluvioglacial deposition, particularly eskers and kames, with limited karstic landforms, notably turloughs (see Section 3.3.5) (Coxon and Drew, 1986). The drift cover in the Robe catchment is very variable. Available maps (Drew and Daly, 1993) indicate sandy tills as the predominant subsoil, other types include: sand and gravel with some clay; blanket peat; clayey till; basin peat; esker sand and gravel; and some patches of exposed limestone pavement. Generally, glacially deposited material is thickest in the east of the catchment, thinning to patchy cover at the shores of Lough Mask in the west. Drew and Daly (1993) estimate average thicknesses of 1-5m, but up over 20m in association with localised drumlin features.

### 3.3.4 Hydrogeology

Whilst much of the catchment exhibits a paucity of karstic landforms, there is evidence of regions of concentrated flow. In tracing experiments between several turloughs and the RS04 spring Coxon and Drew (1986) reported a range of travel times (see Figure 3.6). Up to 120 m $hr^{-1}$ was reported during high flow conditions between two of the turloughs indicating typical karstic conduit flow, whereas one turlough reported flows of 5-10 m $hr^{-1}$ indicating more dispersed fissure flow. The authors were also able to construct a watertable map based on borehole water levels and whilst this map was discontinuous in places it also indicated narrow zones of concentrated flow. Coxon (1986) examined standing water level in four boreholes in the catchment between summer low levels to maximum recharge in winter. The boreholes showed a wide range of response from extreme, to moderate to no response at all. Drew and Daly (1993) note that few data are available concerning water yields from boreholes, but great variation in yield over short distances and vertical localisation of inflows are the norm. Thus, the Robe catchment can be characterised as being highly-karstic in some areas.

A EU STRIDE project produced several aquifer protection maps for Counties Galway, Mayo and Roscommon (Thorn 1995). Whilst many of the maps are lacking basic hydrogeological data, they are used here on the basis of their being the best currently available. The Mayo maps are on a 1:126,720 scale, but a more detailed set of maps on a 1:25,000 scale are available for the Ballindine-Belmont area in the eastern side of the

catchment. Based on these maps the pure limestone bedrock is classified as a regionally important aquifer, whilst the muddy limestone is classified as a poor aquifer.

Vulnerability mapping of Co. Mayo has not been carried out as extensively as in Counties. Clare and Limerick. The STRIDE report highlighted the lack of sufficient basic hydrogeological data in Co. Mayo. Thus much of the catchment is classified unknown vulnerability. However, the detailed Ballindine-Belmont map provides more detailed information for the catchment east of Easting 125,000. Based on this map the majority of the eastern part of catchment is classified with probably high vulnerability due to large areas of undifferentiated glacial till. There are patches of extreme vulnerability associated with bedrock outcrops, turloughs and some gravel deposits. Some raised bog to the north of the catchment is classified with probably moderate to low vulnerability. The southeastern shore of L. Mask where the drift is thin has probably extreme vulnerability.

### 3.3.5 Hydrology

Drew and Daly (1993) highlight the interaction between surface water and groundwater, particularly in the Robe downstream of RS06, where flows from mid-winter to late spring are higher than upstream. Thus, the River Robe is a gaining river under certain stage conditions. In the summer and late autumn the reverse happens and water is lost via the stream bed to groundwater as water table levels are below the level of the river. Both groundwater and surface water in the catchment eventually drain to Lough Mask. Much of the current drainage system is man-made. For example, the spring at RS04 formerly drained into a turlough with no surface outlet, but now is conduited to the River Robe at Ballinrobe. A common hydrological feature of the catchment is the presence of turloughs. These turloughs fill and empty mainly by estavella holes which can act as either springs or swallow holes. They flood within about a week, usually in October, and empty more gradually, the majority being dry usually by the end of June (Coxon and Drew, 1986). Several springs sampled in the project discharge into Lough Mask either via the River Robe or directly to the lake (e.g. RS03). RS05, has been traced from a sink at a turlough within the Robe catchment, but is itself situated outside the Robe catchment proper and eventually drains to Lough Corrib via Cross Springs. Underground connections confirmed by tracing work carried out by Coxon (1986) are presented in Figure 3.6. Table 3.4 summarises the characteristics of the springs sampled for this project.

**Table 3.4 Characteristics of springs sampled in Robe catchment**

| *Spring Name* | *Low flow Discharge* ($m^3 s^{-1}$) | *Positive trace from sink* | *Source of trace* | *Travel times metres* $hr^{-1}$ |
|---|---|---|---|---|
| RS01 | 0.001 | na | na | na |
| RS02 | 0.02* | na | na | na |
| RS03 | 0.05 | Turlough C | Coxon 1986 | na |
| RS04 | 0.027 | Turlough A, B, C | Coxon and Drew 1986 | 47-123 |
| RS05 | 0.017** | Turlough B | Coxon and Drew 1986 | 24-37 |
| RS06 | 0.012 | Cloneen | Drew (pers. Comm) | na |

Note: All flows measured in this study, except where asterisked: * low flow estimate, Doak *et al.* (1995); **mean discharge, Drew and Daly (1993). na = not available.

### 3.3.6 Surface water quality

The EPA's latest report on water quality in Ireland (Lucey *et al.*, 1999) provides the most up to date assessment of lake and river quality in the Robe catchment.

#### Rivers

As mentioned in Section 3.2.6 the above study divides Ireland into a series of hydrometric regions. The Robe catchment is contained within hydrometric region 30, which is dominated by the Lough Mask and Lough Corrib catchments. Figure 3.7 illustrates the trends in river quality in Region 30 during the monitoring periods 1987-90, 1991-94 and 1995-97.

**Figure 3.7 River quality trends in Hydrometric Region 30**

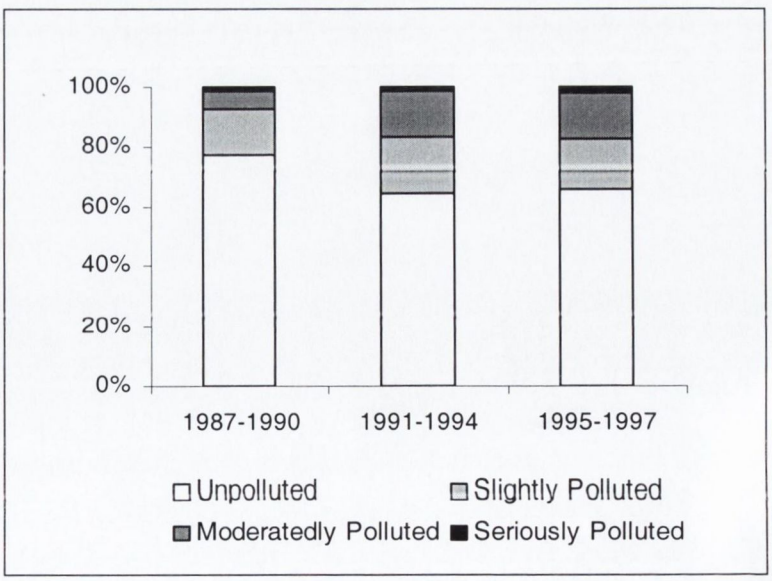


Figure 3.7 indicates the general river water quality trends occurring in the region. Between the 1987-90 and 1991-94 monitoring period there has been a decrease in the percentage of unpolluted river stretches from 77 to 64%, due mainly to an increase of moderately polluted stretches from 6 to 15%. This trend appears to have levelled off during the 1995-97 period, although there has been a slight increase in stretches of seriously polluted water.

### Lakes

Lough Mask is the only major lake in the in the Robe catchment, although there are several turloughs. Table 3.5 lists the trophic status and size of Lough Mask. With a surface area of 80 $km^2$ it is one of the largest lakes in Ireland and important as a game and coarse fishery and also host to a unique Arctic Char population. It is also used for water abstraction. The overall results of the latest monitoring (1995-97) indicate satisfactory quality. Howeve, increased algal growth in open water has been noted (Lucey *et al.*, 1999). No information is available on the nutrient status of the turloughs.

**Table 3.5 Trophic status and size Lough Mask (after Lucey *et al.*, 1999).**

| *Lake* | *Size ($km^2$)* | *Overall Trophic Status* |
|---|---|---|
| Mask | 80 | Mesotrophic |

## *3.4 Limerick Catchments*

### 3.4.1 Introduction

The two major catchments of the Rivers Deel and Maigue were the main focus in Co. Limerick. However, sites outside these catchments within the county were included in order to maximise available hydrogeological information in the form of the Limerick groundwater protection scheme (Deakin *et al.*, 1998) and source protection reports for 18 public supplies (see Appendix B, Table B.2). The long term mean annual rainfall (1961-1990) for the Irish Meteorological Service station at Shannon airport to the north of Co. Limerick is 927 mm.

Figure 3.8 presents the forty sampling locations of all sites in Co. Limerick. The grid references of all sampling locations and their basic characteristics are presented in Appendix A, Table A.3.

### 3.4.2 Bedrock geology

The bedrock geology of Co. Limerick is quite varied. The major rocks in the county can be grouped, in order of age, as: Silurian rocks; Devonian rocks, Lower Carboniferous rocks; and Upper Carboniferous rocks. Examining these rocks topographically, the mountains to the northeast and southeast are composed mainly of Old Red Sandstone with some Silurian rocks. Carboniferous limestones underlie an extensive low-lying plain, which is interrupted by three narrow ridges of folded Old Red Sandstone. West of LD01 lies a steep escarpment which marks the upland areas of the younger Upper Carboniferous sandstones and shales. There are also some volcanic rocks in the east around LB20 and LB29. The individual geologies of each site in Co. Limerick were obtained from the Limerick groundwater protection scheme bedrock maps (Deakin *et al.*, 1998) and from public supply source protection reports published by the GSI.

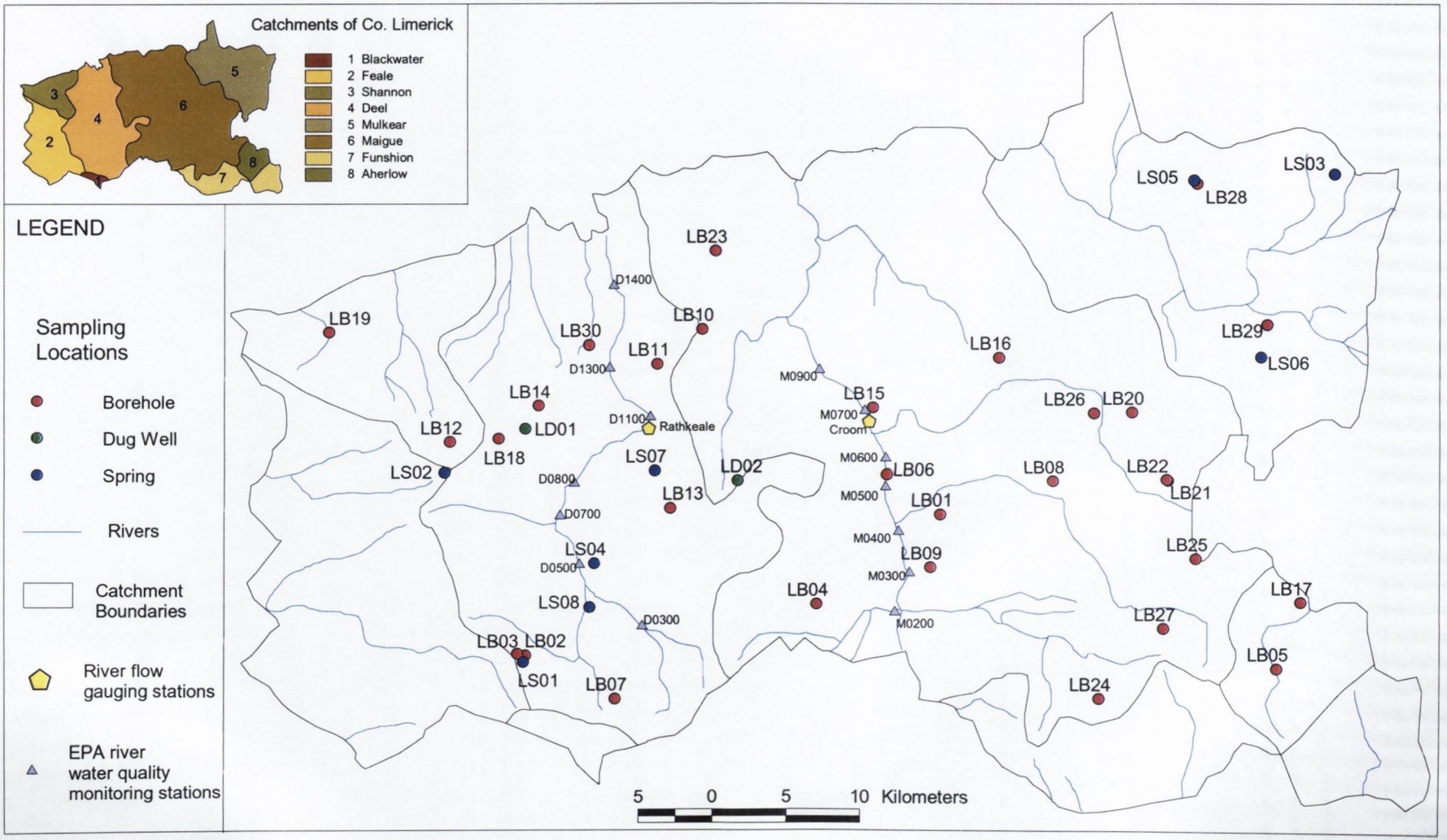
### 3.4.3 Quaternary deposits (subsoils)

There are eight Quaternary deposit types identified in the Co. Limerick groundwater protection scheme: till; sands and gravels; till with gravel; slope deposits; lake sediments; alluvium; peat and marine deposits (Deakin *et al.*, 1998). Limestone till is the dominant Quaternary deposit found at each of the Limerick sites. Alluvial deposits are located near some sites close to rivers. Quaternary deposit thickness varies considerably across the county. Generally, the thickest depoits are tills and till-with-gravel found in the morainic ridges which lie around the edges of the limestone plain, banked up against the upland areas of the Galtys and the Namurian scarp. Depth to bedrock measurements taken from the Quaternary deposit map of the groundwater protection scheme at the Limerick sites range from 1 to 30 m.

### 3.4.4 Hydrogeology

The aquifer map of the Limerick groundwater protection scheme indicates that the majority of sites are located in either regionally important fissured bedrock aquifers or bedrock aquifers that are moderately productive only in local zones. The remainder are poor aquifers that are generally unproductive except for local zones. One site, LB12, is located in a sand and gravel aquifer. Karstification in Co. Limerick is limited primarily in the Waulsortian Limestone, north of Rathkeale and particularly on Aughinish Island

Figure 3.8 Co. Limerick sampling locations. Selected EPA river monitoring and flow guaging stations are also presented.



The Silurian rocks, Muddy Shelf Limestone, Old Red Sandstone and Ballysteen Limestone are all classed as locally important aquifers which are moderately productive only in local zones. The Kiltorcan Sandstone and Waulsortian Limestone are generally classified as a regionally important fissured aquifer. The volcanic rocks are classed as a locally important aquifer which is generally moderately productive. The Clare Shales are classed as a poor aquifer which are generally unproductive. The Upper Namurian Beds are classed as a poor aquifer which is generally unproductive except for local zones. The LB12 site is classified as a locally important sand and gravel aquifer.

A large proportion of the sites are classified with high or extreme vulnerability. Deakin *et al.* (1998) point out that this probably reflects the often-shallow thickness of subsoils in Co. Limerick. Areas where rock is close to the surface include the Galty and Slieve Felim mountains, the upland Namurian scarp, around the volcanic Limerick Syncline in the east, and a large region north of a line from Rathkeale to Croom to LB16. There is a large area of low vulnerability south of LB01, which is mapped as limestone till which reaches depths of up to 80 m in places.

### 3.4.5 Hydrology

The Boundary of Co. Limerick intersects eight river catchments. However, it is the catchments of the Rivers Deel and Maigue that dominate the county and contain 32 of the 41 sites. Both of these catchments are contained within the EPA's Hydrometric Region 24. Estimates of baseflow contribution as a percentage of total flow for the Deel and Maigue from flow data for 1991-94 was 23 and 41% respectively (see Section 8.5.3). This may indicate greater storage capacity in the Maigue aquifers and more quickflow in the Deel.

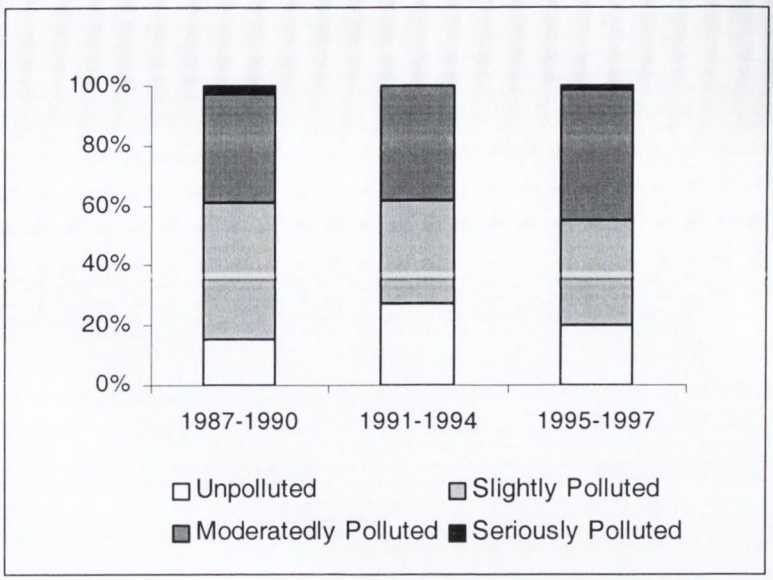
### 3.4.6 Surface water quality

The EPA's latest report on water quality in Ireland (Lucey *et al.*, 1999) provides the most up to date assessment of lake and river quality in Co. Limerick.

#### Rivers

As mentioned above, hydrometric Region 24 includes the Deel and Maigue catchments, the major catchments of Co. Limerick. Figure 3.9 illustrates the trends in river water quality in Region 24 during the monitoring periods 1987-90, 1991-94 and 1995-97.

**Figure 3.9 River quality trends in Hydrometric Region 24 (after Lucey *et al.*, 1999).**




The Deel and Maigue have some of the highest in-river phosphorus concentrations nationally. This is reflected in the small percentage of river stretches classified as unpolluted. 1991-94 saw a slight increase in the percentage of unpolluted river waters, but this was reversed in the latest monitoring period. Indeed, 1995-97 saw an increase in the percentage of moderately polluted and seriously polluted river waters.

### Lakes

Co. Limerick has no major lakes that were sampled by Lucey *et al.* (1999). The only major lake in Co. Limerick is Lough Gur, a 76 ha lake located 4 km north of Bruff in the northern lowland plain. A large concentration of archaeological monuments surrounds the lake. LB26 is located approximately 500 m up gradient of the lake to the east. King and O'Grady (1994) carried out a limnological study of the lake between December 1988 and October 1989. They report the lake as a hardwater eutrophic system

# CHAPTER 4. HYDROCHEMISTRY

## *4.1 Introduction*

The functioning of the studied aquifers will dictate the P concentration and P forms. It is envisaged karstic aquifers with a high degree of concentrated flow will have higher P concentrations and perhaps more particulate P than aquifers closer to the isotropic, homogeneous, diffuse flow model. Slower percolation through aquifer materials should allow more time for sorption and precipitation processes. Springs within the karstic systems of the Robe and Fergus catchments will have varying degrees of diffuse and conduit flow. Conduit flow systems will have more direct connection to both surface water inputs and land sources of P and should therefore, be more vulnerable to P loading.

All these issues are examined in this chapter where the primary aims are threefold. Firstly, the levels of P in groundwaters are examined between each catchment and in the context of surface water eutrophication thresholds. This will assess to what degree groundwater P is a threat and whether this threat is evenly distributed between catchments and within catchments for various site types. Secondly, P fractions are assessed to examine what form dominates in groundwater. The form of P that dominates in groundwater will affect the degree of impact when discharged to surface waters. Thirdly, the influence of groundwater hydrochemistry on P levels is assessed through examining relationships between P forms and various chemical parameters. Electrical conductivity (EC), pH, and dissolved oxygen (DO) were collected in the field during sampling. These parameters are described below.

Electrical conductivity provides an estimate of the amount of dissolved substances in a given water. Electrical conductivity (EC) is a useful field parameter since it can be quickly and reliably taken. Changes in EC can reflect the influence of reharge and interaction with geological materials. As groundwater moves along its flow paths in the saturated zone, increases in dissolved solids normally occurs (Freeze and Cherry, 1979). Variability of EC as expressed by the coefficient of variation of this parameter may relate to the nature of the underground flow system feeding a spring or borehole. High variability may indicate a short underground residence time (Coxon, 1995). This high connectivity between groundwater and recharge may influence P levels and is examined in this chapter in particular reference to the karstic Robe and Fergus catchments.

The pH of a solution is the negative logarithm of the hydrogen ion activity in moles per litre. Rainwater in non-urban areas typically has pH values between 5 and 6 (Freeze and Cherry, 1979). However, chemical transformation will take place as the rainwater travels through the soil and aquifer materials. In natural waters pH is controlled by the concentration of dissolved $CO_2$, $HCO_3^-$ and $CO_3^{2-}$ (Andrews *et al.*, 1996). These species react to maintain the pH within relatively narrow limits. This is known as buffering the pH. In limestone area, such as the Fergus and the Robe one would expect quite strong buffering capacity in the water due to the high bicarbonate levels. However, the sandstones and shales of the Limerick may yield lower pH values which may influence P levels in groundwater.

The presence of DO in groundwaters normally indicates recent exposure to atmospheric influences such as recharge (Lloyd and Heathcote, 1985). The longer the residence time in an aquifer between recharge and discharge the greater the opportunity for attenuation of dissolved solids and particulates, including phosphorus. It is foreseen that groundwaters with high dissolved oxygen levels are probably more vulnerable to P runoff point recharge from surface waters and from point sources on land.

Together, an assessment of these parameters could indicate the degree of control hydrochemistry has on P movement in the saturated zone.

## *4.2 Methods*

### 4.2.1 Monitoring Regime

The objectives of the sampling regime initially focused on successfully locating suitable sites, and providing a good overall network in each catchment. Several of the sites derived from previous studies were found to be either disused or grossly polluted and thus were omitted from the network. Resources permitting, additional sites were located in order to provide reasonable coverage in each catchment.

Sampling commenced in July 1998 in order to quantify the levels of phosphorus that were in the groundwater during the summer, when the risk of eutrophication is highest. After

two subsequent runs in August and September of 1998 the majority of sampling sites were established, along with a baseline of TP levels from which a more targeted strategy was developed. A general sampling run was carried out in February/March 1999 to assess broad seasonal differences.

Starting in late May 1999 until the end of October 1999, a biweekly sampling program was initiated at four representative spring sites in the Robe and Fergus catchments in order to provide detailed temporal data for the summer 1999 period. These sites were RS06, RS01, RS04 and RS03 in the Robe, and FS08, FS05, FS13 and FS18 in the Fergus. These sites were chosen because they had reported significant levels of TP, were evenly distributed within the catchment and in most cases had been subject to water tracing work. Springs were chosen for this detailed temporal work in order to yield phosphorus results derived from a large geographical area, and because by their nature provide immediate input to rivers and lakes in terms of nutrients and discharge. These sites were analysed for TP, TDP and DRP to examine phosphorus fractionation. This sampling program was extended on a monthly basis from November 1999 to February 2000.

Two further general runs were carried out in the Fergus and Robe catchments in June and October 1999, again in order to assess baseline catchment P levels for spatial analysis. A general run of the Limerick sites was fragmented over the summer 1999 period due to difficulties in co-ordinating access to the public supply sites.

SIGMA automatic water samplers were installed for varying time spans at the RS06 Spring in the Robe, and FS05and FS13 in the Fergus. These samplers were programmed initially to recover samples every 8 hrs and subsequently daily to assess temporal changes in more detail at these sites. However, a mechanical failure at the FS05 site resulted in only daily samples been collected.

### 4.2.2 Sampling Procedures

At each site, a sample bottle was half filled, inverted and shaked a few times with the cap on, and emptied. Then the sample was taken, filling the bottle right to the top to avoid bubbles. The cap was screwed on underwater to elimnate bubbles. Each bottle was labelled with site name, date, county and sampler's initials. Some special requirements were needed in the collecting samples at various site types:

*Springs, Karstic Windows and Swallow holes*

A location was chosen closest to the spring source that was flowing and free of weeds. Care was taken to avoid disturbing the spring bottom sediment, which may enter the sample bottle.

*Boreholes*

Samples were generally recovered from either a kitchen tap or an outdoor tap adjacent to the borehole. Preference was given for taps which intercepted the borewater before any storage tank or any type of pre-treatment (e.g., chlorination, water-softener). Occasionally a bailer was used to obtain samples. To ensure that the sample does not comprise water that was simply standing in the well, it is common to purge a number of bore volumes of water prior to sampling (Fetter, 1999). However, these boreholes provided drinking water supply and stock watering, thus the common practice of purging was not practicable. To provide some consistency the pump of each bore was run for approximately 5-10 mins (longer where practicable) or where readings for electrical conductivity and temperature stabilised, before taking the sample. Thus, whilst contamination from stagnant water in the well was a possibility, the sampling procedures employed would have minimised any effect. In addition, these boreholes were in regular use by the landowner, so it is likely that fresh, representative groundwater was being continuously being drawn into the well, at least on a daily basis.

*Dug Wells*

Samples were taken directly in the dug well were possible or otherwise from an adjacent tap. Care was taken to avoid disturbing the bottom sediment.

*Rivers*

A special device was used for sampling rivers which took advantage of the fact that all river sites were bridges. A weighted 5 litre plastic bottle with an opened top end was lowered on a rope into the river until the bottle filled. This device was rinsed once before taking the sample.

*Lakes*

Lakes were only sampled in the Fergus catchment and were only sampled to obtain indicative TP levels, rather than part of a detailed limnological study. As such samples

were taken at the most convenient sites such as weirs and jetties, rather than in the centre of the lake or at depth.

### 4.2.3 Sample Preparation and storage

After sample collection all samples were stored with ice bricks in cooler boxes below 4°C. Samples were prepared each evening approximately 2-5 hours after sample collection. 50ml Pyrex glass digestion flasks with teflon coated wads were used to store samples destined for TP and TDP analysis. 12ml plastic tubes were used to store samples destined for DRP analysis. Since these containers were used directly in the analytical process - i.e. the Pyrex flasks were digested, and mixed reagent was added to the 12ml plastics tubes - loss of P due to adherence onto the sides of containers was minimised.

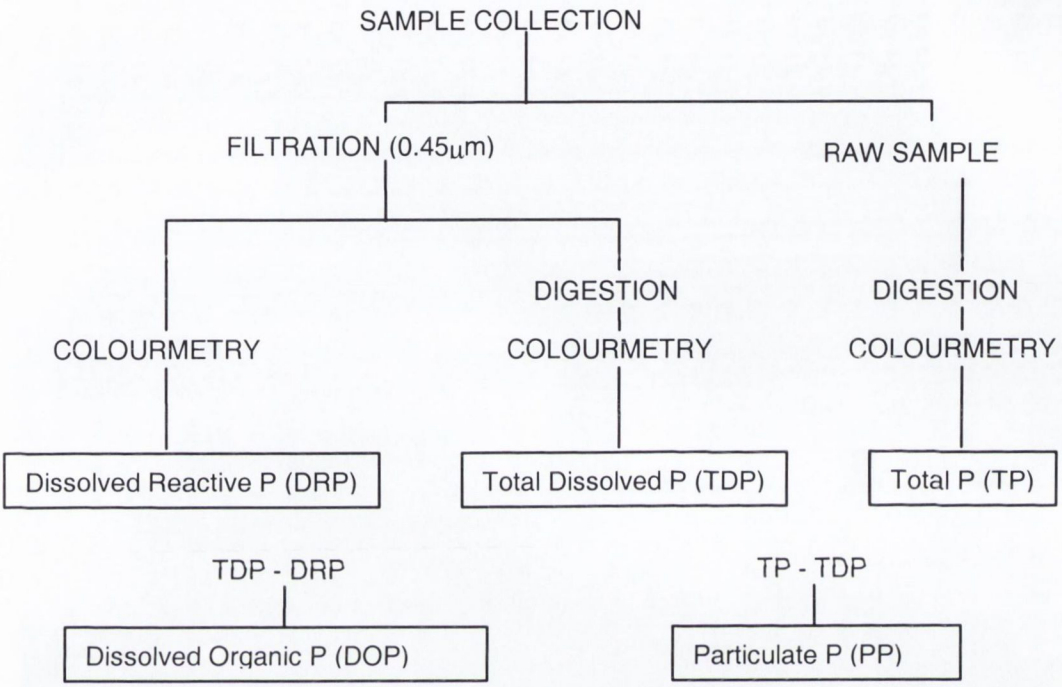
For TP analysis 25ml of raw sample was transferred to a 50ml Pyrex digestion flask. About 100ml of raw sample was than filtered through 0.45µm pore Whatman filter paper using a hand pump. 25ml of the filtrate was transferred to a 50ml Pyrex digestion flask for TDP analysis. 5ml of the filtrate was transferred to 12ml plastic reaction tubes for DRP analysis. 25ml of the filtrate were stored in 50ml polyethylene bottles for cation analysis (4% Lanthanum Chloride (LaCl) added as preservative) and anion analysis (no LaCl added). Dedicated equipment, such as graduated cylinder and filtering apparatus, was used throughout the program and all equipment was washed with deionised water and then raw sample before taking the real sample. The digest flasks and reaction tubes were stored below 4°C in cooler boxes whilst in transit and on returning to the laboratory in a refrigerator. Analysis of samples for DRP was taken as soon as possible. Generally this was within 24hrs after collection.

### 4.2.4 Phosphorus analysis

The phosphorus analysis technique that was employed for this work is derived from Eisenreich *et al.* (1975). The essential ascorbic acid/moybdate colourimetric procedure is as described by Murphy and Riley (1962). Total phosphorus (TP) was measured colourimetrically after digestion with potassium persulfate in the unfiltered samples. The same digestion method was applied to the filtered samples, and resulted in Total dissolved P (TDP). Particulate P (PP) was determined as the difference between TP and TDP. Dissolved reactive P (DRP) was measured colourimetrically on filtered samples that were

not subject to persulfate digestion. These methods are described in detail in Appendix C. Dissolved organic P (DOP) was calculated as the difference between TDP and DRP. Figure 4.1 summarises the various phosphorus fractions measured.

**Figure 4.1 Measured and calculated fractions of phosphorus is water.**




Two spectrophotometers were used in the course of this project. An older spectrophotometer (PYE Unicam SP6-350) with a one centimetre cell was used for the first three sampling events (July, August and September 1999). For all subsequent runs a newer spectrophotometer (Shimadzu UV-120-02) with a four centimetre cell was used. In order to compare the repeatability between both machines all samples were analysed for TP using both machines in the fourth sampling event (February 1999).

### 4.2.5 Other analytes

Nitrogen, chloride and sulphate were measured by chemically suppressed ion chromatography (Dionex system). Determination of these ions followed calibration with five standards. Sodium, potassium, magnesium and calcium were determined by flame atomic absorption (Perkin Elmer 3100) following addition of Lanthanum Chloride to a concentration of 4%. Calibration consisted of four standards and readjustment of calibration was based on one standard using a re-slope factor. Alkalinity was determined by titration to pH 4.5 with 0.01 molar sulphuric acid using a Metrohm burette (E 485).

### 4.2.6 Quality control and quality assurance

*Phosphorus*

Samples were collected in 250ml (for general sampling) and 500ml (for targeted sampling) polyethylene bottles. These sample bottles were initially washed with 10% HCl and thereafter, each bottle was dedicated to each site and washed thrice with tap water and thrice distilled water before each run. Blanks were taken on all runs to ensure this cleaning regime did not contaminate the samples.

A known concentration of standard (20 $\mu g\ l^{-1}$) was made up from a different phosphorus salt to that used for the calibration standards. A large batch of this standard was stored in 250ml containers and stored in a freezer. This facilitated monitoring of the performance of the method and because a separately purchased salt was used provided a degree of quality assurance (QA). On one occasion this standard was taken in the field and processed like a normal sample and later analysed for TP, TDP and DRP.

Quality assurance is a critical component of any scientific study. Robust QA procedures are required to ensure confindence in the reliability of analytical results. It is acknowledged here that more rigorous quality assurance could have been employed by the way of inter-laboratory analysis of blind samples or through the analysis of certified reference materials and of inter-laboratory QA schemes such as AQUACHECK. In defense of the QA procedures adopted, other users of the laboratory successfully carried out the use of certified materials, and schemes such as AQUACHECK would be beyond the means of the laboratory. Overall, whilst the author is confident of the reliability of the P data, on balance, inter-laboratory analysis of blind samples should have been carried out as an additional QA check.

*Anion and cations*

No specific quality control assessment was used for the major ions. However, standards were run after every 10 samples to detect if drift was taking place.

### 4.2.7 Field Meaurements

During the first three sampling events (July, August and September 1998) only electrical conducticity (EC) and temperature were taken in the field at the time of sample collection.

Thereafter, pH and dissolved oxygen (DO) were also taken at all sites. DO and PH were calibrated in the field prior to use. EC was periodically checked against a standard of 5 X $10^{-4}$ M KCl (equivalent to 75 $\mu$S $cm^{-1}$) and a second meter. A WTW Multiline P4 Multimeter was used for all field measurements. Standing water level in the boreholes and dug wells was measured (unless an obstruction prohibited) using a Solinst dip meter. A SIGMA automatic sampler was used at RS06 in the Robe catchment, and at FS05 and FS13 in the Fergus catchment. A maximum of 24 500ml polyethylene bottles were available for each run. These bottles were cleaned with a phosphate-free detergent and then thrice with tap water and thrice with distilled water before each run. To verify this cleaning regime each run included one bottle with deionised water and one with 20 $\mu g\ l^{-1}$ QC standard solution.

## *4.3 Phosphorus Results*

### 4.3.1 Quality control and quality assurance

Detection limits were calculated for DRP, TDP and TP using the methods described by Caulcutt and Boddy (1983). The precision of all the P data was expressed as the standard deviation of the absolute differences between replicate values (APHA, 1989). The detection limit and precision of the measured fractions are presented in Table 4.1.

**Table 4.1 Quality control parameter for the measured P fractions.**

| *Parameter* | *TP ($\mu g\ l^{-1}$)* | *TDP ($\mu g\ l^{-1}$)* | *DRP ($\mu g\ l^{-1}$)* |
|---|---|---|---|
| Detection limit | 2.7 | 2.7 | 1.5 |
| Precision (Standard Deviation) | 1.2 | 1.1 | 0.9 |

The quality control standard of 20 $\mu g\ l^{-1}$ made up from a different salt were read regularly throughout the analysis. Quality control charts for DRP and TP are presented in Figure 4.2 and Figure 4.3. The quality control analysis for total P had an average value of 19.6 $\mu g\ l^{-1}$ and standard deviation of 0.6 $\mu g\ l^{-1}$. The quality control analysis for dissolved reactive P was 19.2 $\mu g\ l^{-1}$ and standard deviation of 1.3 $\mu g\ l^{-1}$. There was a particularly low value during the December 1999 DRP analysis which was attributed to a standard which had

been thawed and stored in the refrigerator for some time. Overall, the accuracy of the quality control standard was satisfactory for both TP and DRP.

**Figure 4.2 Quality control chart for dissolved reactive P. Solid line is the mean result, minor gridlines represent 2 standard deviations.**

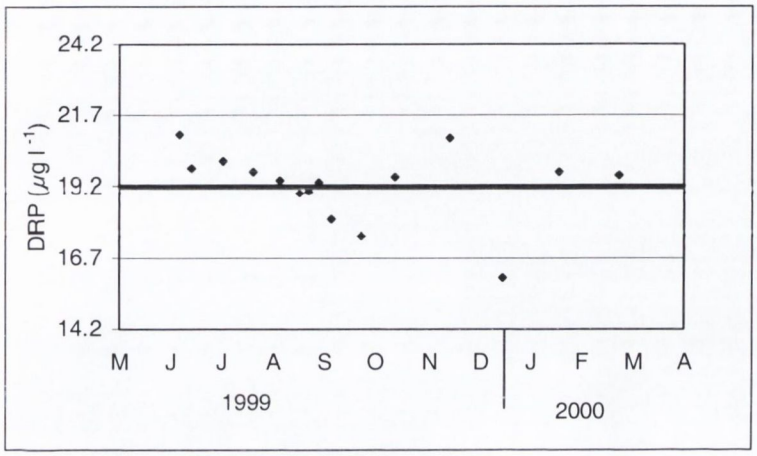
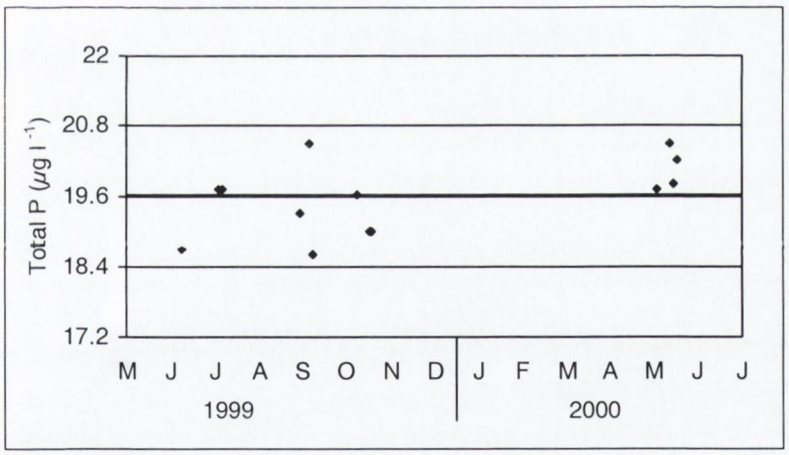



**Figure 4.3 Quality control chart for total phosphorus. Solid line is the mean result, minor gridlines represent 2 standard deviations.**




The QC standard (20 $\mu g\ l^{-1}$) that was taken in the field measured 19.4, 19.6 and 20.1 $\mu g\ l^{-1}$ of TP, TDP and DRP respectively.

### 4.3.2 Total Phosphorus

Figure 4.4 presents mean TP values for all the groundwater sites of each catchment. Similar to the National P dataset, the data is highly skewed to the right. Thirteen of the fourteen of the sites with mean TP greater than 100 $\mu g\ l^{-1}$ were boreholes, the other site was the Kilrush spring in the Robe catchment. Some 44% of the data exceed the river

eutrophication threshold (30 $\mu g\ l^{-1}$ unf. MRP; McGarrigle, 1998). 58% of the data is greater than the lake eutrophication threshold (20 $\mu g\ l^{-1}$ TP; Champ, 1998).

**Figure 4.4 Frequency distribution histogram of mean total P for groundwater sites.**

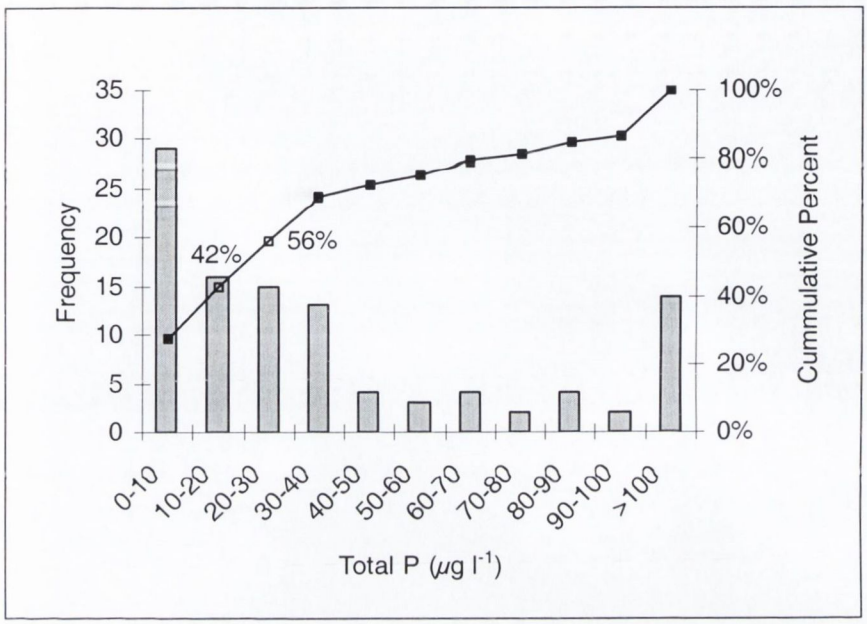



Figure 4.5 presents total P frequency distribution histograms for all three catchment areas. The highly skewed nature of the data is evident in all three catchment areas. For this reason the use of medians rather than means are a more accurate way of summarizing the data. The karstic aquifers of the Robe and Fergus had higher median TP levels than the non-karstic Limerick aquifers. All three catchment areas exhibited a small number of extreme TP levels greater than 200 $\mu g\ l^{-1}$.

Table 4.2, Table 4.3 and Table 4.4 summarise the basic field water chemistry parameters for each catchment. For each site type summary statistics are presented on mean pH, electrical conductivity (EC), dissolved oxygen (DO) and temperature that were measured in the field for each catchment. Mean total P (TP) data is also included. The relationships between P and these key field parameters is examined in more detail later in the chapter. The raw data from which these summary tables are derived are presented in Appendix D.

**Figure 4.5 Total P Frequency distribution histograms for each catchment area.**

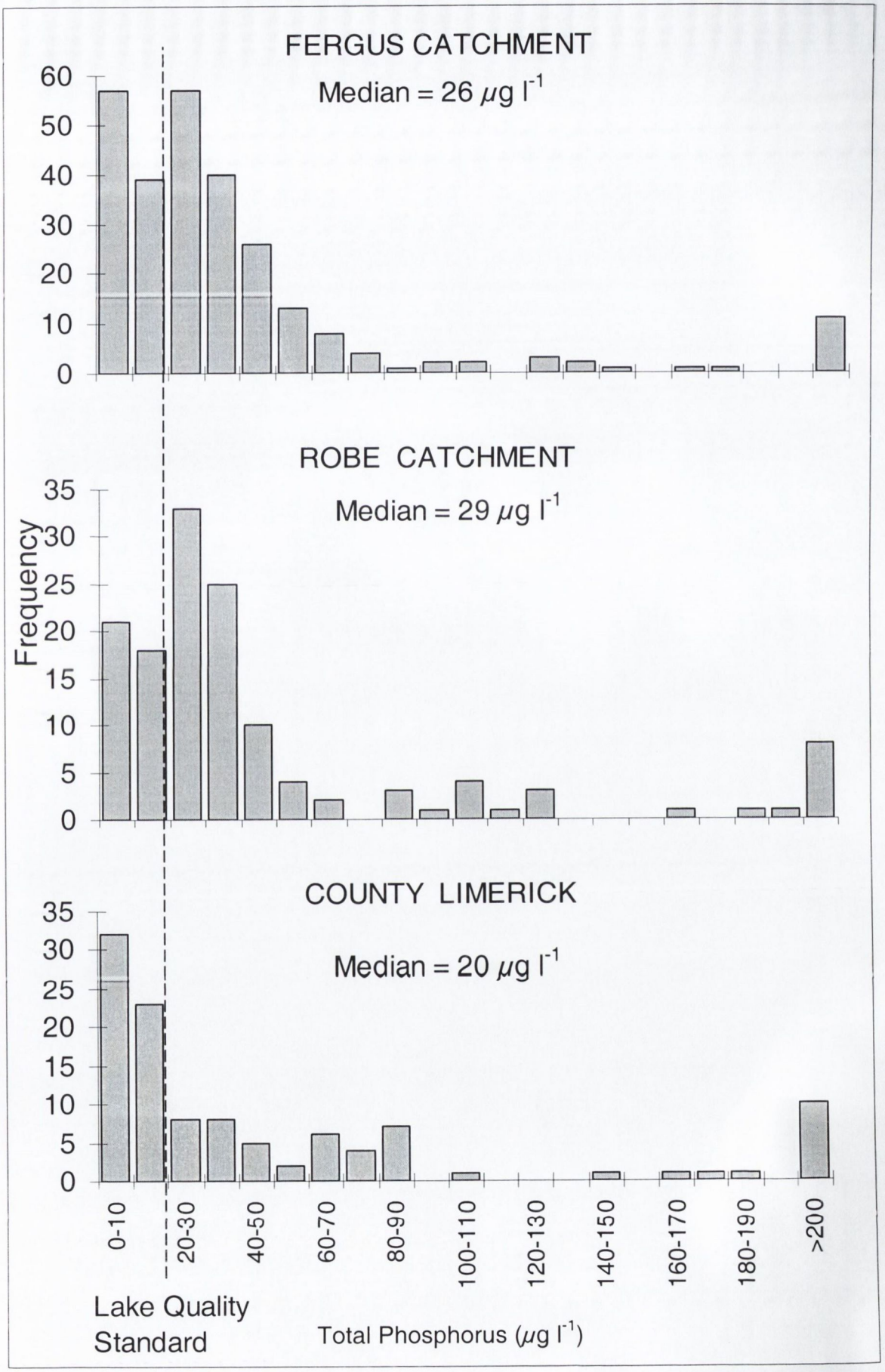


**Table 4.2 Limerick catchments field water chemistry and total P.**

| *Site Type* | *Statistic* | *pH* | *EC ($\mu S\ cm^{-1}$)* | *DO ($mg\ l^{-1}$)* | *Temp (°C)* | *TP ($\mu g\ l^{-1}$)* |
|---|---|---|---|---|---|---|
| Borehole | Mean | 7.10 | 629 | 5.49 | 12.5 | 84.2 |
| | Median | 7.13 | 675 | 5.56 | 12.3 | 37.5 |
| | Max | 7.59 | 874 | 9.29 | 15.4 | 651.3 |
| | Min | 6.17 | 180 | 1.19 | 10.3 | 2.1 |
| | Count | 30 | 30 | 29 | 30 | 30 |
| | SE | 0.05 | 36 | 0.42 | 0.2 | 24.8 |
| Dug Well | Mean | 7.15 | 681 | 6.09 | 12.9 | 85.0 |
| | Median | 7.15 | 681 | 6.09 | 12.9 | 85.0 |
| | Max | 7.24 | 782 | 8.30 | 14.6 | 161.2 |
| | Min | 7.05 | 580 | 3.87 | 11.2 | 8.8 |
| | Count | 2 | 2 | 2 | 2 | 2 |
| | SE | 0.10 | 101 | 2.22 | 1.7 | 76.2 |
| Springs | Mean | 6.89 | 471 | 6.85 | 12.2 | 19.4 |
| | Median | 7.01 | 560 | 6.93 | 12.5 | 8.1 |
| | Max | 7.38 | 1019 | 10.07 | 13.4 | 63.3 |
| | Min | 6.15 | 94 | 2.99 | 9.8 | 3.7 |
| | Count | 8 | 8 | 8 | 8 | 8 |
| | SE | 0.16 | 115 | 0.90 | 0.4 | 8.4 |

**Table 4.3 Fergus catchment field water chemistry and total P.**

| *Site Type* | *Statistic* | *pH* | *EC ($\mu S\ cm^{-1}$)* | *DO ($mg\ l^{-1}$)* | *Temp (°C)* | *TP ($\mu g\ l^{-1}$)* |
|---|---|---|---|---|---|---|
| Borehole | Mean | 7.14 | 675 | 4.70 | 13.6 | 100.6 |
| | Median | 7.13 | 661 | 4.41 | 13.5 | 11.3 |
| | Max | 7.66 | 1136 | 8.34 | 15.3 | 1290.5 |
| | Min | 6.83 | 422 | 2.29 | 11.8 | 3.0 |
| | Count | 18 | 18 | 18 | 17 | 18 |
| | SE | 0.05 | 42 | 0.44 | 0.2 | 70.6 |
| Dug Well | Mean | 6.92 | 426 | 5.41 | 13.6 | 25.1 |
| | Median | 7.10 | 487 | 4.40 | 13.2 | 16.1 |
| | Max | 7.81 | 708 | 8.63 | 15.5 | 91.3 |
| | Min | 5.91 | 149 | 3.00 | 12.2 | 5.6 |
| | Count | 8 | 9 | 8 | 9 | 9 |
| | SE | 0.23 | 58 | 0.81 | 0.4 | 8.8 |
| Spring | Mean | 7.43 | 446 | 7.29 | 13.1 | 31.3 |
| | Median | 7.47 | 439 | 7.49 | 13.2 | 28.8 |
| | Max | 7.63 | 660 | 10.60 | 15.4 | 78.6 |
| | Min | 7.10 | 396 | 2.52 | 10.9 | 5.8 |
| | Count | 18 | 18 | 18 | 18 | 18 |
| | SE | 0.03 | 14 | 0.42 | 0.3 | 3.9 |
| Lake | Mean | 8.10 | 366 | 10.09 | 15.9 | 18.8 |
| | Median | 8.07 | 374 | 10.24 | 16.8 | 20.2 |
| | Max | 8.29 | 402 | 10.76 | 17.1 | 32.7 |
| | Min | 7.92 | 297 | 8.80 | 11.2 | 7.0 |
| | Count | 6 | 6 | 6 | 6 | 7 |
| | SE | 0.06 | 15 | 0.28 | 0.9 | 3.4 |
| River | Mean | 7.56 | 429 | 10.33 | 13.5 | 51.2 |
| | Median | 7.53 | 454 | 10.02 | 13.1 | 46.9 |
| | Max | 7.72 | 462 | 11.41 | 14.9 | 67.8 |
| | Min | 7.43 | 371 | 9.56 | 12.6 | 38.9 |
| | Count | 3 | 3 | 3 | 3 | 3 |
| | SE | 0.09 | 29 | 0.56 | 0.7 | 8.6 |

**Table 4.4 Robe catchment field water chemistry and total P.**

| *Site Type* | *Statistic* | *pH* | *EC ($\mu S\ cm^{-1}$)* | *DO ($mg\ l^{-1}$)* | *Temp (°C)* | *TP ($\mu g\ l^{-1}$)* |
|---|---|---|---|---|---|---|
| Borehole | Mean | 7.34 | 759 | 5.39 | 11.7 | 110.7 |
| | Median | 7.31 | 732 | 4.85 | 11.7 | 20.7 |
| | Max | 7.71 | 922 | 8.50 | 13.1 | 652.0 |
| | Min | 7.01 | 659 | 1.95 | 9.4 | 2.9 |
| | Count | 11 | 11 | 11 | 11 | 11 |
| | SE | 0.05 | 23 | 0.68 | 0.4 | 60.1 |
| Dug Well | Mean | 7.05 | 795 | 5.45 | 12.2 | 17.9 |
| | Median | 7.05 | 795 | 5.45 | 12.2 | 17.9 |
| | Max | 7.10 | 824 | 7.96 | 13.5 | 32.7 |
| | Min | 6.99 | 767 | 2.94 | 10.8 | 3.0 |
| | Count | 2 | 2 | 2 | 2 | 2 |
| | SE | 0.06 | 29 | 2.51 | 1.3 | 14.9 |
| Spring | Mean | 6.99 | 734 | 4.75 | 10.8 | 41.5 |
| | Median | 6.97 | 729 | 4.65 | 10.8 | 31.7 |
| | Max | 7.14 | 773 | 6.57 | 11.0 | 108.4 |
| | Min | 6.92 | 693 | 3.10 | 10.6 | 13.9 |
| | Count | 6 | 6 | 6 | 6 | 6 |
| | SE | 0.04 | 12 | 0.54 | 0.1 | 14.2 |
| River | Mean | 8.06 | 639 | 10.77 | 13.6 | 46.2 |
| | Median | 8.06 | 639 | 10.77 | 13.6 | 46.2 |
| | Max | 8.09 | 654 | 11.00 | 13.7 | 48.5 |
| | Min | 8.04 | 625 | 10.54 | 13.4 | 43.9 |
| | Count | 2 | 2 | 2 | 2 | 2 |
| | SE | 0.03 | 15 | 0.23 | 0.1 | 2.3 |

### 4.3.3 Phosphorus fractions

During the course of the project over 500 samples were taken periodically from 56 springs and 67 wells in the three areas between July 1998 and March 2000. All samples were analysed for total P (TP) and 30% of the samples were also analysed for total dissolved P (TDP) and dissolved reactive P (DRP). Dissolved organic P (DOP) and particulate P (PP) were derived by calculation, i.e., DOP=TDP-DRP and PP=TP-TDP.

Figure 4.6 presents a log-log plot of TDP against DRP. A log scale was used due to the highly skewed nature of the data. There is a strong overall relationship between DRP and TDP. Below 10 $\mu g\ l^{-1}$ there are sites which have more DRP than TDP (i.e. points above the regression line), this is clearly an error as levels get close to the limit of detection. It is likely that this is due to errors associated with TDP analysis, which involves a digestion and is a more complicated process than DRP analysis. There also several sites with far more TDP than predicted by the regression line. These are sites with larger levels of DOP and generally represent boreholes from the Fergus catchment.

Figure 4.7 presents a log-log plot of TP against TDP. Again, there is a very strong relationship between TP and TDP. There are also several sites located below the line with more TP than predicted by the regression, particularly eight sites located around 100 $\mu g\ l^{-1}$ TP. This deviation represents high particulate P levels. All eight sites except one are springs. The turbulent flow in springs may better facilitate the transport of PP.

**Figure 4.6 Log-log TP/DRP plot using all catchment groundwater P data.**

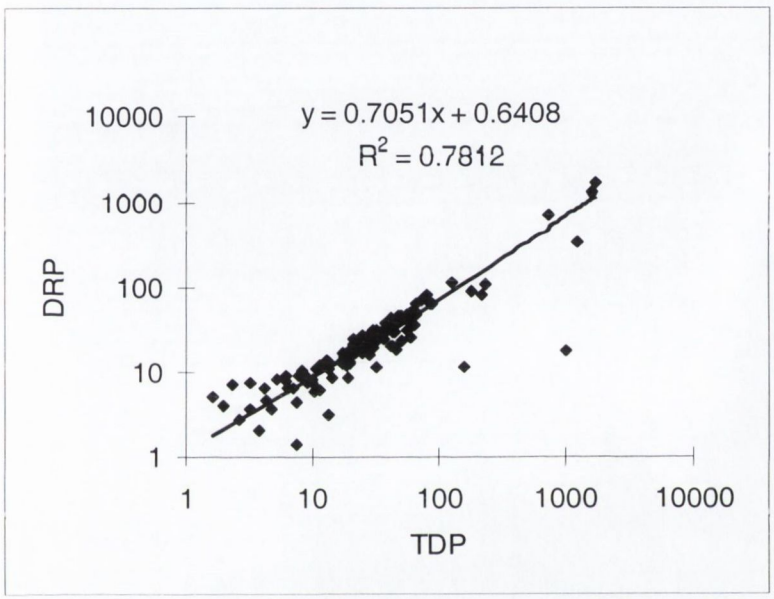
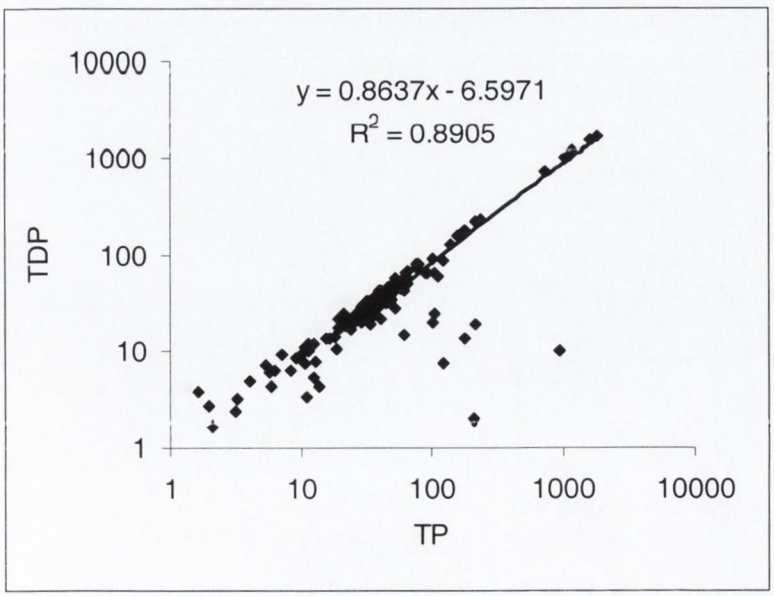



**Figure 4.7 Log-log TP/TDP plot using all catchment groundwater P data.**




The strong positive relationships between TP and the dissolved fractions highlights the dominance of dissolved inorganic P in groundwater. This can also be seen in Table 4.5.

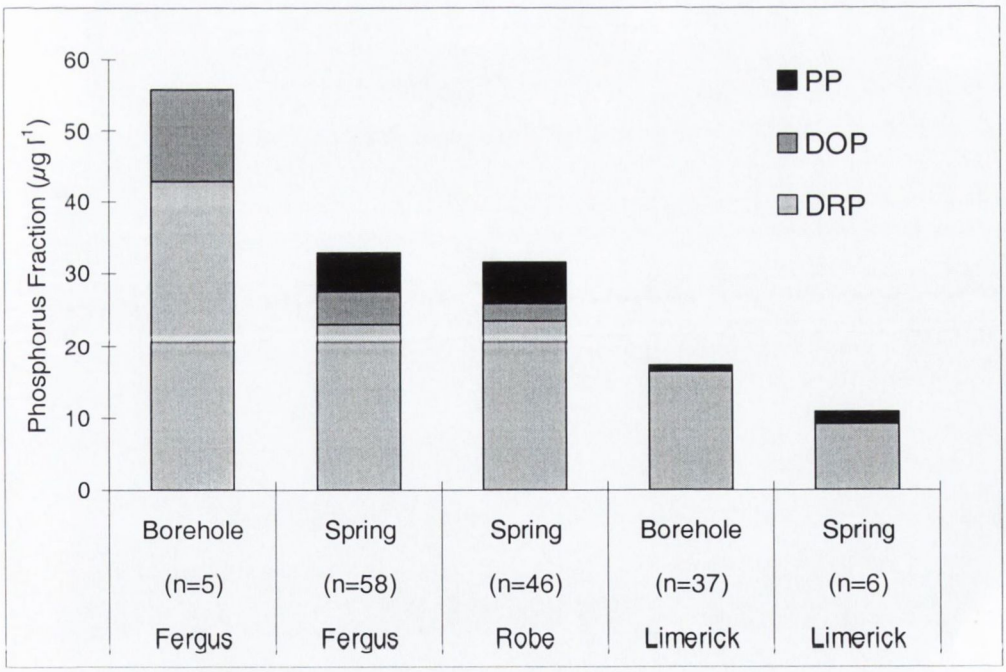
Overall, TP comprised 93% TDP and 81% DRP in boreholes. In springs there is slightly more DOP and PP with TP comprising 83% TDP and 77% DRP.

**Table 4.5 TDP and DRP as a percentage of TP for each catchment**

| | *Borehole TDP* | *Borehole DRP* | *n* | *Spring TDP* | *Spring DRP* | *n* |
|---|---|---|---|---|---|---|
| Fergus | 98 | 78 | 5 | 81 | 75 | 58 |
| Robe | 95 | 95 | 1 | 81 | 71 | 46 |
| Limerick | 86 | 71 | 32 | 88 | 84 | 6 |
| Total | 93 | 81 | 38 | 83 | 77 | 110 |

As apparent in Table 4.5, DRP was the dominant fraction for springs and wells in all catchments. This is also apparent in Figure 4.8 which presents median phosphorus fraction levels for boreholes and springs in each of the catchments. The Robe and Fergus catchments had higher median P than Limerick. Particulate P was higher in springs than in boreholes.

**Figure 4.8 Median phosphorus fraction levels for boreholes and springs.**

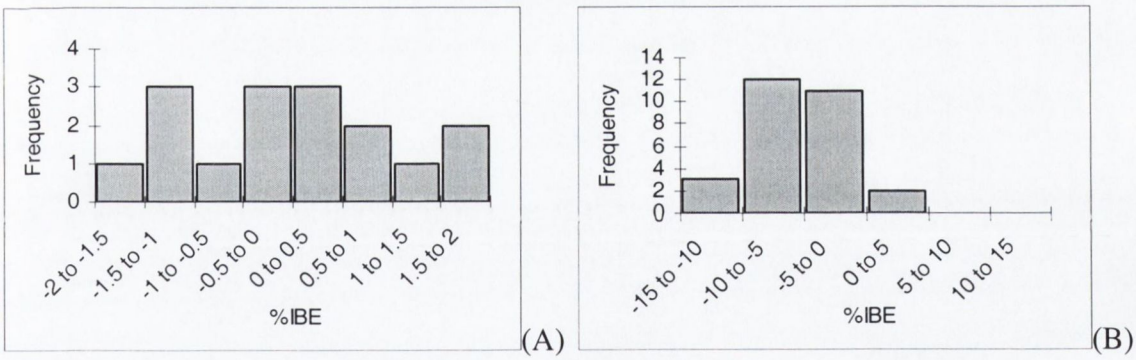


## 4.4 *Basic hydrochemical descriptions of each catchment*

### 4.4.1 Ion balance errors

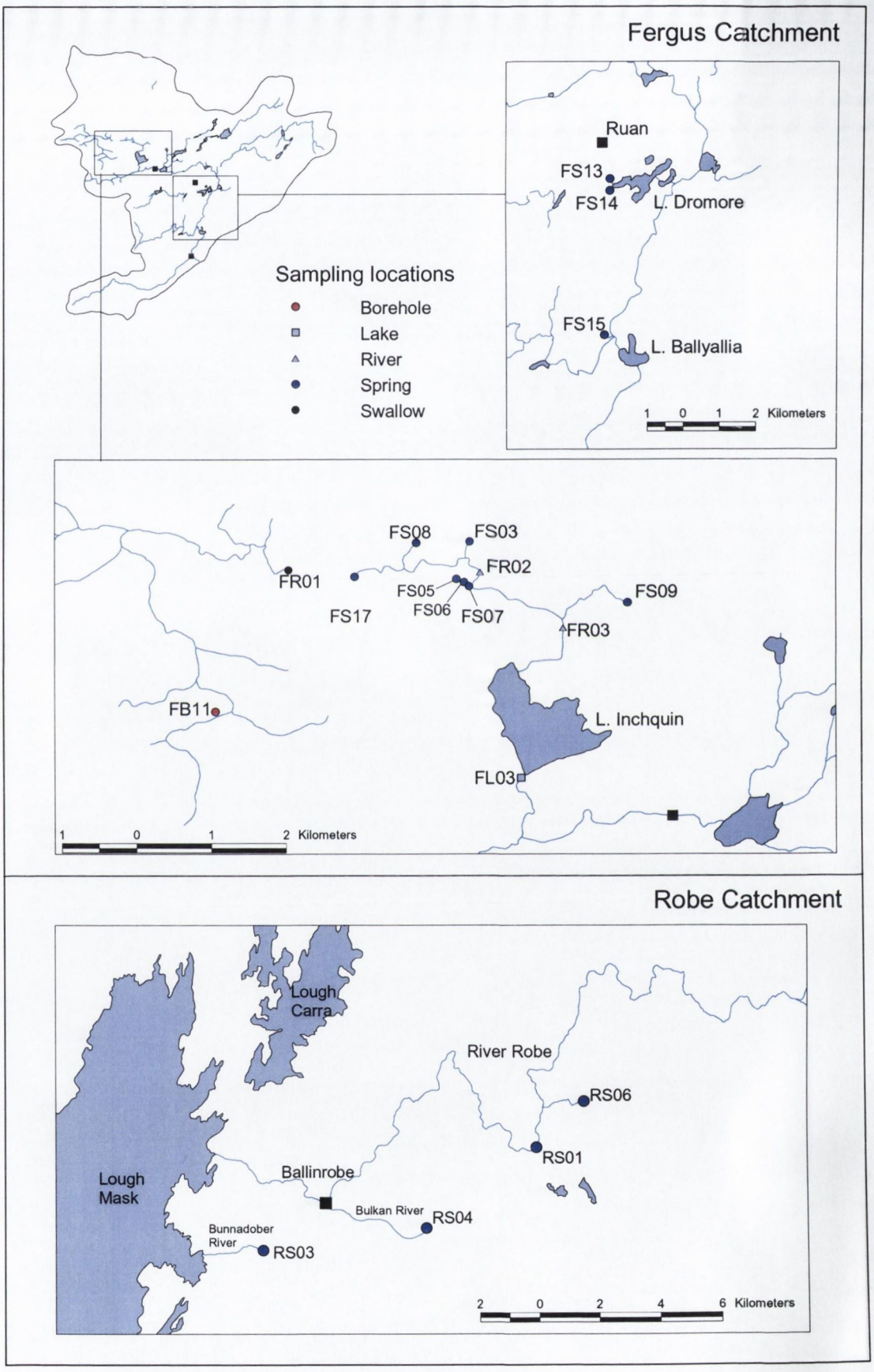
A full analytical suite (major anions and cations) was carried out on the Robe springs and the major springs of the Fergus catchment (including some surface water samples) in September 1999. See Figure 4.10 for locations of these sites. Some of the Fergus sites around Lough Inchquin were also analysed for the major ions during sampling runs in February and June 1999. These data are presented in Appendix D, Tables D.5 and D.6. The Limerick sites were not analysed for ions, however, ion data was sourced from Deakin (1994) and is presented in Appendix D, Table D.4. Ion balance differences for the Fergus/Robe September 1999 run and for the Limerick sites are presented in Appendix D, Table D.7 and D.8. The percentage ion balance difference for the September 1999 in the Fergus and Robe catchments run were satisfactory with an average absolute difference of 0.8% and a maximum absolute difference of 1.7%. Figure 4.9 (A) presents these differences graphically. There were an equal number of negative and positive differences.

**Figure 4.9 Histograms illustrating Ion balance error (IBE) percentages for sites in the Fergus/Robe catchments (A) and sites in Co. Limerick (B).**




In contrast to the September 1999 Fergus and Robe, the ion balance differences for the Limerick sites were larger with an average absolute difference of 4.9% and a maximum absolute difference of 13.3%. Figure 4.9 (B) presents ion balance errors for the Limerick sites. All except two sites had negative ion balance errors, which suggests a more systematic error. Ion balance error calculations were used to verify the quality of the cation and anion data. Lloyd and Heathcote (1985) suggest that ion balance errors should be less than 5% and certainly not greater than 10%. With a maximum error of 1.8% in the Fergus and Robe data these data were well within these thresholds.

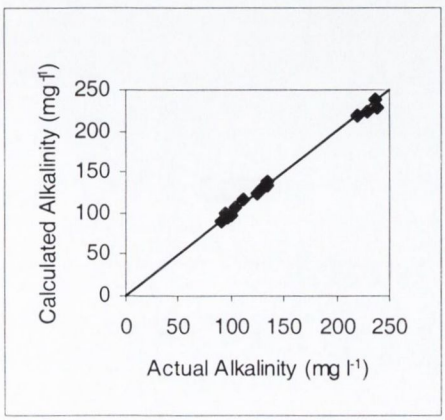
Figure 4.10 Fergus and Robe sites which were subject to anion/cation analysis.



The Limerick data, which was derived from another study (Deakin, 1994), had larger errors. Most of the Limerick sites had negative ions balance errors, suggesting that some anion is being underestimated or some cation over estimated. Fritz (1994) examined ion balance errors on published analyses of ground and surface waters. Overall he found more positive than negative errors (i.e., more cations than anions), which he attributed to alkalinity being measured in the laboratory rather than in the field. Thus, while the sample is being taken back to the lab bicarbonate could be removed from the sample by precipitation of carbonate material. The sample collected for cations however, are generally acidified preventing precipitation and are therefore measured accurately. Fritz (1994) also suggests that under certain conditions alkalinity can also cause a substantial trend towards negative errors. In particular, he suggests that if alkalinity titration is performed in the field, but the sampler titrates on an unfiltered sample, then alkalinity can be over estimated if there are suspended particles of calcite in the titration flask. This strong bias towards negative ion balance errors of the Limerick sites would suggest that such a systematic error has occurred. Nonetheless, the average difference for the Limerick sites was still within the 5% acceptable limit and only three of the sites were greater than 10%.

The alkalinity ($HCO_3^-$) values in Table D.5 for the February and June 1999 runs were not measured in the field but derived by ion balance calculations. Given the satisfactory ion balance errors of the September 1999 sampling run (see Table D.8) it was considered reasonable to adopt a calculation method. As a check, alkalinity values for the September run were plotted against calculated values using the ion balance. As is evident from Figure 4.11 actual and calculated alkalinity compare very well.

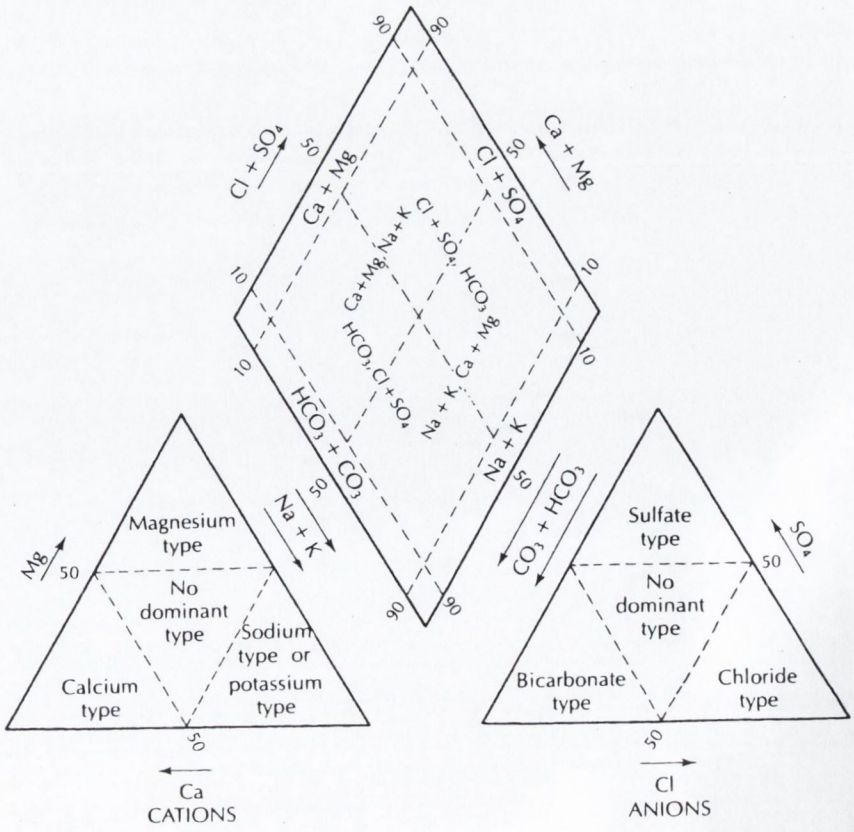
**Figure 4.11 Actual versus calculated alkalinity for the Fergus & Robe Sept. 1999 run.**



### 4.4.2 Major ionic composition

As mentioned above, the major cations and anions were not analysed for the Limerick sites. However, such data was available for the Limerick public supply groundwater sources from Deakin (1994) and is presented in Table A.1. Piper trilinear diagrams (Fetter, 2001) were constructed to examine the hydrochemical facies prevalent in each catchment area (Figure 4.12). A trilinear diagram can show the percentage composition of three ions. By grouping $Na^+$ and $K^+$ together, the major cations ([$Na^+$ & $K^+$], $Ca^{2+}$, $Mg^{2+}$) can be displayed on one trilinear diagram (the lower left triangle of Figure 4.12). Likewise, if $CO_3^{2-}$ and $HCO_3^-$ are grouped the major anions ([$CO_3^{2-}$ & $HCO_3^-$], $Cl^-$, $SO_4^{2-}$) can also be displayed on one trilinear diagram (the lower right triangle of Figure 4.12). The diamond field between the two triangles is used to represent the composition of water with respect to both cations and anions. The cation point is projected onto the diamond field parallel to the side of the triangle labeled magnesium, and the anion point is similarly projected parallel to the side of the triangle labeled sulphate. The intersection of the two lines is plotted as a point on the diamond field (Fetter, 2001). In this way the dominant ions of a given water can be idenitifed. This allows for the comparison of water-types between several sites in one graphical format.

**Figure 4.12 Hydrogeochemical classification system for natural using the trilinear diagram (Fetter, 2001).**



For Limerick, the sites were grouped according to generic geological groups to clearly show the different hydrochemical facies (see Table 4.6).

**Table 4.6 Generic geologies for Limerick trilinear diagram.**

| *Geology* | *Generic Geological Grouping* |
|---|---|
| Silurian | Sandstone/mudtsone |
| Old Red Sandstone | Sandstones |
| Kiltorcan Sandstone | Sandstones |
| Mellon House Beds | Limestones |
| Ballysteen Limestone | Limestones |
| Waulsortian Limestone | Limestones |
| Herbertstown Limestone | Limestones |
| Muddy Shelf Limestone | Limestones |
| Volcanics | Volcanics |
| Namurian | Shales |

Figure 4.13 presents a trilinear diagram for sites in County Limerick. The majority of the sites have Ca-$HCO_3$ type waters that reflect the dominance of limestone aquifers in the county as confirmed by Deakin *et al.*'s (1998) study of Limerick groundwater. A minority of sites deviates from this type, most notably those with Namurian geologies (LB19 and LB12) and to a lesser degree some of the Sandstone and Silurian aquifers. It should be noted that the mineral composition of a given groundwater will also reflect overlying glasical deposits as well as bedrock lithology

Figure 4.14 presents $Na^+/Cl^-$ and $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ plots for the Limerick sites. There are strong linear relationships between these ions. As was evident in the trilinear diagram for Limerick, the two Namurian sites of LB19 and LB12 deviate from these trends due principally to lower calcium and higher sodium (see Table D.4).

**Figure 4.13 Limerick Trilinear Diagram**

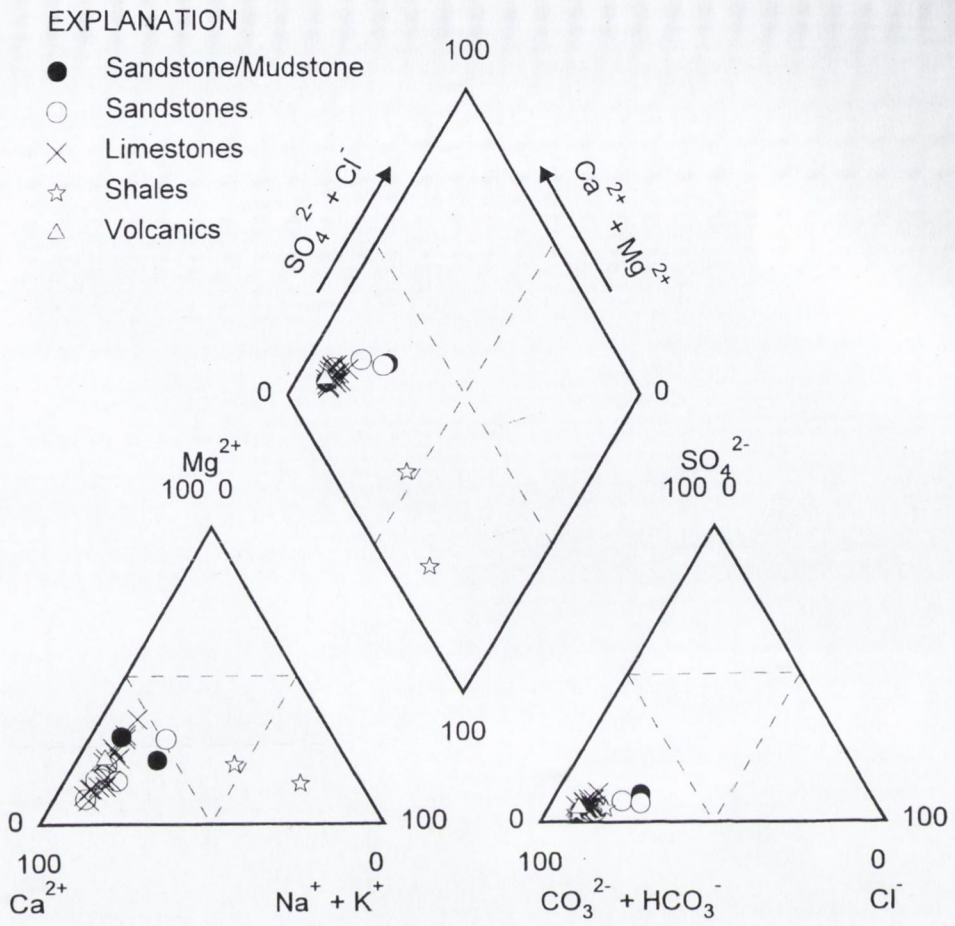



**Figure 4.14 $Na^+/Cl^-$ and $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ plots for the Limerick sites. Note: $Na^+$ on log axis; Clear diamonds are LB19 and LB12.**

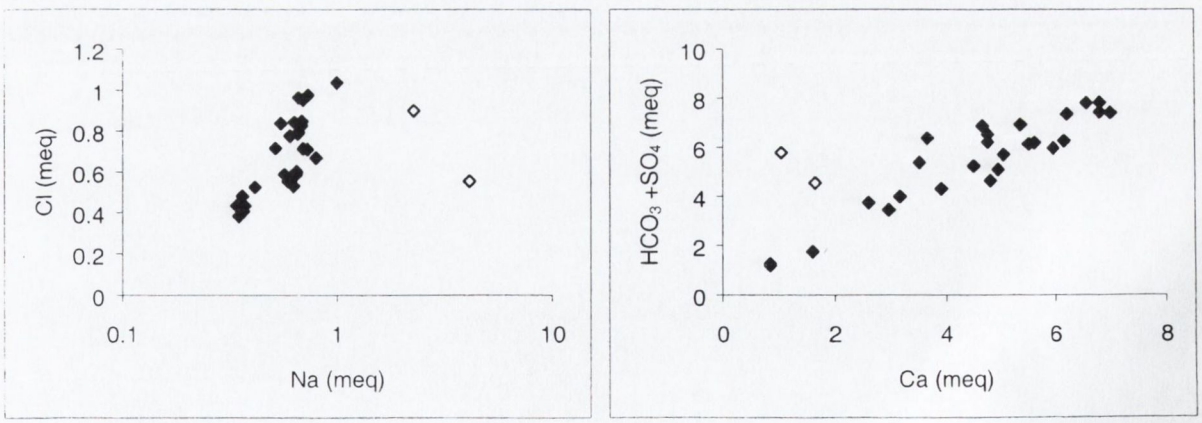
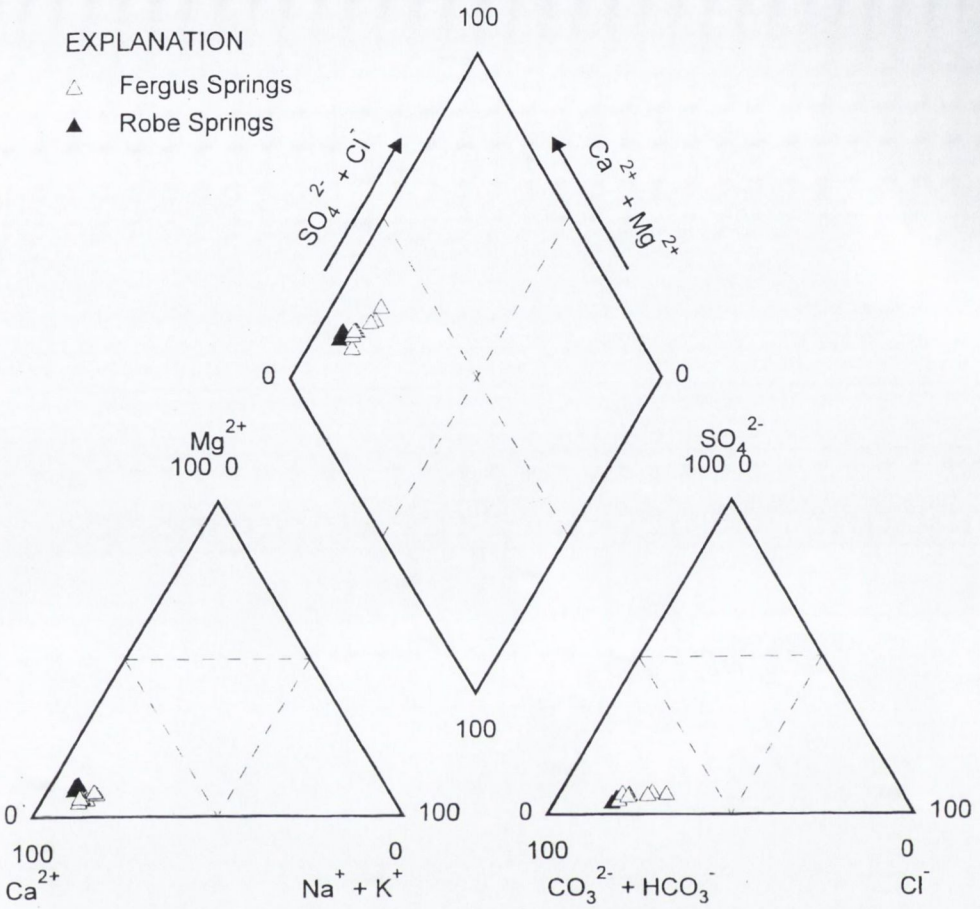



Figure 4.10 presents the locations of the sites in the Fergus and Robe catchments that were subject to anion/cation analysis. Table D.6 (Appendix D) presents the ion data for the September 1999 sampling runs in the Fergus and Robe catchments.

**Figure 4.15 Fergus and Robe Trilinear diagram**




The $Ca\text{-}HCO_3$ water type once again dominates both catchments especially the Robe springs. Three springs, FS13, FS14 and FS18, are slightly less dominated by bicarbonate waters. These springs are located further downstream of the other springs and derive much of their water from point recharge at sinks (see Figure 4.10). Therefore, the trilinear diagram could reflect the effect of surface water mixing.

Figure 4.16 presents a trilinear diagram for sampling runs of the Fergus sites during February, July and September 1999. All runs exhibit the familiar $Ca\text{-}HCO_3$ water, however sites sampled in February are all noticeably less dominated by bicarbonate ions. This could reflect the greater recharge experienced during winter and thus less contact time in the aquifer. There is one outlier that clearly has a water type far different from the other Fergus sites. It is a borehole (FB11) located on the Namurian Shale in the west of the catchment. This is reflected in the greater influence sodium and magnesium.

**Figure 4.16 Fergus Trilinear diagram temporal. Solid symbols are surface water.**

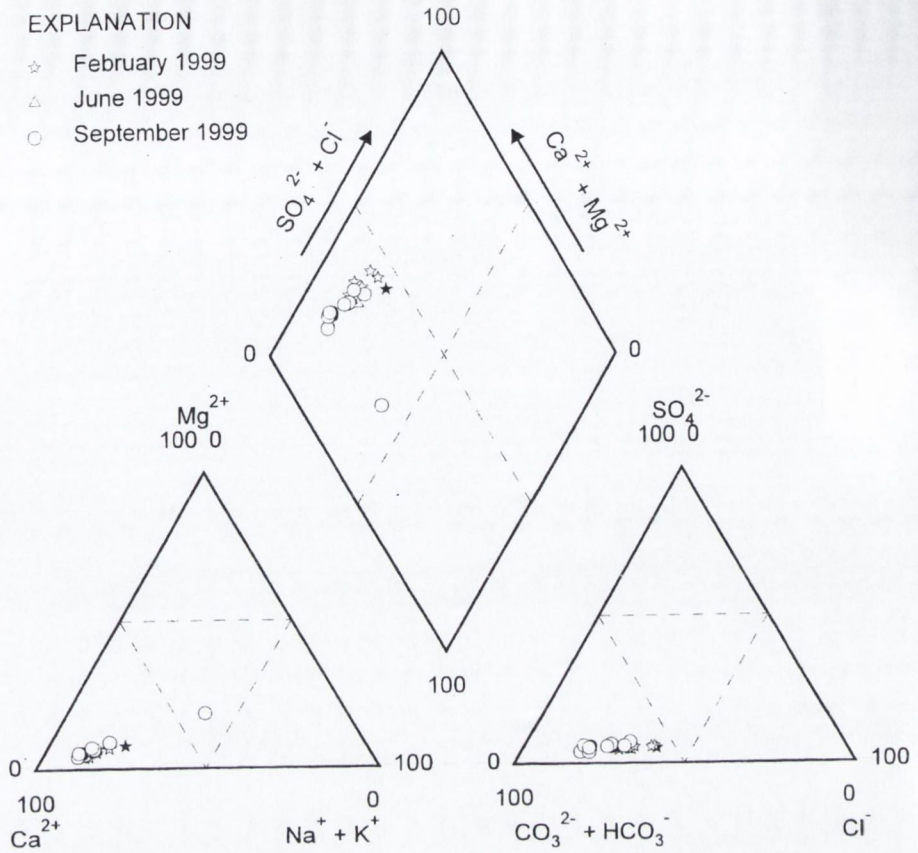
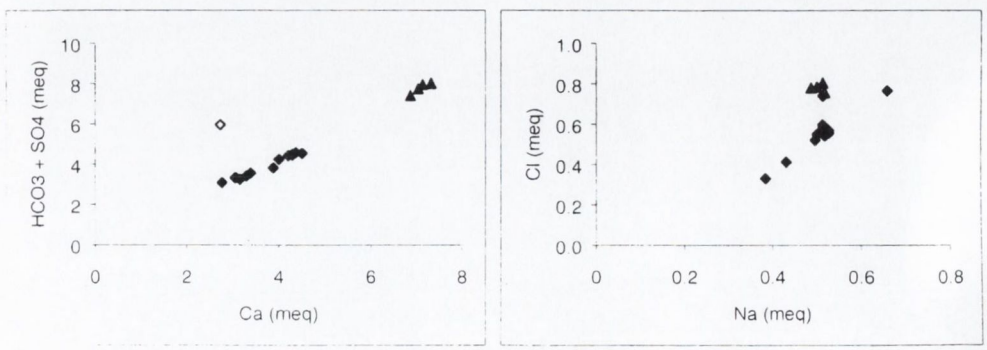



Figure 4.17 presents $Na^+/Cl^-$ and $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ plots for the Fergus and Robe sites. The linear relationships between $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ is apparent for both catchments, the exception being FB11 which was identified in the trilinear as being more influenced by sodium. The $Na^+/Cl^-$ plots also generally indicate linear trends. The FB11 was removed from this graph due to extreme sodium levels. The Robe springs are less clear, particularly due to RS06, which may reflect the impact of a pollution incident the previous month.

**Figure 4.17 $Na^+/Cl^-$ and $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ plots for the Fergus (♦) and Robe (▲) sites. Note: open diamond is FB11; the open triangle is RS06.**



### *4.5 Field parameters distribution maps*

Distribution maps of pertinent parameters provide useful preliminary information about a groundwater system together with water quality (Lloyd and Heathcote, 1985). Figure 4.18 presents distribution maps for mean EC, pH and DO for each site in Co. Limerick. Total P ranges classes are also presented.

Typically one would expect higher EC values down gradient in a aquifer. McKenzie *et al.* (2001) examined 16 springs in Ethiopia and found that total dissolved solids increased down gradient and attributed this to the fact that recharge from precipitation at higher elevations moves downward and laterally to spring-discharge points down slope, resulting in the discharge down slope having the longest subsurface residence time. This pattern is generally apparent for EC in the Deel and Maigue catchments (see Figure 3.8 for location of these catchments). In particular the three mountain springs of LS01, LS02 and LS03 all have very low EC (111, 94 and 159 $\mu$S cm$^{-1}$ respectively). In these cases the lower EC levels in upland areas are probably due to different geologies rather. Thus, the non-carbonate nature of their geologies (see Section 5.4) results in lower $Ca^{2+}$ and $HCO_3^-$.

Given the dominance of limestone geologies in Co. Limerick it is not surprising that pH values at or above neutral are commonest. Exceptions are characterized with non-limestone geologies. These are LB02/LB03/LS01 (6.15 – 6.86 pH units; Namurian), LB17 (6.17 pH units; Kiltorcan Sandstone), LB03 (6.84 pH units; Silurian), LB14 (6.6 pH units; Clare Shales) and LS02 (6.2 pH units; Namurian).

Dissolved oxygen was the most difficult parameter to measure accurately in the field. This may reflect the lack of any clear distribution pattern.

Figure 4.19 presents distribution maps for mean EC, pH and DO for each site in the Robe catchment. Levels of EC range at groundwater sites are clearly distinguished from the two River Robe sites which have the lowest EC levels. The River Robe sites are also have noticeably higher pH and DO levels. The spring sites have lower EC and pH but higher DO than the borehole sites. These factors could reflect chemical changes occurring in the aquifer as the water emerges at springs and becomes exposed to the atmosphere.

Figure 4.20 presents distribution maps for mean EC, pH and DO for each site in the Fergus catchment. For clarity the maps do not include the sites near Lisdoonvarna (FS15/16/19/20/21) or at Carron Turlough (FL07). See Appendix D, Table D.1 for data at these sites.

Spring EC levels in the Fergus catchment are noticeably lower than the Robe springs. The EC and pH levels at sites located on the Namurian shale are generally lower than for groundwater sites located on the Limestone. On the Limestone itself there is wide variability between sites.

The Lakes stand out with clearly higher pH, DO and lower EC than groundwater sites. The river sites also have higher DO. However, Fergus River pH and EC levels are comparable to the spring sites. This probably reflects that high degree of connectivity between the Fergus river and discharging springs and the fact that a large proportion of the total flow in the Fergus is groundwater derived. The boreholes and dug wells stand out with lowest pH, DO and highest EC levels.

Figure 4.18 Co. Limerick water chemistry distribution maps.

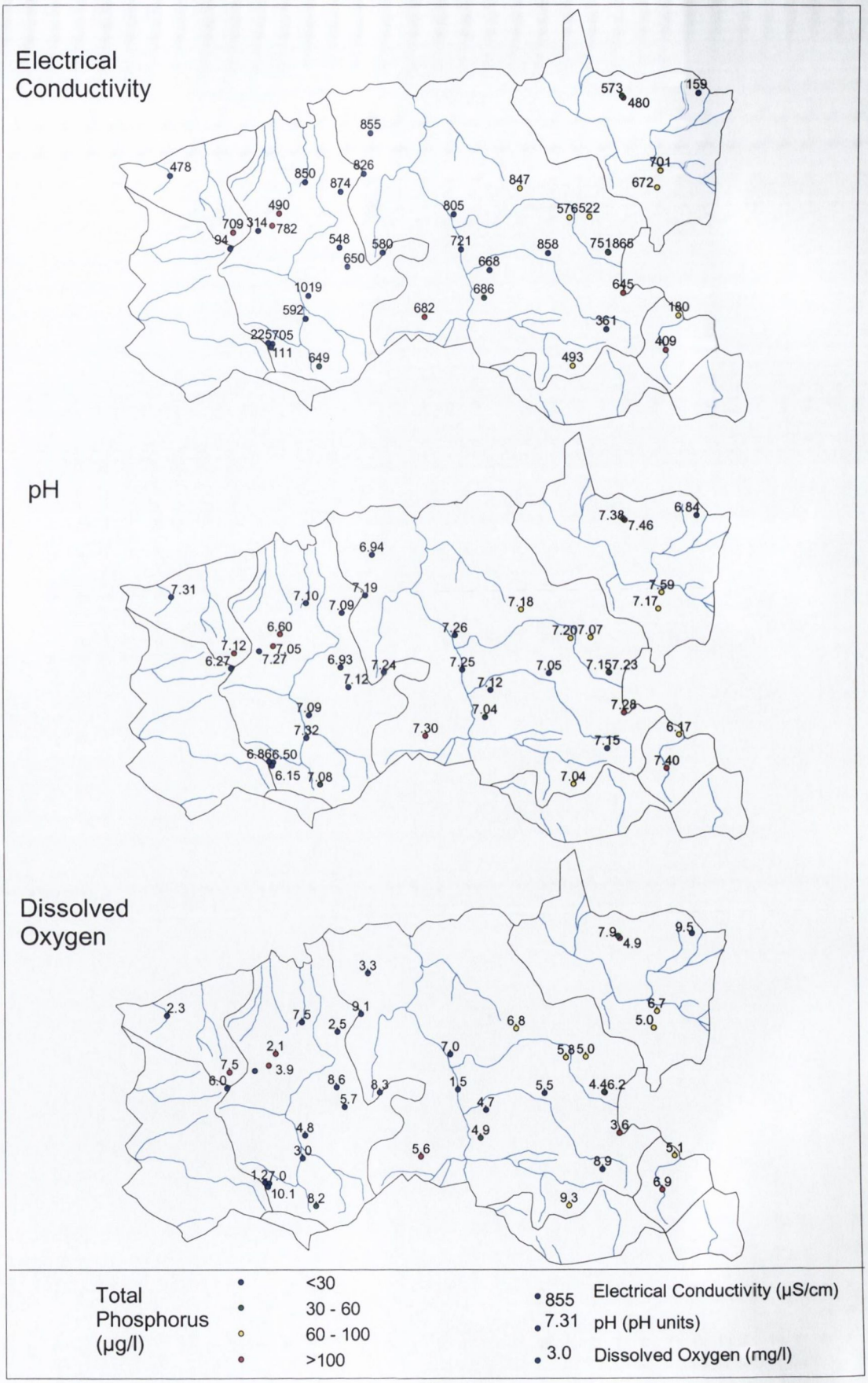


Figure 4.19 Robe catchment water chemistry distribution maps.

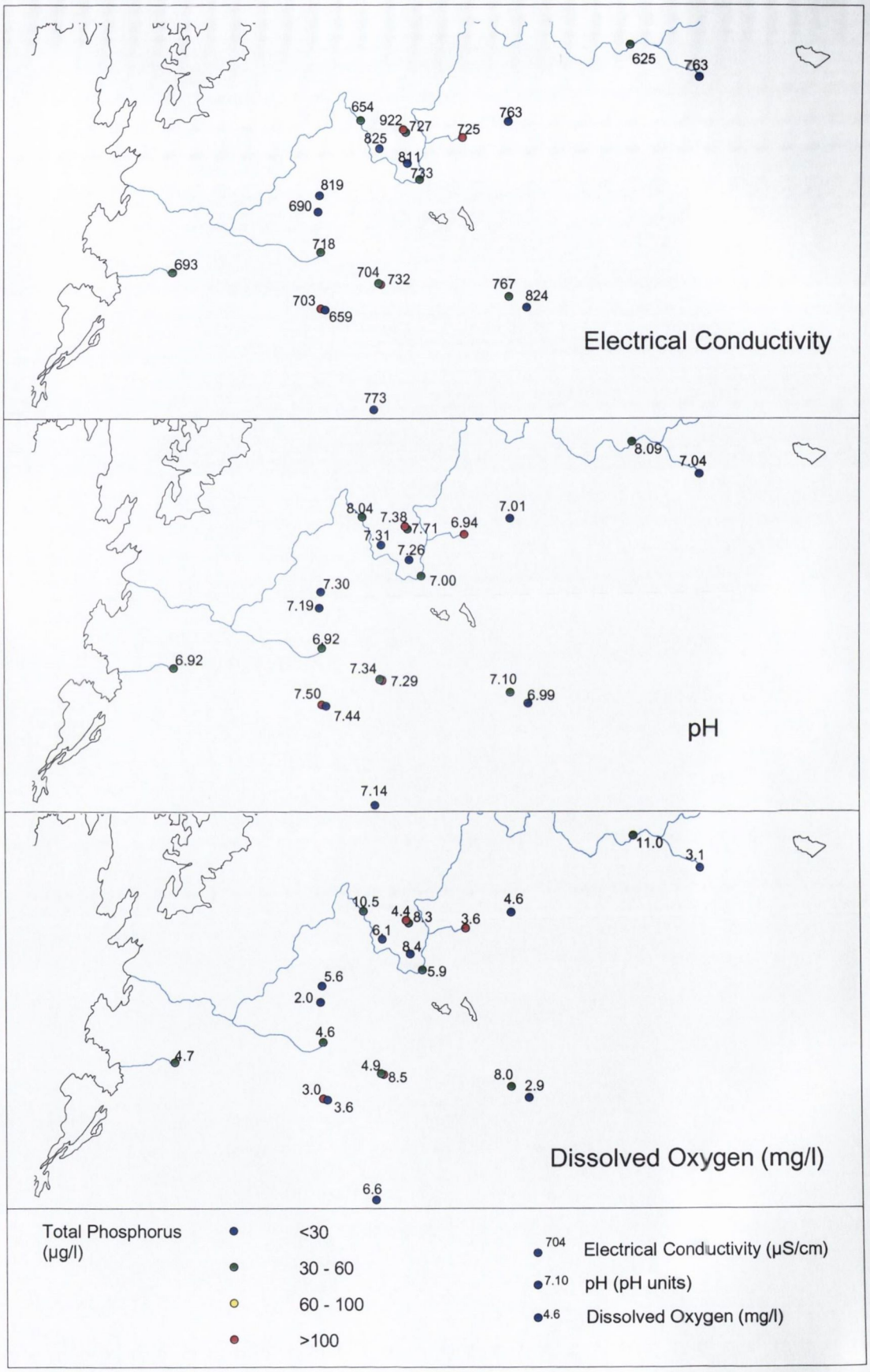
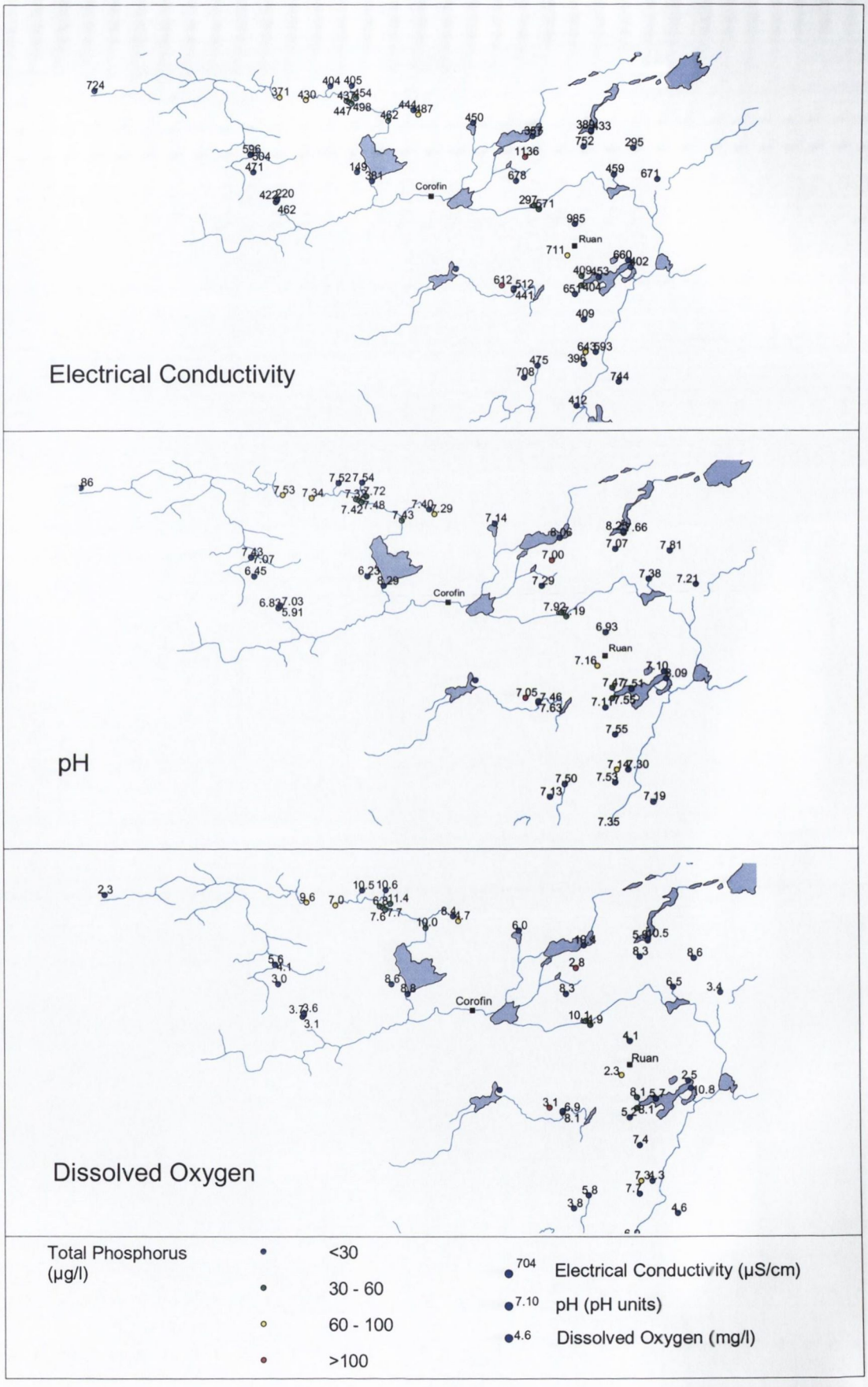


Figure 4.20 Fergus catchment water chemistry distribution maps.



## *4.6 Relationships between phosphorus fractions and other water chemistry parameters*

### 4.6.1 Introduction

Three approaches were adopted in the assessment of the influence of field water chemistry parameters on P levels. The first and second approaches examine mean total P data and mean water quality data for each site, whilst the third approaches assess the raw data only. A brief explanation of these approaches follows.

Since total P was the most commonly analysed P fraction, the first approach, which includes almost all sites, assesses the relationship between mean EC, pH, DO and TP at each site (see Section 4.6.2). The second approach focuses on sites where the three P fractions were analysed (TP, TDP and DRP) and examines their relationship with mean EC, pH and DO (see Section 4.6.3). This generally includes all the Limerick sites and the major springs of the Fergus and Robe catchments. Finally, the third approach examines the P fractions with the major anions and cations (see Section 4.6.4). This includes the major springs of the Robe and Fergus catchment and some Fergus surface waters.

Two additional assessments were carried out at the end of this chapter. Firstly, examination of the TP data was carried out using the variability of EC as a measure of vulnerability of spring and borehole sites in the Fergus and Robe catchments. Secondly, calcite and hydroxyapatite saturation indices were calculated for sites in the Robe and Fergus. Calcite saturation can be used to characterize whether a spring is fed by diffuse or conduit flow (Shuster and White, 1971). The diffuse flow systems tend to have values near saturation whereas the conduit flow systems tend to be undersaturated. It is expected that diffuse flow systems should contain less P than those fed by conduit flow. Hydroxyapatite, along with other P minerals, has been seen to control the magnitude of phosphate in septic tank plumes. Whilst, equilibrium conditions are not expected in karst systems, they may indicate evolutionary trends of water in the system. Areas of where apatite was mined in east of the Fergus catchment may yield more phosphate saturated waters.

### 4.6.2 Assessment of total phosphorus and EC, DO and Ph

#### *4.6.2.1 Electrical conductivity*

In the figures below TP has been log-transformed due to the highly skewed nature of the data. For the Fergus catchment there was a general increase in TP with EC, however this correlation was only significant ($r=0.584$, $p<0.01$) when five boreholes (FB17, FB12, FB07, FB13, and FB16) were removed (see Figure 4.21). These boreholes had the lowest mean TP levels of all boreholes in the Fergus catchment ($\leq 6\ \mu g\ l^{-1}$).

**Figure 4.21 Mean EC and Log TP in the Fergus catchment. The correlation is improved when five boreholes (open diamonds) are removed.**

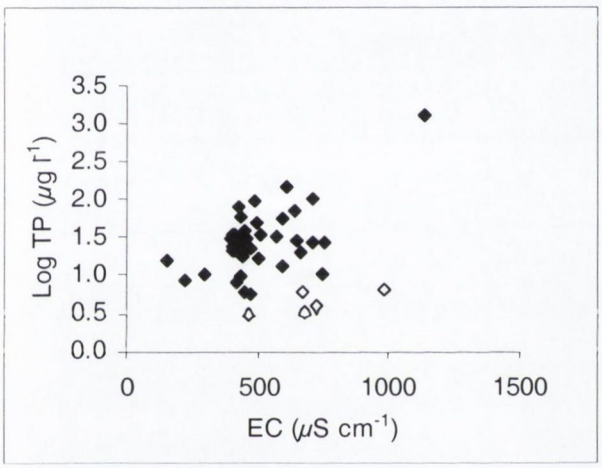



**Figure 4.22 Mean EC and Log TP in the Co. Limerick.**

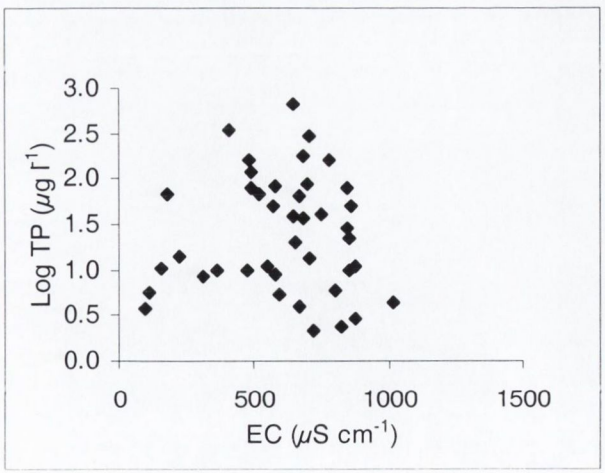
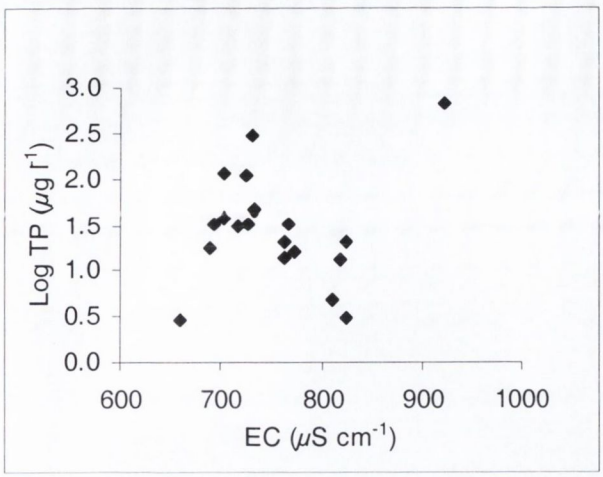


**Figure 4.23 Mean EC and Log TP in the Robe catchment.**




In Co. Limerick, there are no clear relationships between EC and TP (see Figure 4.22). This could reflect the fact that the data includes a number of catchments and a more diverse range of geologies than the Robe or Fergus.

As mentioned in Section 4.3 the Robe catchment has a much narrower EC range that the other two catchment areas. The combined data does not exhibit any clear trends (see Figure 4.23). However, when the lowest and highest EC sites (RB03 and RB07 respectively) are removed a significant negative correlation is derived ($r=-0.636$, $p<0.01$).

### *4.6.2.2 pH*

As mentioned in the introduction to this chapter, in limestone areas, such as the Fergus and the Robe one would expect quite strong buffering capacity in the water due to the high bicarbonate levels. In the Fergus catchment the majority of sites lie between 7 and 8 pH units. All sites with values below pH 7 are generally located on the Namurian Shale. There was no clear relationship between pH and total P in the Fergus data (see Figure 4.24).

In Co. Limerick, again most of the sites have a narrow mean pH range between 7 and 7.5. Sites with pH less than seven are generally located on non-limestone geology. There were no clear trends in the Limerick pH and TP data (see Figure 4.25).

The Robe had the narrowest pH range, almost only 0.5 of a pH unit (see Figure 4.26). There were no clear trends between pH and TP.

**Figure 4.24 Mean pH and Log TP in the Fergus catchment.**

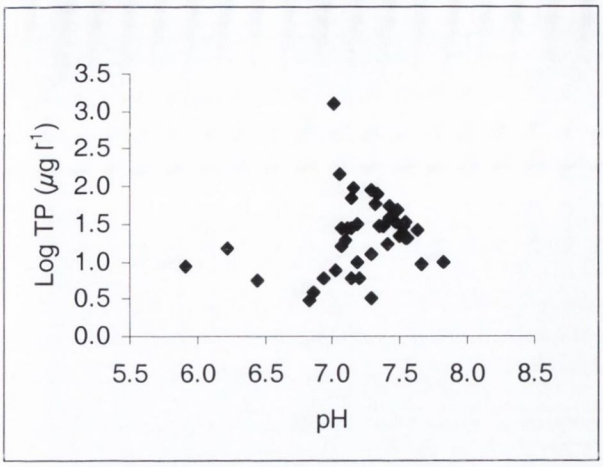



**Figure 4.25 Mean pH and Log TP in the Co. Limerick sites.**

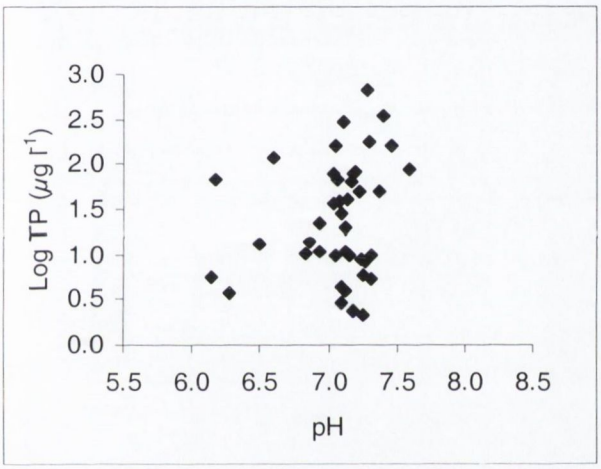
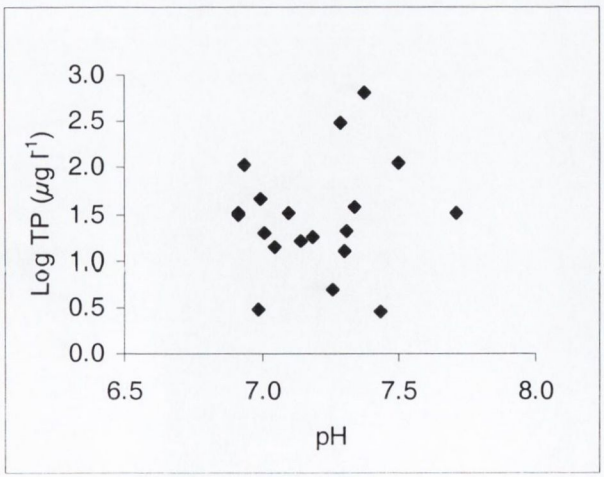



**Figure 4.26 Mean pH and Log TP in the Robe catchment.**



### 4.6.2.3 *Dissolved oxygen*

Ideally, a DO meter that is sealed from the atmosphere is required for accurate measurements. This was not practicable for this project; therefore the DO readings are only presented here for comparative purposes. As evident in Figure 4.27, there were no clear trends between mean DO and TP in the Fergus catchment. However, two distinct populations of DO levels are apparent (see Figure 4.28). The first, with levels less than 6 mg $l^{-1}$ DO, comprised mainly of boreholes. In this group, excluding three extreme TP values (FB06, FB03 and FB14), there is a significant positive correlation ($r=0.602$, $p<=0.01$). The second group, with levels greater than 6 mg $l^{-1}$ DO, comprised mainly of springs. In this second group, excluding two TP values close to the limit of detection (FB12 and FS12), there is a significant negative correlation ($r=-0.521$, $p<0.05$).

**Figure 4.27 Mean DO and Log TP in the Fergus catchment.**

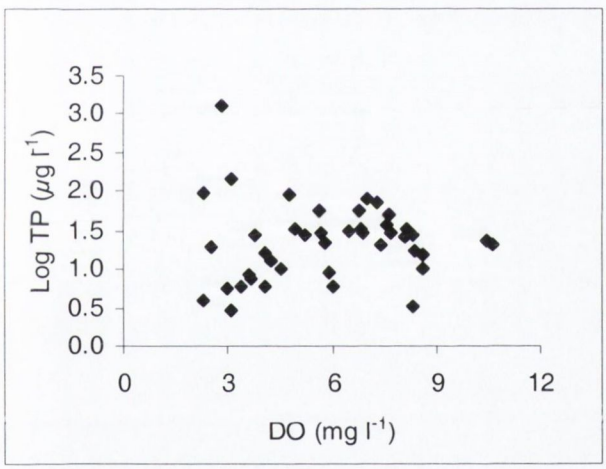
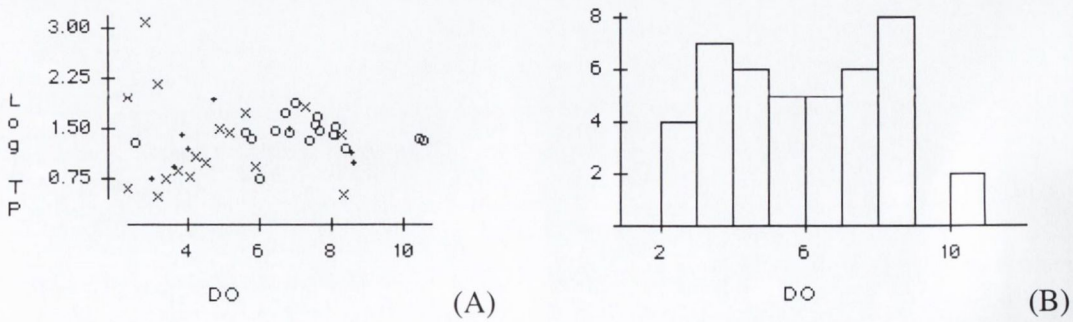
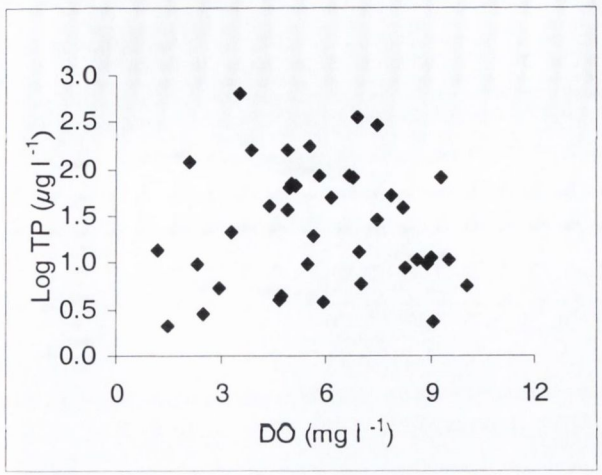



**Figure 4.28 (A) As above Figure with boreholes (x) springs (o) and dug wells (+). (B) DO frequency distribution histogram.**



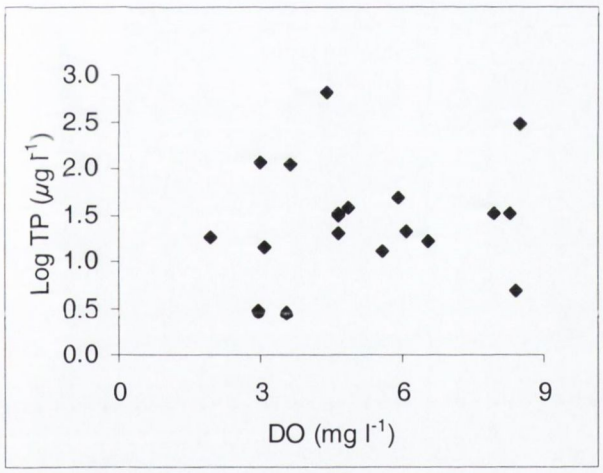

There were no clear relationships with DO and TP in the Limerick sites (see Figure 4.29).

**Figure 4.29 Mean DO and Log TP in the Limerick catchment.**




The Robe catchment did not exhibit any clear relationship between DO and TP, other than the fact that the two lowest TP levels had low DO concentrations (see Figure 4.30).

**Figure 4.30 Mean DO and Log TP in the Robe catchment.**




### 4.6.3 Assessment of phosphorus fractions and EC, DO and pH at selected sites in each catchment.

In this section fewer sites are examined, but advantage is taken of the fact that several forms of phosphorus were analysed. All three catchment areas are included in this analysis.

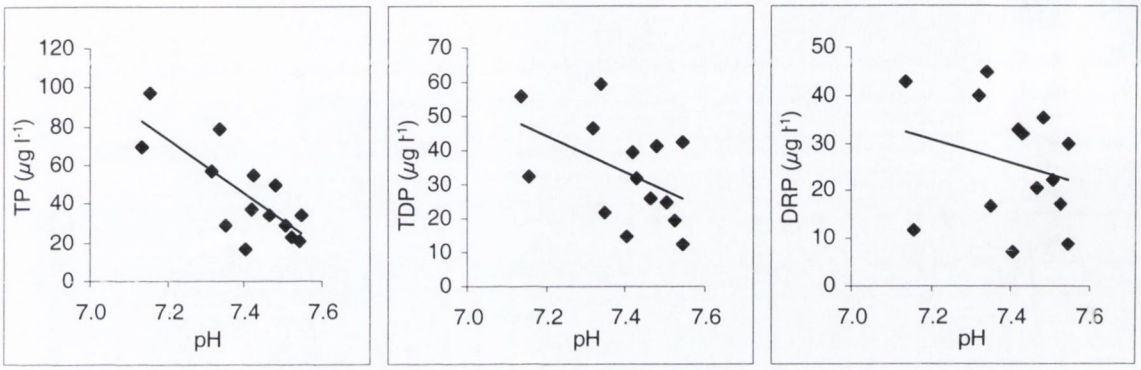
#### *4.6.3.1 Fergus catchment*

The Fergus sites examined are all the springs from Figure 4.10, plus FS04, plus three boreholes (FB06, FB11 and FB01).

*pH*

All three phosphorus fractions in the Fergus catchments exhibited general negative trends with pH (see Figure 4.31). However only TP and pH had a significant correlation ($r=-0.764$, $p<0.01$).

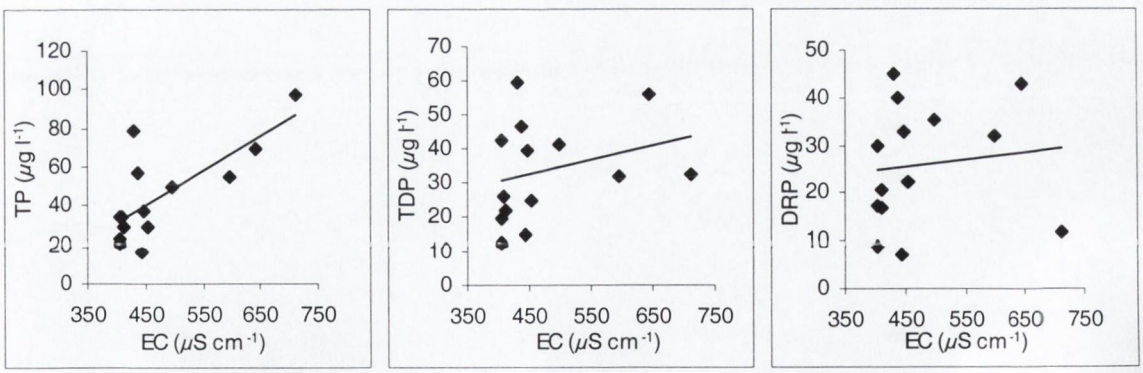
**Figure 4.31 Mean TP, TDP, DRP and pH at selected sites in the Fergus catchment. Regression lines shown.**




*ELECTRICAL CONDUCTIVITY*

There was a general positive trend between EC and TP ($r=0.746$, $p<0.01$). However, as evident in Figure 4.32 there was no significant correlation between TDP or DRP and EC

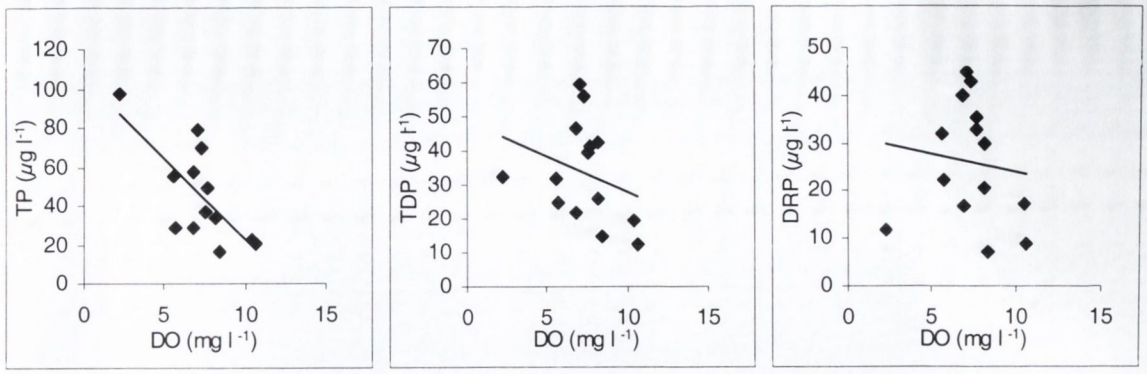
**Figure 4.32 Mean TP, TDP, DRP and EC at selected sites in the Fergus catchment. Regression lines shown.**




*DISSOLVED OXYGEN*

There was a general negative trend between the P fractions and DO (see Figure 4.33). As above, only the TP and DO correlation was statistically significant ($r=-7.25$, $p<0.01$).

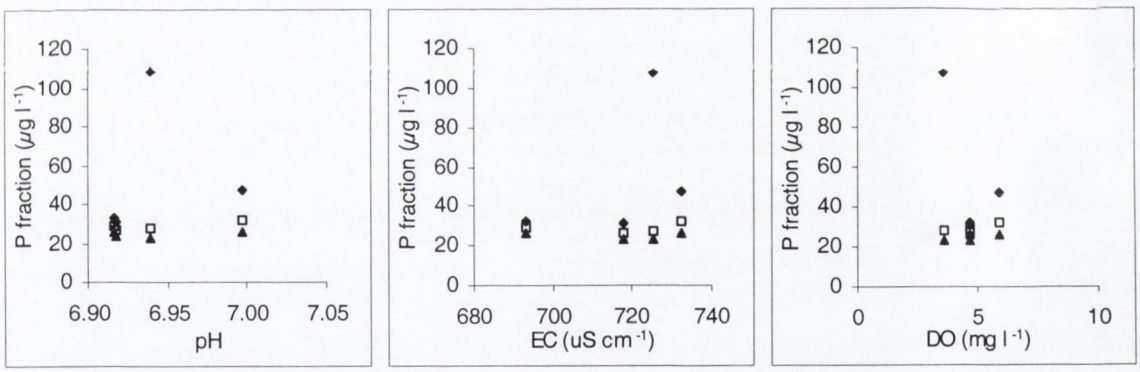
**Figure 4.33 Mean TP, TDP, DRP and DO at selected sites in the Fergus catchment.**




### 4.6.3.2 *Robe catchment*

Due to the small number of sites with sufficient numbers of P fraction analyses all fractions are plotted together for each field parameter (see Figure 4.34). There were no significant relationships on account of the small sample size. The outlier TP value in each graph is from RS06, its elevated value for this fraction is due to a pollution event which increased the particulate load to the spring dramatically.

**Figure 4.34 Mean TP, TDP and DRP with pH, EC and DO. (TP = diamonds, TDP = squares, DRP = triangles).**



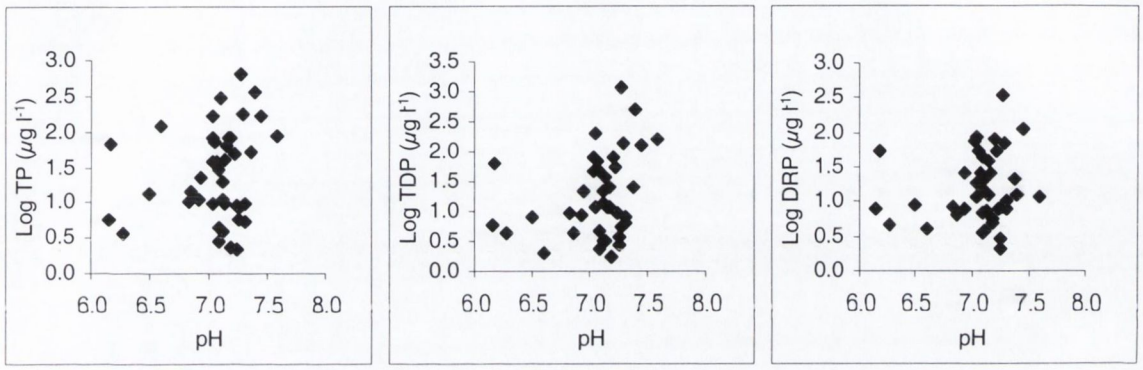

### 4.6.3.3 *Limerick catchments*

As mentioned above the sites in Co. Limerick incorporated several catchments and more disparate geologies than the Fergus or Robe, and were not sampled as regularly.

*pH*

Five sites stand out with pH values of 6.6 or less (see Figure 4.35). All these sites are located on non-limestone geology where the buffering capacity would not be as effective as sites on limestone. The other sites exhibit strong buffering and are grouped between a narrow pH range. There are no clear trends between each of the P fractions and pH.

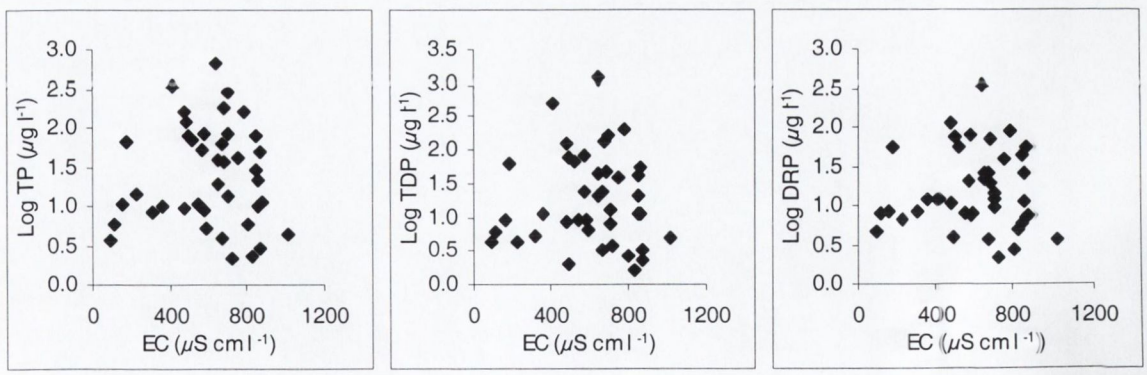
**Figure 4.35 Mean TP, TDP, DRP and pH at the Co. Limerick sites.**




*ELECTRICAL CONDUCTIVITY*

It is not unexpected that a wide range of conductivities would be found in Co. Limerick given the variety of geologies. Figure 4.36 clearly illustrates this with EC ranging from approximately 100 – 1000 $\mu$S cm$^{-1}$. At the lower end of this range there appears to be a positive relationship at least with TP, but otherwise no clear trends are apparent.

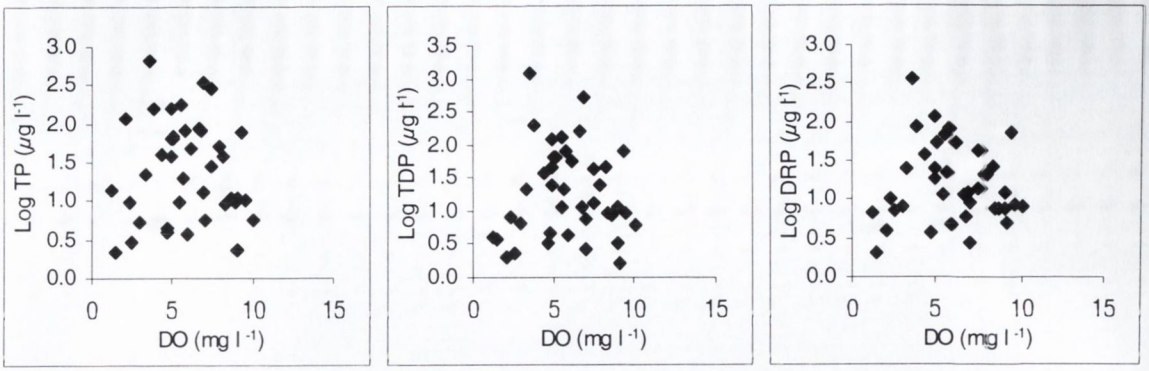
**Figure 4.36 Mean TP, TDP, DRP and EC at the Co. Limerick sites.**




*DISSOLVED OXYGEN*

There is a large range of DO values between 0 and 10 mg l$^{-1}$ (see Figure 4.37). No clear relationships between DO and P fractions are apparent.

**Figure 4.37 Mean TP, TDP, DRP and DO at the Co. Limerick sites.**




### 4.6.4 Phosphorus fractions and major ions at selected sites in the Fergus catchments.

This section examines the relationships between the major ions and P fractions. In February 1999 and June 1999 (see Table D.5, Appendix D) selected sites of the Fergus catchment were analysed for the major anions and cations. In September 1999 (see Table D.6) the major anions and cations were analysed for the major springs of the Robe and Fergus catchment and some surface waters of the Fergus catchment. Figure 4.10 shows the locations of these sites. Total P was only analysed for in February 1999, and TP, TDP and DRP were analysed for in June and September 1999.

Best correlations were achieved in the September 1999 run when the Robe sites were omitted. The September 1999 TP value for FS09 was uncharacteristically high (217 $\mu g\ l^{-1}$) and was thus omitted from this analysis. As seen in Figure 4.17, the water chemistry of the FB11 borehole is divergent from the norm in the Fergus catchment. Omitting FB11 improved the correlations. Excluding these sites, Pearson Product-Moment correlations were calculated for each sampling run (see Table 4.7, Table 4.8 and Table 4.9).

**Table 4.7 Pearson Product-Moment correlations for TP and major ions in the Fergus catchment in February 1999. (Bold = p<0.05; Bold+underline = p<0.01).**

| | TP | pH | Temp | EC | DO | K/Na | Ca | Na | Mg | K | Cl | NO3 | SO4 | HCO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TP | 1 | | | | | | | | | | | | | |
| pH | -0.39 | 1 | | | | | | | | | | | | |
| Temp | -0.65 | -0.05 | 1 | | | | | | | | | | | |
| EC | -0.56 | -0.29 | **0.89** | 1 | | | | | | | | | | |
| DO | -0.28 | **0.87** | -0.26 | -0.48 | 1 | | | | | | | | | |
| K/Na | 0.60 | -0.59 | -0.53 | -0.23 | -0.30 | 1 | | | | | | | | |
| Ca | -0.71 | 0.08 | 0.63 | 0.65 | 0.19 | -0.07 | 1 | | | | | | | |
| Na | **0.79** | -0.11 | **-0.79** | **-0.89** | 0.16 | 0.43 | -0.66 | 1 | | | | | | |
| Mg | **0.92** | -0.39 | -0.64 | -0.49 | -0.36 | 0.43 | **-0.81** | 0.67 | 1 | | | | | |
| K | **0.82** | -0.44 | **-0.77** | -0.62 | -0.11 | **0.88** | -0.41 | **0.81** | 0.66 | 1 | | | | |
| Cl | **0.77** | -0.11 | -0.24 | -0.19 | -0.22 | 0.23 | -0.49 | 0.36 | 0.74 | 0.36 | 1 | | | |
| NO3 | -0.53 | -0.23 | **0.91** | **0.98** | -0.46 | -0.25 | 0.62 | **-0.88** | -0.50 | -0.63 | -0.10 | 1 | | |
| SO4 | 0.25 | -0.65 | 0.40 | 0.56 | -0.56 | 0.41 | 0.36 | -0.18 | 0.15 | 0.18 | 0.42 | 0.56 | 1 | |
| HCO3 | -0.66 | 0.06 | 0.51 | 0.53 | 0.26 | 0.02 | **0.99** | -0.54 | **-0.78** | -0.29 | -0.54 | 0.49 | 0.32 | 1 |

**Table 4.8 Pearson Product-Moment correlations for P fractions and major ions in the Fergus in June 1999. (Bold = p<0.05; Bold+underline = p<0.01).**

| | TP | TDP | DRP | pH | Temp | EC | DO | K/Na | Ca | Na | Mg | K | Cl | NO3 | SO4 | HCO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TP | 1 | | | | | | | | | | | | | | | |
| TDP | **0.93** | 1 | | | | | | | | | | | | | | |
| DRP | **0.74** | **0.94** | 1 | | | | | | | | | | | | | |
| pH | -0.53 | -0.57 | -0.55 | 1 | | | | | | | | | | | | |
| Temp | -0.21 | -0.51 | **-0.71** | 0.40 | 1 | | | | | | | | | | | |
| EC | 0.44 | **0.71** | **0.85** | -0.49 | **-0.88** | 1 | | | | | | | | | | |
| DO | **-0.73** | **-0.79** | **-0.77** | 0.62 | 0.23 | -0.44 | 1 | | | | | | | | | |
| K/Na | 0.62 | 0.52 | 0.40 | -0.43 | 0.14 | 0.26 | -0.58 | 1 | | | | | | | | |
| Ca | 0.23 | 0.52 | **0.71** | -0.50 | **-0.94** | **0.92** | -0.25 | 0.11 | 1 | | | | | | | |
| Na | **0.81** | 0.59 | 0.29 | -0.17 | 0.14 | 0.02 | -0.25 | 0.37 | -0.16 | 1 | | | | | | |
| Mg | **0.86** | **0.68** | 0.41 | -0.24 | 0.02 | 0.14 | -0.32 | 0.45 | -0.02 | **0.98** | 1 | | | | | |
| K | **0.84** | 0.66 | 0.42 | -0.40 | 0.15 | 0.21 | -0.53 | **0.89** | 0.01 | **0.75** | **0.79** | 1 | | | | |
| Cl | **0.70** | 0.51 | 0.26 | 0.04 | 0.29 | -0.06 | -0.23 | 0.42 | -0.27 | **0.91** | **0.89** | **0.71** | 1 | | | |
| NO3 | -0.53 | -0.29 | -0.01 | -0.17 | -0.49 | 0.34 | 0.14 | -0.15 | 0.57 | **-0.83** | **-0.75** | -0.49 | **-0.90** | 1 | | |
| SO4 | **0.66** | **0.80** | **0.84** | -0.37 | -0.53 | **0.80** | -0.50 | 0.62 | 0.67 | 0.36 | 0.49 | 0.59 | 0.43 | -0.04 | 1 | |
| HCO3 | 0.28 | 0.55 | 0.72 | -0.53 | **-0.95** | **0.92** | -0.26 | 0.12 | **1.00** | -0.09 | 0.05 | 0.05 | -0.24 | 0.54 | 0.67 | 1 |

**Table 4.9 Pearson Product-Moment correlations for P fractions and major ions in the Fergus in September 1999. (Bold = p<0.05; Bold+underline = p<0.01).**

| | TP | TDP | DRP | pH | Temp | EC | DO | K/Na | Ca | Na | Mg | K | Cl | NO3 | SO4 | HCO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TP | 1 | | | | | | | | | | | | | | | |
| TDP | **0.82** | 1 | | | | | | | | | | | | | | |
| DRP | **0.67** | **0.96** | 1 | | | | | | | | | | | | | |
| pH | **-0.63** | **-0.72** | **-0.65** | 1 | | | | | | | | | | | | |
| Temp | -0.19 | **-0.62** | **-0.76** | 0.49 | 1 | | | | | | | | | | | |
| EC | 0.45 | **0.74** | **0.83** | -0.38 | -0.64 | 1 | | | | | | | | | | |
| DO | 0.10 | -0.03 | -0.04 | -0.31 | -0.32 | -0.12 | 1 | | | | | | | | | |
| K/Na | **0.58** | 0.31 | 0.10 | -0.52 | 0.18 | -0.26 | 0.45 | 1 | | | | | | | | |
| Ca | 0.30 | **0.67** | **0.81** | -0.28 | **-0.73** | **0.97** | -0.08 | -0.37 | 1 | | | | | | | |
| Na | **0.62** | 0.35 | 0.16 | -0.14 | 0.44 | 0.27 | -0.32 | 0.36 | 0.06 | 1 | | | | | | |
| Mg | **0.62** | 0.49 | 0.32 | -0.37 | 0.25 | 0.39 | -0.26 | 0.44 | 0.19 | **0.93** | 1 | | | | | |
| K | **0.70** | 0.33 | 0.08 | -0.38 | 0.44 | -0.07 | 0.03 | **0.82** | -0.27 | **0.81** | **0.80** | 1 | | | | |
| Cl | 0.48 | 0.29 | 0.08 | -0.07 | 0.44 | 0.12 | -0.45 | 0.39 | -0.08 | **0.85** | **0.81** | **0.75** | 1 | | | |
| NO3 | 0.22 | **0.67** | **0.83** | -0.36 | **-0.95** | **0.77** | 0.09 | -0.30 | **0.87** | -0.32 | -0.16 | -0.45 | -0.34 | 1 | | |
| SO4 | **0.71** | **0.67** | 0.56 | -0.26 | -0.04 | **0.67** | -0.25 | 0.20 | 0.52 | **0.86** | **0.85** | **0.59** | **0.72** | 0.19 | 1 | |
| HCO3 | 0.27 | **0.61** | **0.77** | -0.25 | **-0.74** | **0.95** | -0.03 | -0.42 | **0.99** | 0.02 | 0.14 | -0.32 | -0.15 | **0.85** | 0.47 | 1 |

The key trends in these correlations can be summarized into relationships within the ions (excluding P), relationships between the ions and each of the P fractions, and relationships between P fractions and the field parameters.

In the first case, alkalinity (as $HCO_3^-$) was strongly correlated with calcium all three runs. EC was strongly correlated with calcium in the June and September runs, but with sodium in the February run. The relationship between EC/alkalinity and calcium are expected given the dominance of limestone in these aquifers. The relationship between sodium and TP in February 1999 may reflect periods when recharge to the aquifer involves greater interaction with the Namurian Shale.

Several strong relationships were present between ions and the P fractions. TP was significantly correlated (positive) to sodium, magnesium and potassium in all three runs. TP was positively correlated with sodium/potassium ratios in all three runs, but these relationships were only significant in the September run. Nitrate was only correlated (positive) with DRP and TDP in the June run. Sulphate was significantly correlated (positive) with TDP in both the June and September runs, and with DRP in June only.

Calcium was significantly correlated (positive) with DRP in both runs, and with TDP in June only.

The field parameters (pH, DO and EC) also yielded some interesting relationships. All P fractions were negatively correlated with pH, but these relationships were only significant in the September run. DO was only significantly correlated (negative) with all fractions in the June run. EC was significantly correlated (positive) with TDP and DRP, but not TP.

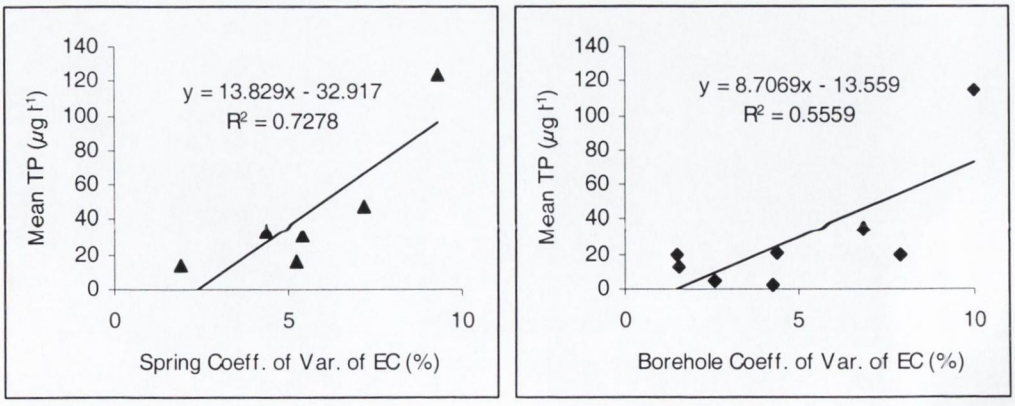
### 4.6.5 Coefficient of variation of EC and TP

As introduced in Section 4.1, coefficients of variation (CV) of EC can relate the nature of the underground flow system feeding a groundwater source. Sites with a large EC variation (and subsequently a large coefficient of variation percentage) are likely to have a shorter underground residence time (Coxon, 1995).

CVs of EC were calculated for both springs and boreholes in the Robe and Fergus catchments. Table C.1, Appendix C, presents the calculations of these data. Only sites with at least three EC/TP values were included in this analysis. Two boreholes, RB02 and FB03, had grossly elevated mean TP values (300 $\mu g\ l^{-1}$ and 1186 $\mu g\ l^{-1}$ respectively), and were omitted from this analysis.

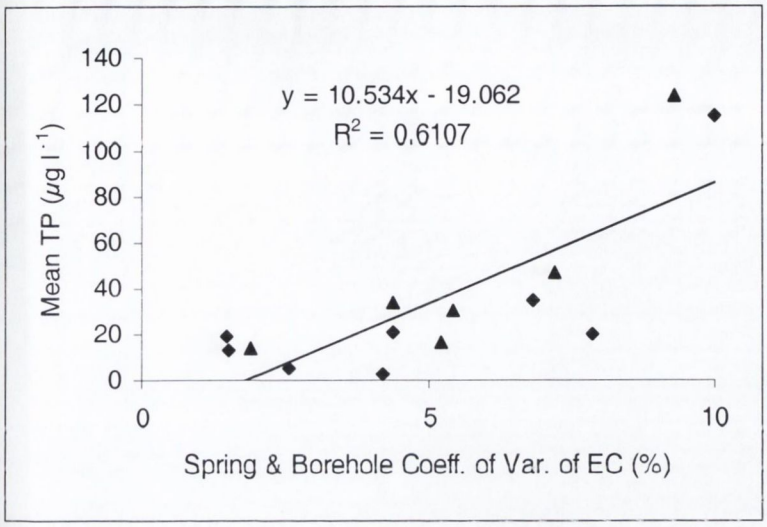
Significant positive relationships were found between coefficients of EC variation and TP for both springs and boreholes in the Robe catchment (see Figure 4.38).

**Figure 4.38 Coefficient of variation of EC and TP for Robe Springs and Boreholes.**



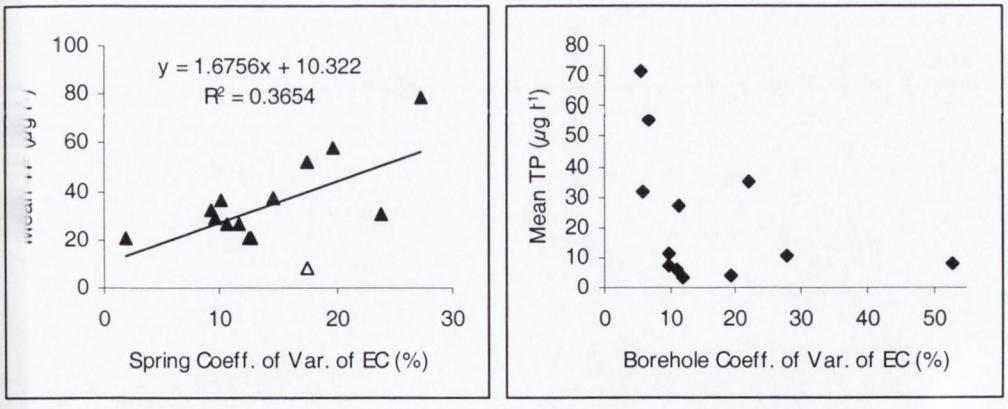

Combining boreholes and springs in the Robe (see) also yielded a significant positive relationship (p=0.001).

**Figure 4.39 Coefficient of variation of EC and TP for combined Robe Springs (▲) and Boreholes (◆).**



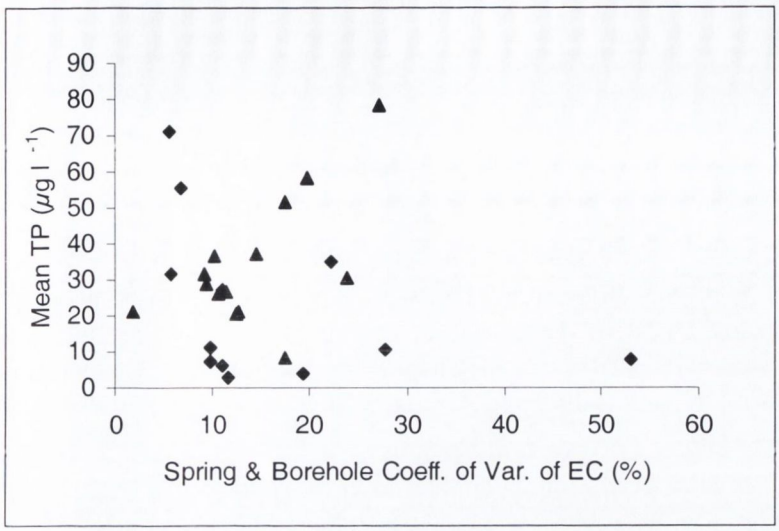

In the Fergus catchment, the springs yielded significant positive relationships, but the boreholes did not (see Figure 4.40). The clear triangle in the spring graph is FS12, which had very low mean TP levels (8 $\mu g\ l^{-1}$). If this point is removed, the $R^2$ value improves to 0.4. It is also noticeable that the range of the EC coefficients of variation in the Fergus catchment (0-50%) is much wider than that of the Robe catchment (0-10%).

**Figure 4.40 Coefficient of variation of EC and TP for Fergus Springs and Boreholes.**




Combining spring and borehole data does not improve any relationships (see Figure 4.41).

**Figure 4.41 Coefficient of variation of EC and TP for combined Fergus springs (▲) and boreholes (◆).**




### 4.6.6 Saturation Indices of Calcite and Hydroxyapatite.

Saturation indices (SI) are an estimate of the state of saturation of a water with respect to a given mineral. SI's can be expressed as Log (IAP/K), where IAP is the ion activity product and K is the solubility product for the mineral at a given temperature. A solution is said to in equilibrium with respect to a given mineral if Log (IAP/K) = 0, supersaturated if Log (IAP/K)>0 and under saturated if Log (IAP/K)<0. IAP can be calculated manually using water chemistry data (Fetter, 2001) or by the using geochemical modelling packages such as PHREEQE (Parkhurst, 1985).

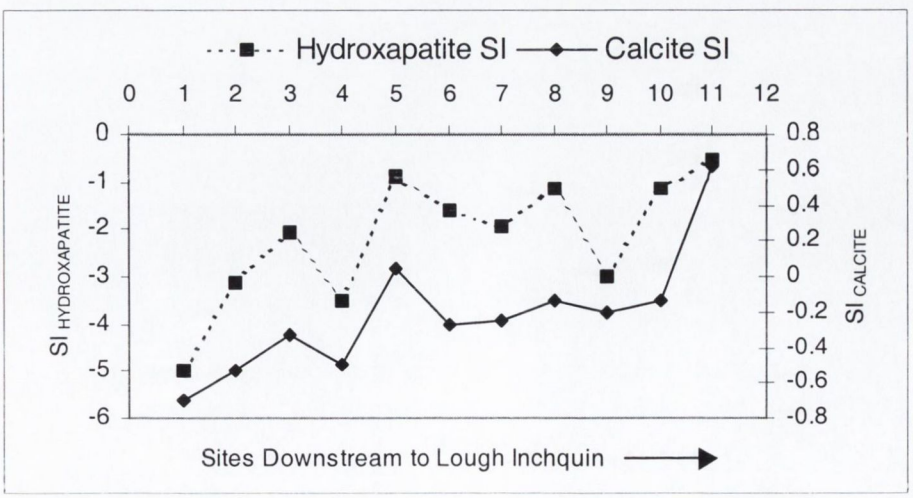
Calcite saturation is particularly important in limestone aquifers in that it estimates the degree to which the water is dissolving or precipitating calcium carbonate. Hydroxyapatite is one of the main the calcium phosphate minerals. Several authors have examined the importance of hydroxyapatite in controlling groundwater movement of P (see Introduction chapter). Table 4.10 lists the calcite and hydroxyapatite saturation indices (SI) as calculated by PHREEQC using the data listed in Table A.4. Overall, the Robe springs are a lot closer to calcite equilibrium than the Fergus sites. All sites were undersaturated with respect to hydroxyapatite.

**Table 4.10 Calcite and hydroxyapatite saturation indices for Fergus and Robe sites.**

| *Site Name* | *Sampled* | *Catchment* | *Site Type* | *Calcite SI* | *Hydroxapatite SI* |
|---|---|---|---|---|---|
| FB11 (1) | 05/10/99 | Fergus | Borehole | -0.7 | -4.99 |
| FR01 (2) | 06/09/99 | Fergus | Sink | -0.53 | -3.11 |
| FS17 (3) | 06/09/99 | Fergus | Spring | -0.33 | -2.08 |
| FS03 (4) | 06/09/99 | Fergus | Spring | -0.5 | -3.49 |
| FR02 (5) | 06/09/99 | Fergus | River | 0.05 | -0.88 |
| FS05 (6) | 06/09/99 | Fergus | Spring | -0.27 | -1.61 |
| FS06 (7) | 06/09/99 | Fergus | Spring | -0.25 | -1.94 |
| FS07 (8) | 06/09/99 | Fergus | Spring | -0.13 | -1.15 |
| FS09 (9) | 06/09/99 | Fergus | Spring | -0.2 | -3.01 |
| FR03 (10) | 06/09/99 | Fergus | River | -0.14 | -1.14 |
| FLO3 (11) | 06/09/99 | Fergus | Lake | 0.62 | -0.56 |
| FS13 | 12/09/99 | Fergus | Spring | -0.38 | -2.0 |
| FS14 | 12/09/99 | Fergus | Spring | -0.29 | -1.5 |
| FS18 | 12/09/99 | Fergus | Spring | -0.29 | -1.97 |
| RS06 | 04/09/99 | Robe | Spring | -0.15 | -4.74 |
| RS01 | 04/09/99 | Robe | Spring | -0.06 | -2.85 |
| RS04 | 04/09/99 | Robe | Spring | -0.09 | -2.64 |
| RS03 | 04/09/99 | Robe | Spring | -0.21 | -2.95 |

The Fergus and Robe sites in this table are ordered in their position downstream of the catchment. For the Fergus catchment this order is maintained in Figure 4.42 downstream to Lough Inchquin (FL03). From the FB11 to the east of the catchment there is a steady increase in the Calcite SI at the groundwater sites until Lough Inchquin is reached and the water is supersaturated with respect to calcite. A similar trend is apparent for the hydroxyapatite SI's.

**Figure 4.42 Calcite and hydroxyapatite saturation indices in the Fergus catchment downstream to Lough Inchquin (see Table 4.10 for codes of sites).**



The relationship between these two minerals are further examined in Figure 4.43. Lough Inchquin has been omitted and the regression lines refer to the Fergus sites only. A plot of hydroxyapatite versus calcite is presented in Figure 4.43 (A). There is a clear positive relationship between the two minerals. The RSO6 spring has clearly lower hydroxyapatite than the other Robe springs, probably reflecting the impact of the pollution event which occurred just previous to when the sample was taken (see Section 6.5.2). Figure 4.43 (B) indicates that the dissolution of hydroxyapatite is strongly pH dependent.

**Figure 4.43 Fergus (◆)and Robe (▲) sites plotting (A) Calcite versus hydroxyapatite saturation indices and (B) hydroxyapatite versus pH. RS06 (△).**

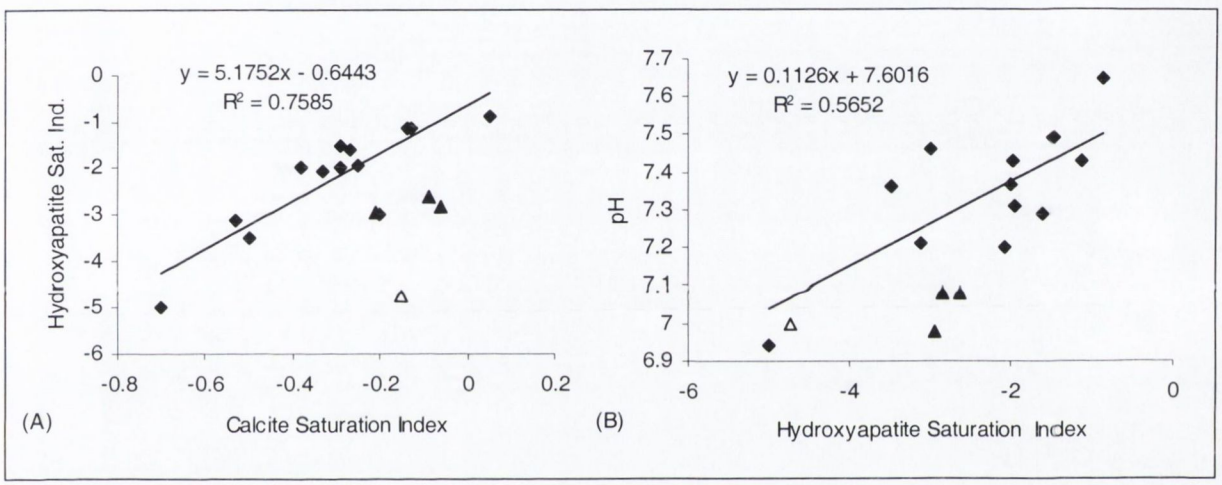
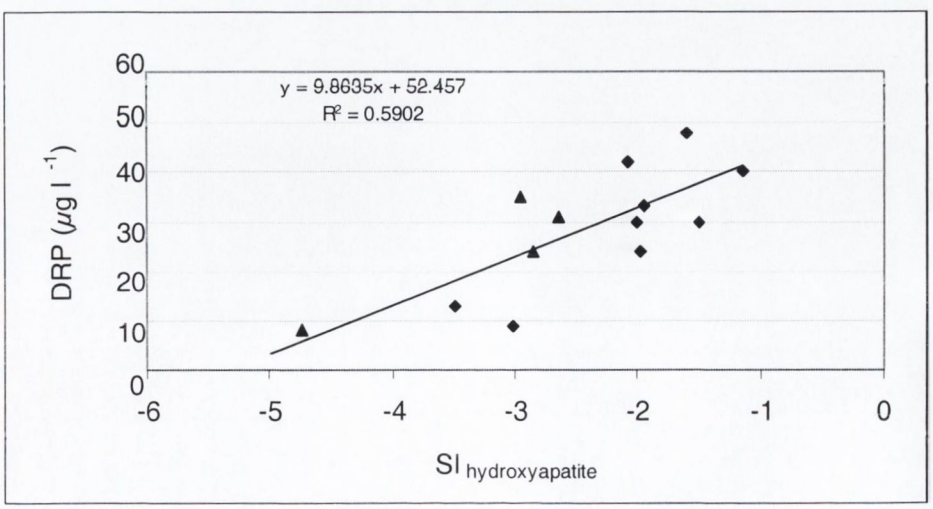



Figure 4.44 plots the saturation index (SI) for hydroxyapatite against dissolved reactive P for the Fergus and Robe springs.

**Figure 4.44 Dissolved reactive P (DRP) and hyroxyapatite saturation indices for Robe (▲) and Fergus (◆) springs.**



The surface water sites and FB11 borehole have been removed from this analysis so as to focus solely on the springs. The springs from these two catchments exhibit a significant positive relationship (p=0.0022) with DRP increasing as the SIs for hydroxyapatite increases.

## *4.7 Discussion*

### 4.7.1 Total phosphorus concentrations

Overall, the distribution of TP in the three catchment areas was highly skewed and the concentrations were generally low. However, some 44% of the data exceed the river eutrophication threshold (30 $\mu g\ l^{-1}$ unf. MRP; McGarrigle, 1998). 58% of the data is greater than the lake eutrophication threshold (20 $\mu g\ l^{-1}$ TP; Champ, 1998). Mean total P data varied considerably between catchments and site types. In general, boreholes had high mean values and low median values and high standard errors, due to the mean being dramatically increased by a few grossly elevated sites. In contrast the mean and median of springs compared well and had low standard errors. The TP at dug wells of the Robe and Fergus catchments also had low standard errors. Only the dug wells of the Limerick and Robe catchments showed good comparison between mean and median, although this is probably simply an artifact of small sample size. The Limerick groundwater median TP levels are very low at the springs (8.1 $\mu g\ l^{-1}$) but close to eutrophication thresholds at the boreholes (37.5 $\mu g\ l^{-1}$). Median TP levels at the Fergus boreholes and dug wells were very low (11.3 and 16.2 $\mu g\ l^{-1}$ respectively) however, the springs were higher (28.8 $\mu g\ l^{-1}$). Similarly in the Robe catchment median TP levels for boreholes and dug wells (20.7 and 17.9 $\mu g\ l^{-1}$ respectively) were lower than for springs (31.7 $\mu g\ l^{-1}$).

### 4.7.2 Phosphorus fractions in groundwater

Clearly TDP and DRP comprised the majority of TP. Therefore, it would seem that dissolved forms of P are the dominant P fraction in these groundwaters. However, it is acknowledged that this statement is restricted to the dissolved forms dictated by the methods adopted. Therefore, as mentioned in Section 1.4, these dissolved forms may or may not include colloidal P or particulate P less than 0.45 $\mu m$. Nonetheless, in situations where groundwater P is contributing to surface water loading, it is doing so in the form most readily taken up by plants. In Irish lakes TP is usually higher in winter and lower in

summer (Gibson *et al.*, 1996). This concurs with a recent assessment of eleven Irish lakes where lowest median TP levels (12 $\mu g\ l^{-1}$) occurred in July and August (EPA, 2001). This coincides with when groundwater contribution to rivers and lakes is highest. Therefore, the form of P in groundwater will be important. This is discussed in further detail in Chapter Eight. The karst aquifers (Robe and Fergus) had higher DRP, DOP and PP levels than the non-karstic Limerick aquifers. This could reflect the influence of point recharge from surface waters via swallow holes, combined with less attenuation of P in karst systems due to rapid conduit flow. Springs had more PP than wells probably due to more turbulent flow.

### 4.7.3 Groundwater type and its influence on phosphorus levels

The trilinear diagrams indicated that Ca-$HCO_3$ was the main water type in each catchment. Limestone was clearly the dominant geological influence on the water chemistry in the Robe and Fergus catchment. Whilst the geologies in Limerick were more varied, limestone was also the main controlling geology. The linear relationships between $Na^+/Cl^-$ and $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ indicate that neither ion exchange nor sulphate reduction are complicating the carbonate chemistry and that simple solution is the main process (Lloyd and Heathcote, 1985).

The majority of the groundwater sites have pH values close to neutral. The surface water sites of the Robe and Fergus catchments have slightly more alkaline pH due to greater equilibrium with atmospheric $CO_2$. The springs of the Limerick and Robe catchments have slightly more acidic waters (mean pH of 6.89 and 6.99 respectively) than the Fergus springs (mean pH of 7.43). This could reflect the highly karstic nature of the Fergus catchment and greater influence of surface waters via point recharge.

Groundwater electrical conductivity (EC) in boreholes was quite variable in the Limerick and Fergus catchments (180-874 and 422-1136 $\mu S\ cm^{-1}$ respectively). This would reflect the range of geologies in Co. Limerick and the high degree of karstification in the Fergus catchment (and adjacent shales). The Robe boreholes had a much narrower EC range (659-922 $\mu S\ cm^{-1}$) possibly due to less karstification and thus less direct impact of recharge. The Robe catchment has a paucity of allogenic recharge, deriving all its recharge from limestone rocks unlike the other catchment areas. So even where point recharge exists

along highly karstified routes, the EC is likely to be higher than with point recharge in the Fergus catchment originating on the shale.

Groundwater dissolved oxygen (DO) levels were lowest in the boreholes except for the Robe catchment where the springs had slightly higher DO than the boreholes (mean DO of 4.75 and 5.39 mg $l^{-1}$ respectively). As expected the surface waters sampled in the Robe and Fergus catchments all had mean DO levels greater than 10 mg $l^{-1}$.

### 4.7.4 The influence of specific chemical parameters on groundwater phosphorus

Several approaches were adopted to analyse the influence of water chemistry parameters on phosphorus in groundwater. Total P was the most commonly analysed P fraction and therefore offered greatest scope for using all site data. There was a general increase in TP as EC increased in the Fergus catchment, but no clear trend emerged in the other catchments. Examination of the P fractions only yielded clear trends in the Fergus catchment. Overall TP increased as pH and EC increased and as DO decreased. These trends were also apparent in the sites analysed for ions of the Fergus and Robe catchments.

Electrical conductivity was strongly correlated with calcium highlighting the influence calcium carbonate dissolution is having on ionic concentration. Electrical conductivity was also strongly correlated with $HCO_3$ during the June and September 1999 runs, emphasizing the dominance of carbonate chemistry in the Fergus system. The presence of dissolved oxygen (DO) in groundwaters normally indicates previous and fairly recent exposure of the water to atmospheric influences such as recharge (Lloyd and Heathcote, 1985). Carlyle and Hill (2001) reported a weak inverse relationship between DO concentrations and groundwater SRP in a sand aquifer in Ontario, Canada. The Fergus catchment and to a lesser extent the Robe catchment exhibited an increase in TP between 0-6 mg $l^{-1}$ DO range. This could represent the influence of recent recharge to flush P fractions through the karstic conduits. There were some negative correlations between pH and P fractions, particularly the dissolved forms. This trend was primarily over a narrow pH range (7 - 7.5). On face value this would indicate that slightly more alkaline groundwater yields higher P levels. However, the narrow pH range indicates strong buffering in these limestone catchments.

Sodium – potassium (K/Na) ratios are often used to examine agricultural impacts on groundwaters (Daly, 2000). The background Na/K ratio in most groundwaters less than

0.4. The K/Na ratio of soiled water and other wastes derived from plant organic matter is greater than 0.4, and thus, can be used to indicate contamination by plant organic matter. All sites had K/Na ratios below 0.4 and therefore no conclusion can be made on the source of P in the catchments. Whilst there were positive correlations between TP and Na:K in all three runs, only the September run was statistically significant.

### 4.7.5 Dissolved solids variability and groundwater phosphorus

Coefficient of variation of EC at the Robe spring and boreholes correlated well with TP. The Fergus springs (but not boreholes) were also well correlated. Shuster and White (1971) used coefficient of variation of hardness as a means of distinguishing between diffuse and conduit flow springs. The Coefficient of variations for the Robe springs were much lower (<10%) than the Fergus springs (0-30%). The Robe range is similar to ones calculated by Doak *et al.* (1995) at Ballindine and Belmont. Coxon (1995) calculated a range of 5-13% for Fergus springs, however, these springs were located south of L. Inchquin and comprised fortnightly sampling over one year, unlike in this study which was concentrated around the May – October period. This would tend to indicate that the Robe springs are fed by more diffuse flow than the Fergus springs. Indeed, the calcite saturation indices corroborate this distinction (see paragraph below). However, Coxon (1986) argues that the model proposed by Shuster and White is based on allogenic (non-limestone as in the case of the Fergus shale) rather than autogenic (as in the Robe) conduit flow recharge. Therefore, it cannot be conclusively stated that the flow to the Robe springs is not conduit derived. Previous studies have indicated that the Robe springs have characteristics common to diffuse and conduit flow systems (Coxon, 1986; Coxon and Drew, 1986). Nonetheless, the relationship with TP indicates that sites with high EC variability are more vulnerable to elevated P levels. This is particularly in the case of springs in both catchments and also of boreholes in the Robe.

### 4.7.6 Calcite and hydroxyapatite saturation indices

The Fergus springs were all undersaturated with respect to calcite. Therefore one would expect that these waters are likely to dissolve calcium carbonate. Whilst the Robe springs also have negative calcite saturation index (-0.21 to -0.06), they are all much closer to equilibrium than the Fergus springs. Furthermore, Lloyd and Heathcote (1985) note that, due to errors associated with calcite SI calculation, a value within ± 0.2 units of zero may indicate equilibrium. This would tend to indicate a conduit flow system for sites in the

Fergus and a diffuse flow system in the Robe. However, as discussed above, this interpretation cannot be taken in isolation.

Several authors have examined hydroxyapatite, particularly with respect to septic tank plumes. Robertson (1995) examination of P concentrations in septic tank plumes identified groundwaters supersaturated with respect to hydroxyapatite and suggests that precipitation of such mineral is limiting the magnitude of P in the plume. All the Robe and Fergus springs were undersaturated with respect to hydroxyapatite. This is not surprising given the insolubility of this mineral. The study of Muldoon *et al.* (1990) also found that out of 109 wells sampled in Wisconsin all were undersaturated with respect to hydroxyapatite. However, the sites in the Fergus up to Lough Inchquin indicated a degree of evolution as the water traveled through the catchment. Upstream, much of the Fergus is shale-derived water, which will not have been in contact with aquifer materials for long periods. Travelling downstream the Fergus increasingly receives more limestone-derived water. This could explain the reduction in undersaturation of both calcium minerals along this flow path. Water at Lough Inchquin was close to saturated with hydroxyapatite, therefore it is likely that precipitation of the mineral is among the factors limiting P levels at this stage. The strong relationship between calcite and hydroxyapatite was clearly demonstrated. Hydroxyapatite was also strongly pH dependent. In their study, Muldoon *et al.* (1990) hypothesize that because calcite is so plentiful and soluble it probably controls the dissolution of hydroxyapatite. The positive relationship between DRP and hydroxyapatite SI is difficult to interpret since all SI's are undersaturated. It may be explained by the relationship between DRP and calcium which were positively correlated for the Fergus sites.

# CHAPTER 5. HYDROGEOLOGICAL CONTROLS ON PHOSPHORUS IN GROUNDWATER

## *5.1 Introduction*

The intrinsic characteristics of aquifers determine the degree to which solutes and particulates are transported in groundwater. Aquifer materials will vary in their ability to retard this movement. Acid-base reactions, redox reactions, solution-precipitation reactions and adsorption all contribute to controlling the water chemistry of groundwater, the dominating process being a function of aquifer mineralogy, the hydrogeological environment and the history of groundwater movement (Lloyd and Heathcote, 1985). The nature of the unsaturated or vadose zone will determine the extent of solute and particulate migration of contaminants from ground level to the water table. In Ireland, the vulnerability of groundwater is primarily determined by the dual parameters of Quaternary deposits (permeabilities) and thickness, and presence of karst features (Daly and Warren, 1998). This chapter examines the control a range of hydrogeological parameters has on phosphorus concentrations in groundwater.

Since the main focus of P research has been on the overland flow pathway from land to surface waters, few researchers have examined hydrogeological parameters. Emphasis has been on the soil layer. For P to enter groundwater it must be leached from the surface layers, and be transported through the vadose zone to the saturated zone. Sims *et* al. (1998) reviewed research on P leaching and export in subsurface runoff and noted that P movement from subsoil to surface water depends on the depth of P leaching and the hydrology of the watershed. The concentration of P carried in the subsurface and groundwater runoff will be influenced by the time of contact with any component in the soil profile and in the case of groundwater, contact with bedrock (Ryden *et al.*, 1973). Leaching of phosphorus from soils has been identified in areas which have the following characteristics: coarse textured soils (Eghball, 1996) and sandy soils (Zhu *et al.*, 1994) with high permeability (Chen *et al.*, 1996), and in phosphorus saturated soils (Breeuwsma and Reijerink, 1992).

Research into hydrogeological controls on P leaching has focused on the water table. The study by Takatert *et al.* (1999) in a forest in the Rhine Plain of eastern France found that temporal variations in nutrient concentrations in groundwater were directly related to

variations in groundwater level during an annual hydrological cycle. In particular they found that DRP concentrations were lower in deep groundwater (piezometers at 4.5m depth below ground level) than in shallow groundwater (piezometers at 2m depth below ground level). This was attributed to the creation of reducing conditions as groundwater levels rose. A study by Ahmad *et al.* (1994) in the Kelantan Plain, Malaysia also found that generally the water table strongly influenced the redox potential which in turn controlled P levels. In the Netherlands, Breeuwsma *et al.* (1995) point out that unlike nitrogen, phosphate is strongly adsorbed in most soils. Therefore, leaching to groundwater is not likely except where the soil P levels are high and in shallow water tables. Breeuwsma and Reijerink (1992) report on a study in the Netherlands under such circumstances where during winter 80% of groundwater monitoring sites exceeded the quality threshold of 150 $\mu g\ l^{-1}$ of TP. In contrast, during the summer, when water tables are lower, only 18% of groundwater sites exceeded the threshold. Kilroy *et al.* (1997) found, in agricultural areas in southwestern USA, significantly higher concentrations of orthophosphate in shallow aquifers (wells ≤ 50ft; median, 220 $\mu g\ l^{-1}$ ortho-P) than in samples from deep aquifers (wells >50ft; median, 50 $\mu g\ l^{-1}$ ortho-P). In contrast, Spruill *et al.* (1998) found lower P in shallow groundwater than deeper groundwater and attributed this phenomenon to naturally occurring geological P.

This chapter aims to examine the hydrogeological characteristics of the studied sites in conjunction with their phosphorus concentrations. Several major hydrogeological parameters are examined in the subsections that follow. Some of the parameters have been grouped for convenience. The major hydrogeological areas studied were:

- abstraction rates/depth to standing water
- Quaternary deposits
- Bedrock geology/aquifer classification
- Aquifer vulnerability

Whilst much of the analysis is of an exploratory nature, several hypotheses are tested. Greater thickness of the unsaturated zone should increase the time required for soil P to travel from the soil surface to the water table. Therefore, one would expect higher groundwater P concentrations at sites with shallow water tables. Typically in soils there is a logarithmic decline in soil P levels with depth (Sims *et* al. 1998). However, preferential flow has been shown to act as mechanism for P to bypass the soils P retention capacity

(Dils, 1997; Stamm *et al.*, 1998). In Ireland, the Quaternary deposits below the soil are considered the single most important natural feature in influencing groundwater vulnerability to pollution (Daly and Warren, 1998). While the thickness of these deposits should be important, their permeability and type should also influence P concentrations in groundwater. Sand and gravel aquifers and sandy tills are expected to yield higher P levels due to high permeability. Groundwater beneath fine textured materials is expected to have lower phosphorus levels due to poorer drainage.

In the karstic aquifers, however, point recharge may negate the attenuating properties of Quaternary deposits. In the Republic of Ireland the majority of bedrock types are of Carboniferous age or older and all have fissure permeability only (Daly and Warren, 1998). It is expected that the karstic aquifers should have higher groundwater P than non-karstic aquifers due to the effects of conduit flow and point recharge. The areal extent of aquifers may also influence groundwater P levels. Sites located in poor aquifers of limited extent may have insufficient recharge to dilute contaminants, including P. Whilst the limestone aquifers may facilitate greater P attenuation through precipitation and adsorption reactions the non-limestone aquifers, the flows systems (conduit versus diffuse) may also play an important role.

Overall, the hydrogeological characteristics of these sites will determine the vulnerability of the groundwater to pollution. While hydrogeology is unlikely to control all facets of P movement to groundwater, it will be of interest to see if the vulnerability of these aquifers correlates with groundwater P levels.

## *5.2 Abstraction rates and depth to standing water*

### 5.2.1 Introduction and methods

This section examines the influences of abstraction rates and depth to standing water (DSW) on groundwater P levels. They are both related by the fact that higher abstraction rates will result in a lowering of the water table as water is drawn from the aquifer to the well. The acknowledgement is made that pumping required to abstract water may have influenced the DSW measured here. Information on abstraction rates was only available for the 19 Limerick sites for which source protection reports had been prepared (see Appendix B). This data, expressed in cubic metres of water per day, reflects the productivity of the

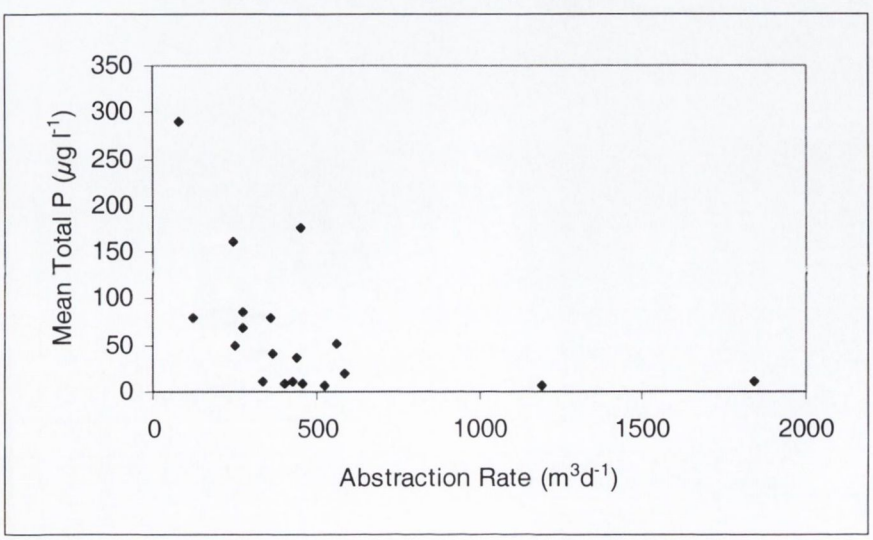
aquifer. Abstraction rates may indicate aquifers which are most likely to transmit P from through the aquifer.

Depth to standing water was measured at each borehole and dug well during each sampling visit using a SEBA dip meter. All depth to standing water levels are expressed as metres below ground level measured from the top of the well casing. For some sites this procedure was not practicable due lack of access to the well head or the danger of trapping the dip meter probe amongst the pipes of in-borehole pumps. The maximum length of the dip meter tape is 50m. It is likely that the DSW measured does not represent the natural potentiometric level in many cases but a lowered head due to pumping. Due to time constraints in obtaining access to the groundwater public supplies, the wells were not allowed to recover for longer than 10 minutes. Fifteen of the Limerick sites for which source reports are available have information on static water levels as opposed to pumping water levels. This information was used to compare known static water levels and measured DSW. It is envisaged that greater DSW depths, and hence greater unsaturated zone should result in a reduction in groundwater P levels.

### 5.2.2 Abstraction rates results

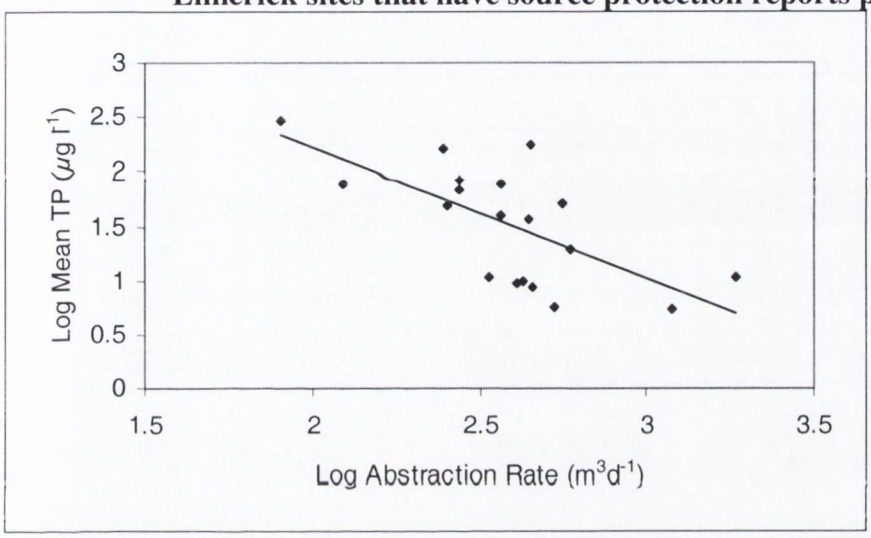
Abstraction rates were only available for the 19 Limerick sites for which source protection reports had been prepared. Figure 5.1 illustrates a logarithmic decline in mean total P at these sites as the daily abstraction rates decrease.

**Figure 5.1 Abstraction rate and mean total P levels at the 19 Limerick sites that have source protection reports prepared.**



A log-log plot of the same data is presented in Figure 5.2. A significant negative relationship is apparent between total P and abstraction rate with a Pearson product-moment correlation coefficient of –0.67 (p=0.01). A regression between log abstraction rate and log TP yields an $R^2$ value of 45.2% (p=0.0016). These trends are discussed in Section 5.2.4 below.

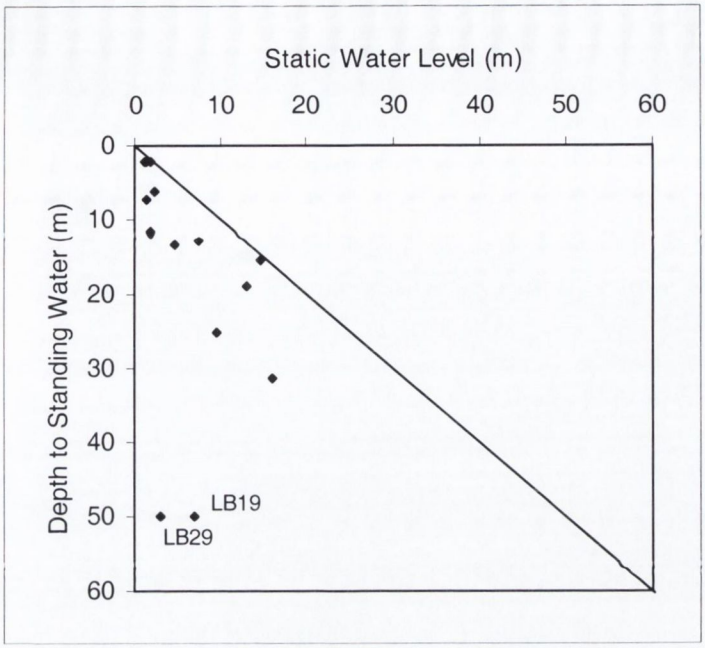
**Figure 5.2 Log-log graph of mean total P and daily abstraction rates for the 19 Limerick sites that have source protection reports prepared.**




### 5.2.3 Depth to standing water

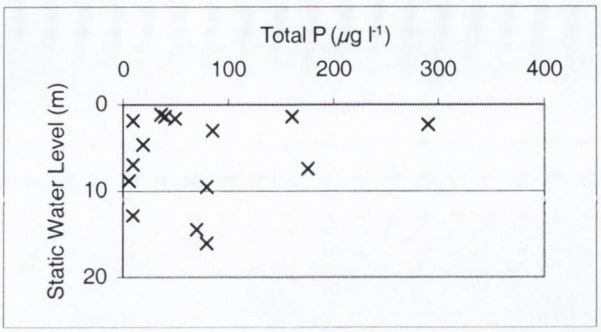
The fifteen Limerick sites for which static water levels were available are plotted against mean measured DSW in Figure 5.3. This figure illustrates that whilst there is a weak linear trend, in most cases the average measured DSW is lower than the known static water level. These transgressions probably represent a reduced head due to pumping at the borehole and the measured DSW are only partially recovered pumping levels. In the case of LB19 and LB29, both reported standing water levels greater than 50m, the maximum length of the dip meter. These are clearly gross deviations from the static water level and represent drawdown though pumping.

**Figure 5.3 Known below ground level static water levels and average measured depth to standing water for 15 of the Limerick boreholes.**




Due to the discrepancy between DSW and static water levels in the Limerick sites only the fifteen above sites were used to examine the effects of unsaturated zone thickness and groundwater TP (see Figure 5.4). Elevated TP levels greater than 100 $\mu g\ l^{-1}$ all have static water levels less than 10m. However, otherwise there are no clear trends.

**Figure 5.4 Static water levels and groundwater TP in Limerick sites.**




The Fergus and Robe boreholes are all private schemes and would generally only be used periodically during the day. Therefore it is likely that measured DSW values for these catchments are more accurate representations of the static water table level. Figure 5.5 presents all recorded DSWs and total P concentrations for boreholes and dug wells in the Fergus and Robe catchment. All grossly elevated TP values (> 100 $\mu g\ l^{-1}$) are reported for sites with a DSW less then 10 metres. The McMahon bore in the Fergus catchment represents in the three data points located on the 50m DSW which was greater than the maximum length of the dip meter. It is likely that it reflect drawdown rather than static water levels.

**Figure 5.5 Depth to standing water (DSW) and total P concentrations for boreholes and dug wells in the Fergus (◇) and Robe (+) catchments.**

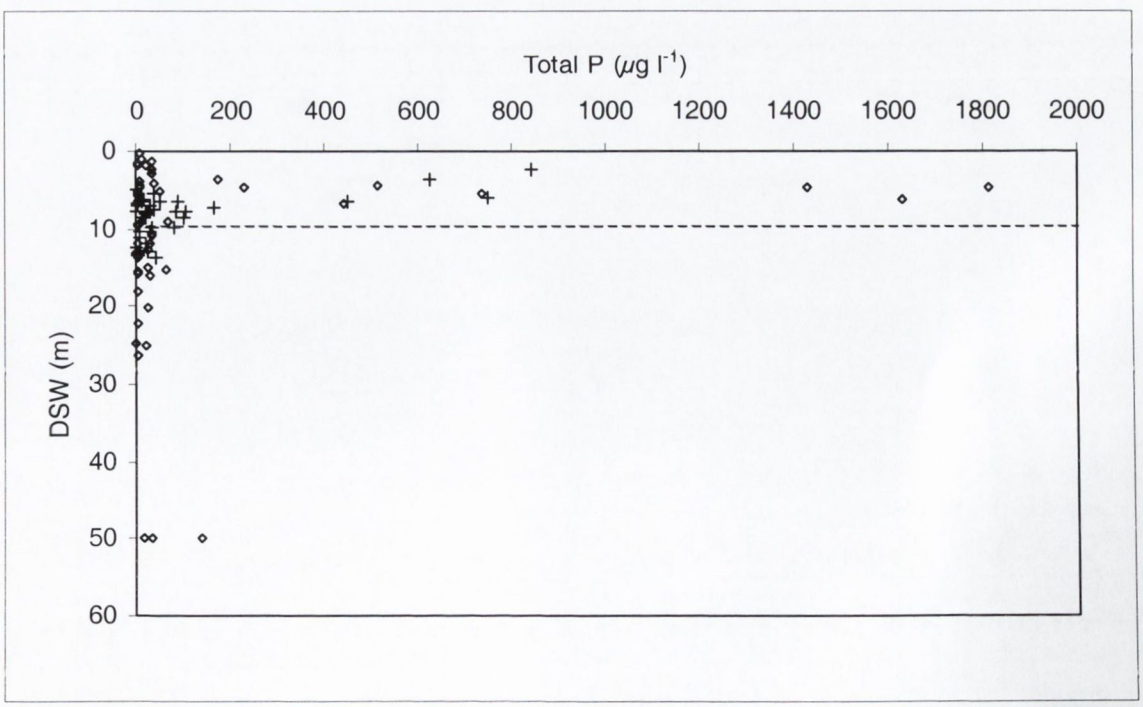


Figure 5.6 and Figure 5.7 presents total P and DSW data for sites in the Robe and Fergus catchments during the duration of the sampling program. Only sites with four or more DSW measurements were included. DSW at the RB01, RB02 and RB10 boreholes exhibit a positive relationship with TP levels. However, the other Robe sites do not exhibit such a trend. Indeed, in the case of boreholes RB04, RB08 and RB05 there is a marked increase in TP around July 1999 when these sites have a lowering of standing water levels.

In the Fergus catchment, boreholes FB03, FB06, FB09 and to a lesser extent FB12 show some control of DSW on TP levels. The FB02 and FB11 do not exhibit such pattern. FB02 is situated close to the River Fergus and river levels may impact the DSW and TP. FB11 had three of four DSW greater than 50m and thus is very likely to be impacted by drawdowns.

**Figure 5.6 Total P (solid line) and depth to standing water (DSW; dashed line) time series for Robe boreholes.**

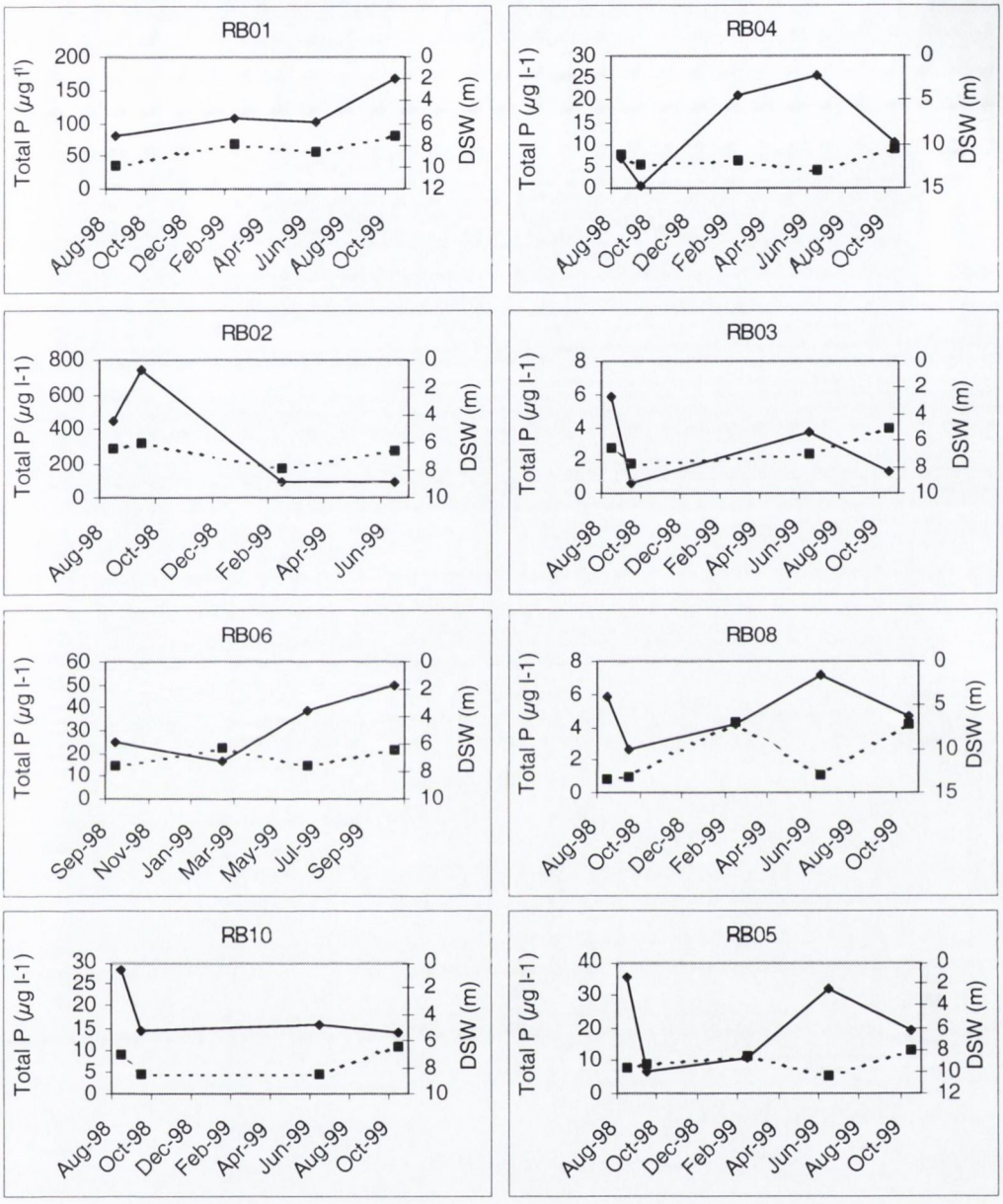
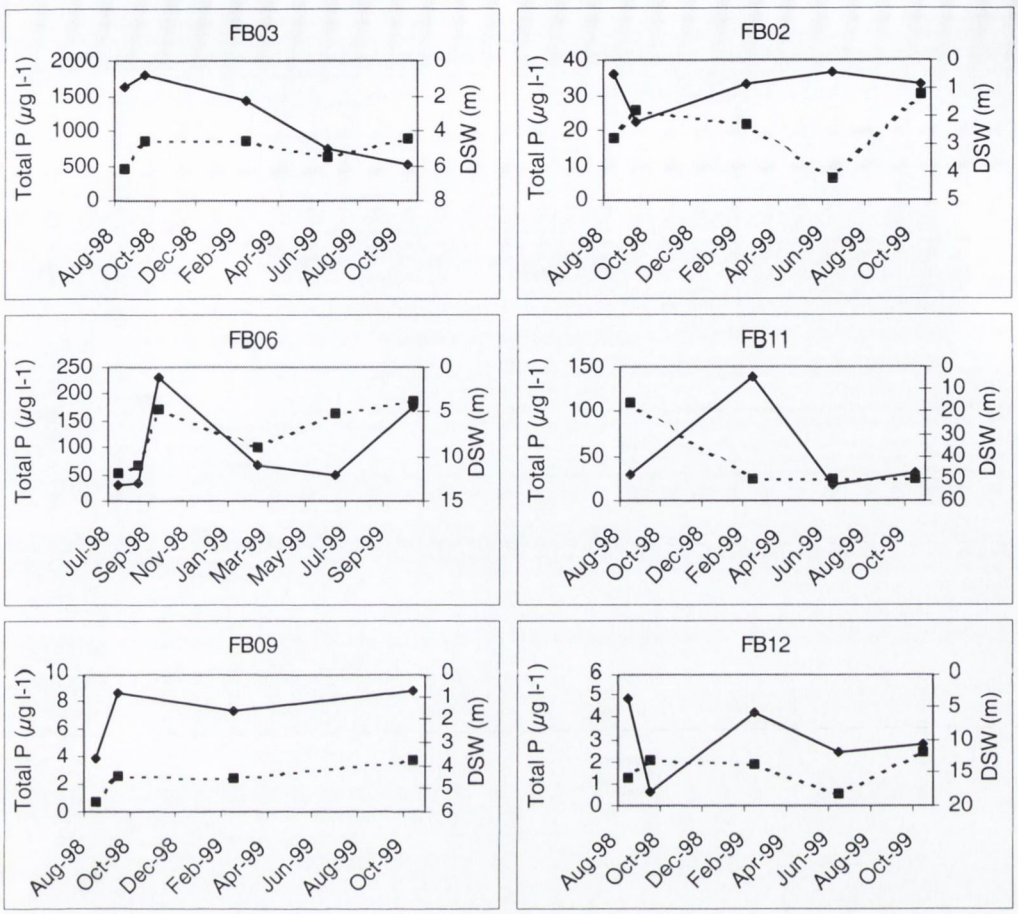


**Figure 5.7 Total P (solid line) and depth to standing water (DSW; dashed line) time series for Fergus boreholes.**




## 5.2.4 Discussion

There was a negative correlation between TP and daily abstraction rate. Sites with larger abstraction rates (greater than 500 $m^3d^{-1}$) tend to have lowest TP values. This relationship was also borne out in the national dataset albeit a weaker one (see Section 2.3.4). This fact may reflect a dilution effect due to a larger zone of contribution (ZOC). In addition pollution events within the zone of contribution will be flushed from the aquifer at a quicker rate than sites with lower abstraction rate. However, this assumes that P sources are often localised, i.e. point sources. If the source of P were diffuse across all farmland then one would not expect any difference with a larger ZOC. On balance, it is likely that the aquifers with higher abstraction rates may have lower P levels due greater mechanical dispersion properties.

Figure 5.3 indicated the discrepancy between depth to standing water and actual static water levels. This difference is probably greatest at the public supply sites where large volumes are required to be continuously pumped. This fact may have clouded any relationships between DSW and TP because water levels in a pumped well will be lower than in other parts of the ZOC depending on hydraulic gradient and saturated zone permeability. What is apparent from the data is that highly elevated TP levels (greater than 100 $\mu g\ l^{-1}$) are generally are found at sites where the DSW is less than 10m.

Where four or more DSW recordings were available at the Robe and Fergus sites it can be seen that generally higher TP is reported at sites with higher DSW. This may reflect a similarity between the relationship between TP and river flow, i.e. rather than groundwater recharge diluting the groundwater P, higher P values may be associated with recharge events. This point is examined in more detail for the springs in the Fergus and Robe catchments (Chapter Six). Pumping and seasonal factors may also be influencing these trends. TP increases in July 1999 at boreholes RB04, RB03, RB08 and RB05 may be attributed to increased agricultural activity during these periods rather than any water table influence. Indeed, during this period DSW was low at these sites.

## *5.3 Quaternary deposits*

### 5.3.1 Introduction and methods

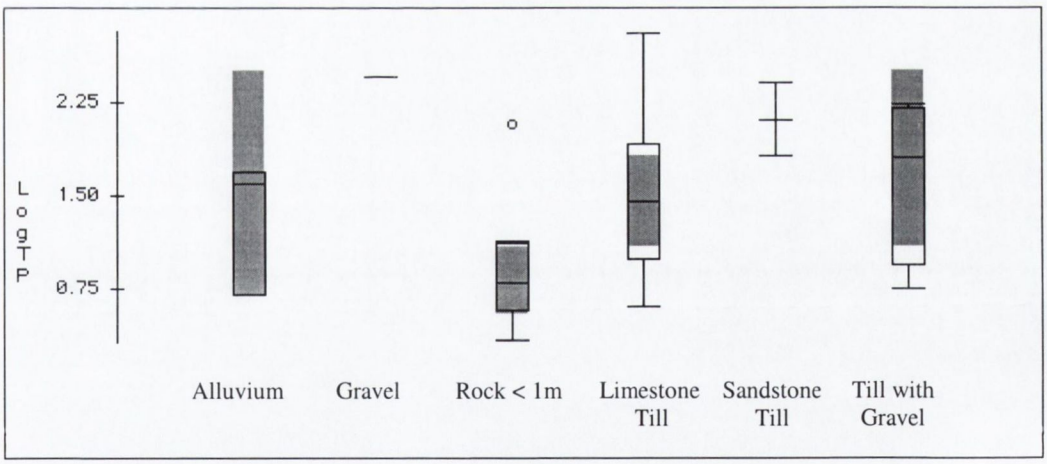
Quaternary deposits were examined in each county separately because of the distinct nature of the information sources for each catchment area. The Fergus and Limerick areas were examined using the GSI Groundwater Protection Scheme maps (Deakin *et al.*, 1998; Deakin and Daly, 2001). The classifications of Quaternary deposits used in this analysis are those used in these protection schemes. No protection schemes have been carried out in Co. Mayo. For this reason the Robe was examined using the STRIDE maps. It is anticipated that less permeable deposits such as the Namurian tills (shale and sandstones) will result in more groundwater P than the more permeable deposits such as sand and gravels and till with gravel. Depth to bedrock information was only available for the Limerick sites. It is expected that the thicker the overburden, the greater the attenuating

potential, and thus less vulnerable the groundwater. Therefore, lower P levels would be expected in areas with thicker subsoils.

### 5.3.2 Limerick Quaternary deposits results

Figure 5.8 presents TP boxplots of each subsoil type in the Limerick sites. The TP data has been log-transformed to allow for parametric statistics. Only two sites were located in sandstone till (LB05 and LB17) and one in gravels (LB12). All other sites were located in either alluvium, limestone till, till with gravel or in sites where rock is within 1m of the surface. Of these four major subsoil types, the sites located in till with gravel had the highest median TP levels. Sites in areas where rock is within 1m of the surface had lowest median TP levels. Sites in alluvium and till with gravel display a large variation and are not statistically different from the other subsoil types. Sites located in areas where rock is within 1m of the surface were significantly different in TP than sites located in limestone tills (p=0.0155).

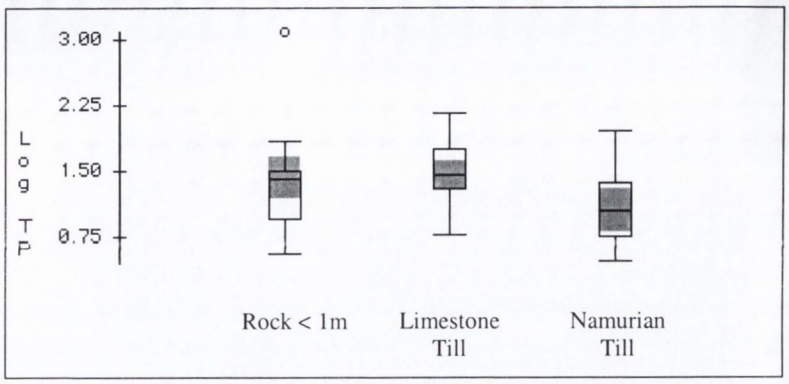
**Figure 5.8 Boxplots showing groundwater log TP levels for Quaternary deposit types in the Limerick sites.**




### 5.3.3 Fergus Quaternary deposits results

Figure 5.9 presents TP boxplots of each subsoil type in the Fergus sites. Springs, boreholes and dug wells were used for this analysis. The TP data has been log-transformed to allow for parametric statistics. Lowest median TP levels were in sites located in till derived from Namurian rocks, which were significantly different from those located in limestone till (p=0.009). Sites located in areas where rock within 1m of the surface were not significantly different from either limestone or Namurian till.

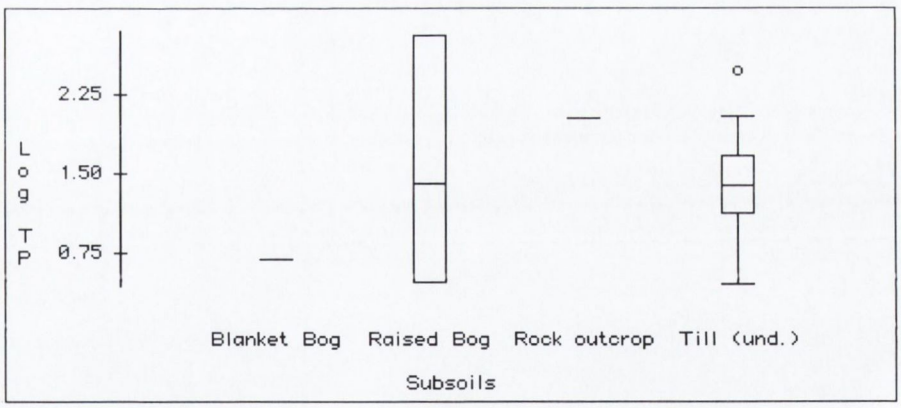
**Figure 5.9 Boxplots showing groundwater log TP levels for Quaternary deposit types in the Fergus sites.**




### 5.3.4 Robe Quaternary deposits results

The STRIDE maps generally located the Robe sites in either undifferentiated limestone till (Till (und.)) or raised bog. There was no statistical difference between TP values from these subsoils. One site was located in blanket bog (RB08) and one in a rock outcrop (RS06).

**Figure 5.10 Mean TP boxplots of Quaternary deposits for the Robe sites.**

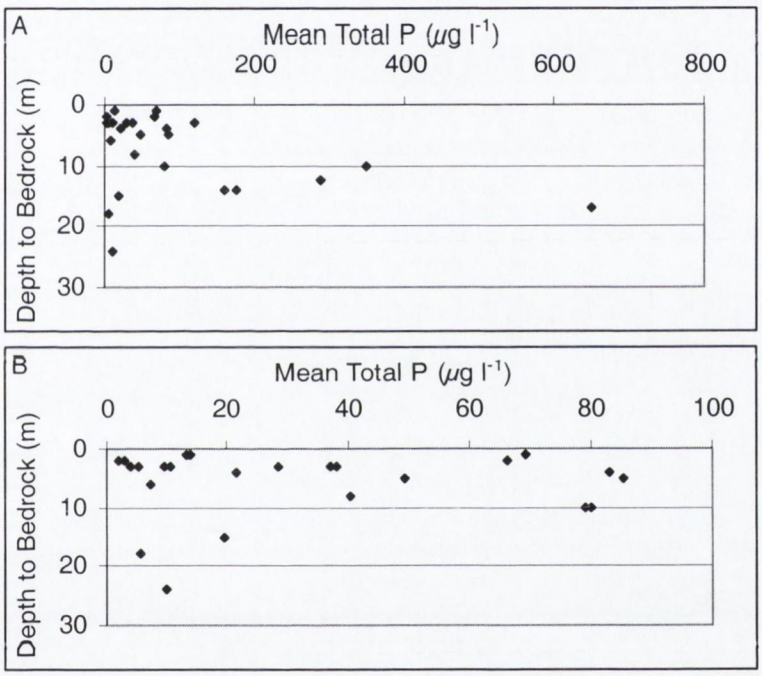



### 5.3.5 Depth to bedrock results

Only the Limerick Groundwater Protection Scheme maps are sufficiently detailed to allow an assessment of the impact subsoil thickness had on groundwater P levels. The majority of the groundwater sites in the Fergus catchment are located in areas designated as having shallow rock, that is where rock is less than 1 metre from the surface. Only nine of the Fergus sites were located within 1km of known depth to rock data points. Even less information is available for the Robe catchment.

Depth to bedrock (DTB) information was obtained either from source reports or from the Limerick Groundwater Protection Scheme maps. For boreholes DTB data represents depth to bedrock at the wellhead and not necessarily representative of bedrock depth in the zone of contribution. In Figure 5.11 graph A indicates a logarithmic decline in TP with DTB. However, in graph B, where the six sites with elevated TP (>100 $\mu g\ l^{-1}$) have been removed, it can be seen that in Limerick the majority of sites have depths to bedrock between 0 and 10m. Within this band there is no clear trend.

**Figure 5.11 Limerick borehole depth to bedrock data and mean TP levels. (A) presents all borehole data. (B) presents borehole data < 100 $\mu g\ l^{-1}$ TP.**




## 5.3.6 Discussion

In Limerick till with gravel had highest TP levels (excluding two minor deposit groups). However, this subsoil group has large variability and is not statistically different from the other deposit groups. Deakin *et al.* (1998) designate this type of deposit as having assumed high permeability. However the authors acknowledge that these areas may be underlain by both till and sand/gravel, but were unable to delineate the boundaries of the two deposits. Therefore the actual permeability will vary depending on the underlying lithology, and in some cases this deposit could be designated with moderate or more rarely low permeability. This could account for the variation in this group. The other two major

deposit classes were limestone till and areas where rock was within 1m of the surface (Rck). Limestone till was significantly higher in TP than areas under Rck. This is opposite to what conventional wisdom would suggest. Typically, areas with little or no overburden would have only minor attenuating capacity. Whilst this is probably true, land may also be less suitable for intensive agriculture.

Much of the Fergus catchment was covered in areas where rock was within 1m of the surface. The remainder of sites located in limestone till or Namurian till. The Namurian tills, which had significantly lower TP levels than the limestone till, overly the Namurian rocks in the west of the catchment. Deakin (2000) notes that these subsoils have a high proportion of clay present in the deposit matrix which is derived from the underlying shales and shaly mudstones. Using BS5930, the author classifies the till as being sandy clay or clay. These low permeability tills would conduct less water and contaminants than the more permeable Limestone Till and provide more opportunities for adsorption and precipitation of P.

The STRIDE maps did not provide sufficient classification of tills in the Robe catchment to accurately facilitate comparisons. However, the location of the RS06 spring at a rock outcrop highlights the vulnerability of the groundwater in the immediate vicinity of this site. More detailed Quaternary studies are required in this catchment before the true vulnerability of the groundwater can be assessed.

A general decline in TP as Quaternary deposit thickness increases is apparent from the Limerick data. Sites with Quaternary deposits greater than 10m generally have lower TP. However, this relationship is far from clear. Furthermore, in sites with less than 10m of overburden, the majority of the Limerick sites, there is no clear relationship with TP levels. Therefore it is likely that other factors are at play, such as Quaternary deposit permeability, at a finer resolution than the subsoil classes used for the groundwater protection scheme. Although there were sites with large depths to bedrock and low TP, there were also sites in shallow depth to bedrock with low TP. Therefore, thick Quaternary deposits may equate to low TP, but thin Quaternary deposits may equate to either high or low TP. Therefore, it is probable that non geological factors, such as agricultural intensity and soil P levels. In addition, depth to bedrock data at the wellhead may not be good reflection of overburden thickness across the zone of contribution to the source. Detailed site specific analysis of

ZOC overburden thickness would be required to improve the resolution of TP/depth to bedrock relationships. This level of detailed research was beyond the scope of this project.

## *5.4 Bedrock geology and aquifer classification*

### 5.4.1 Introduction and methods

This section examines the bedrock geologies specific to the aquifers sampled. These geologies are based on the Limerick and Clare groundwater protection schemes (Deakin *et al.*, 1998; Deakin and Daly, 2001). The emphasis is on the hydrogeological aspects of bedrock geology which may influence the movement of P in groundwater. The presence of apatite in the Namurian shales in the west of the Fergus catchment may influence P levels. However, any dissolution of apatite may be insignificant compared to the influence of the low permeability Namurian Quaternary deposits in preventing anthropogenic P inputs reaching groundwater. The karst limestones in the Fergus catchment are likely to transmit high P levels due to effects of point recharge and conduit flow. In Limerick greater diversity may allow better comparison between geologies. The lack of hydrogeological information in the Robe catchment, including bedrock geology will limit the degree of analysis possible. The aquifer classification system used in this assessment is that adopted by the GSI, (Daly and Warren, 1998) and is presented in Table 5.1.

**Table 5.1 Aquifer classification used by the Geological Survery of Ireland (Daly and Warren, 1998).**

| *Aquifer Category* | *Subdivision (code)* |
|---|---|
| Regionally Important Aquifers (R) | (i) Karstified aquifers (Rk)<br>($Rk^c$) Development potential limited by concentration of flow<br>($Rk^d$) Good development potential<br>(ii) Fissured bedrock (Rf)<br>(iii) Extensive sand/gravel aquifers (Rg) |
| Locally Important Aquifers (L) | (i) Sand/gravel (Lg)<br>(ii) Bedrock which is Generally Moderately Productive (Lm)<br>(iii) Bedrock which is Generally Moderately Productive only in local zones (LI) |
| Poor Aquifers (P) | (i) Bedrock which is Generally Unproductive except for Local Zones (PI)<br>(ii) Bedrock which is Generally Unproductive (Pu) |

The GSI define these categories on the basis of a number of factors and are described by Deakin and Daly (2001) as:

(1) Lithological and/or structural characteristics of geological formations which indicate an ability to store and transmit water. Clean washed and sorted sands and gravels for example, are more permeable than poorly sorted glacial tills. Clean limestones and sandstones are also more permeable than muddy limestones, and sandstones interbedded with shales, respectively. Areas where folding and faulting has produced extensive joint systems tend to have higher permeabilities than areas where this has not occurred.

(2) Hydrological conditions of groundwater storage and movement. For example, the presence of large springs can indicate a good aquifer; the absence of surface drainage can suggest high permeability; and high groundwater base flows indicates good aquifer potential.

(3) Information from boreholes, such as high permeabilities from pumping tests, specific capacities (pumping rate per unit drawdown), and well yields.

It is envisaged that higher permeability aquifers will tend to have highest P levels. The large regionally important aquifers may offer greater dilution potential of contaminants than poor aquifers, but karstification and associated point recharge in some of these aquifers be more important regarding P movement.

### 5.4.2 Co. Limerick results

*(i) Bedrock geology in Co. Limerick*

The general geology of Co. Limerick is presented in Figure 5.12. Table 5.2 lists the bedrock lithologies for the groundwater sampling sites of Co. Limerick. A wide of range of bedrock classes are found in the Limerick sites. The most common lithologies of the sites are the Ballysteen and Waulsortian Limestone with five and eight sites respectively.

**Figure 5.12 Limerick Geology (from Deakin, 1994).**

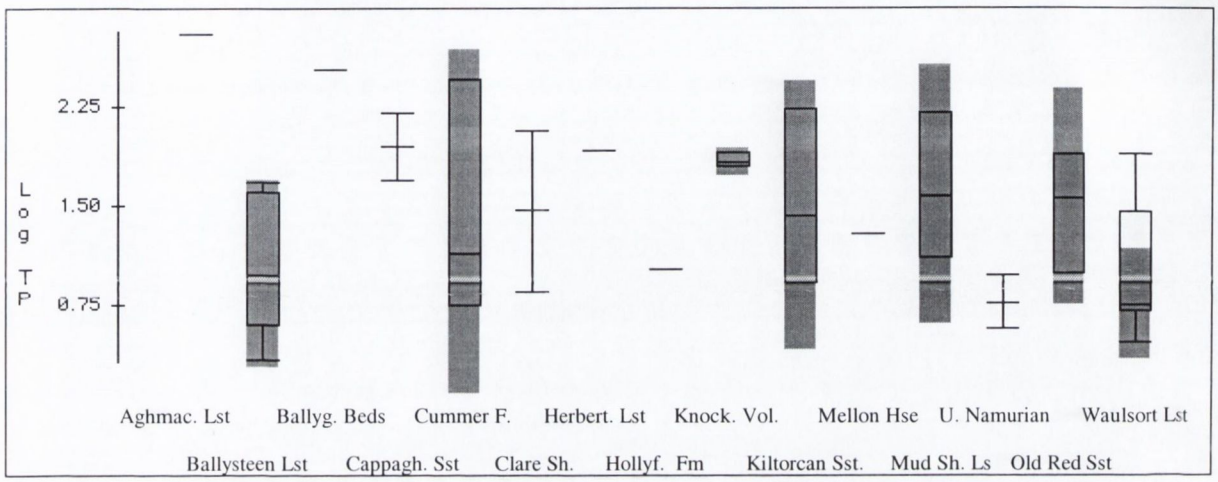
**Table 5.2 Lithological descriptions for site locations in Co. Limerick.**

| *Age* | *Formation* | *Aquifer Class* | *Description* | *Code* | *No sites* |
|---|---|---|---|---|---|
| Upper Carboniferous (Namurian) | Upper Namurian Beds | PI | Alternating sandstones, siltsones & shales. | NAMu | 2 |
| | Clare Shales | Pu | Soft, pyrtic, olive &black fossiliferous shales. | CS | 2 |
| | Cummer Flagstones | LI | Alternations of bedded, muddy, coarse siltstones & mudstones | CF | 3 |
| Lower Carboniferous | Muddy Shelf Limestone | LI | Black shales, shaly limestone & shaly mudstones. | msl | 3 |
| | Knockroe Volcanics | Lm | Tuffs & basaltic lava flows, some fracturing. | KRf | 3 |
| | Aghmacart Limestone | LI | Dark grey, generally fine grained limestone with thin shales and with frequent chert bands towards the bottom. | AG | 1 |
| | Herbertstown Limestones | Rf | Clean, pale blue limestones, thickly bedded, well sorted, medium to coarse, oolitic and skeletal grainstones. | HE | 1 |
| | Waulsortian Limestone | $Rk^c$/Rf | Massive blue or gray limestones. More thinly bedded with shales at the base, and shaley and cherty towards the top. Some karstification and dolomitisation. | WA | 8 |
| | Ballysteen Limestone | LI | Dark muddy fossiliferous limestones. | BA | 5 |
| | Mellon House Beds | LI | Transitional zone of fine sandstones, dark grey siltstone, & shale with some limestone. | MH | 1 |
| Devonian | Kiltorcan Sandstone | Rf | Thickly bedded white and yellow coarse sandstones, red fine grained sandstones and purple, red and green mudstones, shales and conglomerates. | KT | 4 |
| | Cappaghwhite Sandstone | LI | Coarse conglomerates overlain by red sandstones and interbedded black mudtsones | CA | 2 |
| | Old Red Sandstone | LI | Purple, red & grey sandstones, siltstones & conglomerates with interbedded mudstones. | ORS | 3 |
| Silurian | Ballygeana Beds | LI | Dark silty sandstones. High proportion of interbedded mudstones, siltsones and shales. | BN | 1 |
| | Hollyford Formation | Lg | Dark, grey-blue muddy sandstones, dark mudstones and well bedded, grey-green siltsones which are interbedded. | HF | 1 |

Adapted from Deakin *et al.* (1998)

Figure 5.13 presents mean TP boxplots for the bedrock lithologies of the Limerick sites. There is a wide variation within many of the categories. This is probably influenced by the small sample size in many of the categories. The Knockroe volcanics (KRf) were significantly higher in TP than the Waulsortian Limestone (WA) (p=0.0191).

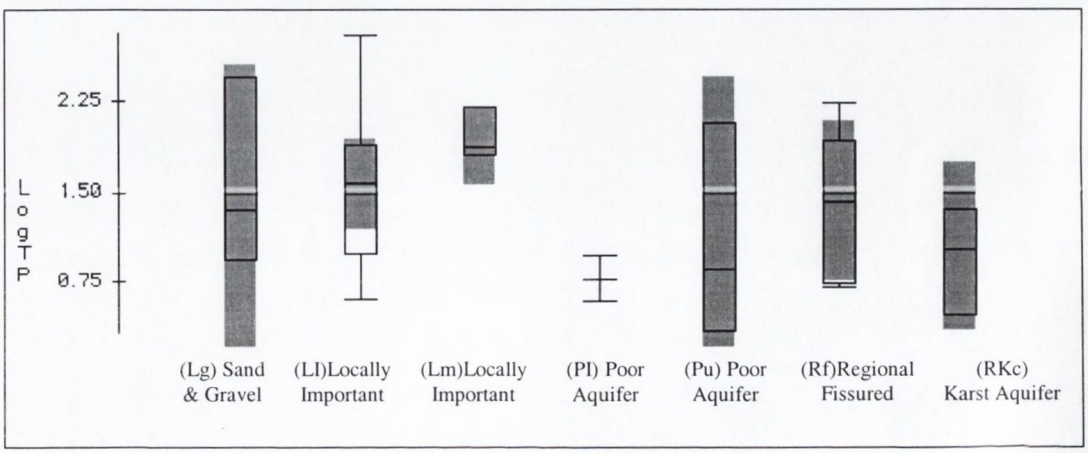
**Figure 5.13 Mean TP boxplots for bedrock lithologies of Limerick sites. See Table 5.2 for explanation of bedrock types.**




(ii) *Aquifer classification in Co. Limerick*

The aquifer classification of the geologies encountered in the Limerick sites is included in Table 5.2. The majority of Limerick sites are located in locally important aquifers which are moderately productive only in local zones (LI). Figure 5.14 presents log TP boxplots for each aquifer type in the Limerick sites. There is no significant difference between the aquifer types. Excluding extreme mean TP values (greater than 100 $\mu g\ l^{-1}$) or by examining only the 19 sites for which source reports are available did not indicate any refining of the boxplots in Figure 5.14.

**Figure 5.14 Mean TP boxplots of Limerick sites. (See Table 5.1 for aquifer details).**



### 5.4.3 Fergus catchment results

(i) *Bedrock geology in the Fergus catchment*

Figure 5.15 presents a general geology map of the Fergus catchment. Bedrock analysis in the Fergus catchment examined 48 groundwater sites. Tubber limestone was the most common lithology (see Table 5.3). The Burren limestone with its two members (Ailwee and Maumcaha) was the second largest group with 12 sites.

**Table 5.3 Lithological descriptions for site locations in the Fergus catchment derived from the Clare groundwater protection scheme bedrock map.**

| *Age* | *Formation (Member)* | *Description* | *Aquifer Class* | *Code* | *No. of Sites* |
|---|---|---|---|---|---|
| Upper Carboniferous | Gull Island Siltstone | Grey silstones and sandstones | LI | GL | 9 |
| Lower Carboniferous | Slievenagasha Limestone | Pale grey, coarse grained limestone with chert bands and fossiliferous horizons | $Rk^c$ | SL | 6 |
| | Tubber Limestone | Fossiliferous, medium grey, clean fine and medium grained limestones with shaly partings, cherts and dolomites | $Rk^c$ | TU | 17 |
| | Burren Limestone | Pale to medium gray fossiliferous clean medium to coarse grained limestone. Clay wayboards towards the top | $Rk^c$ | BU | 5 |
| | Maumcaha Member | Massive clean, unbedded minestone with poor jointing | $Rk^c$ | BUmc | 2 |
| | Ailwee Member | Thickly bedded, clean limestones, separated by clay wayboards | $Rk^c$ | BUaw | 5 |

Adapted from Deakin and Daly (2001)

Figure 5.16 presents mean TP boxplots for bedrock in the Fergus catchment. The extreme outlier borehole EB has been removed from this figure (mean TP = 1291 $\mu g\ l^{-1}$). An ANOVA comparing the bedrock types and log mean TP results in significant differences (p=0.016) when the EB outlier is removed from the TU bedrock category. Examining these differences further, the Gull Island Siltstone (GL) had lowest TP levels. GL had significantly lower TP levels than the Slievenagasgha Limestone (p=0.0103) and the Ailwee Member (p=0.0183). GL was also significantly lower than the Burren Limestone when the PHB outlier is removed. Whilst GL had median TP levels lower than the Tubber limestone, this difference was not statistically different.

Figure 5.15 Fergus catchment geology.

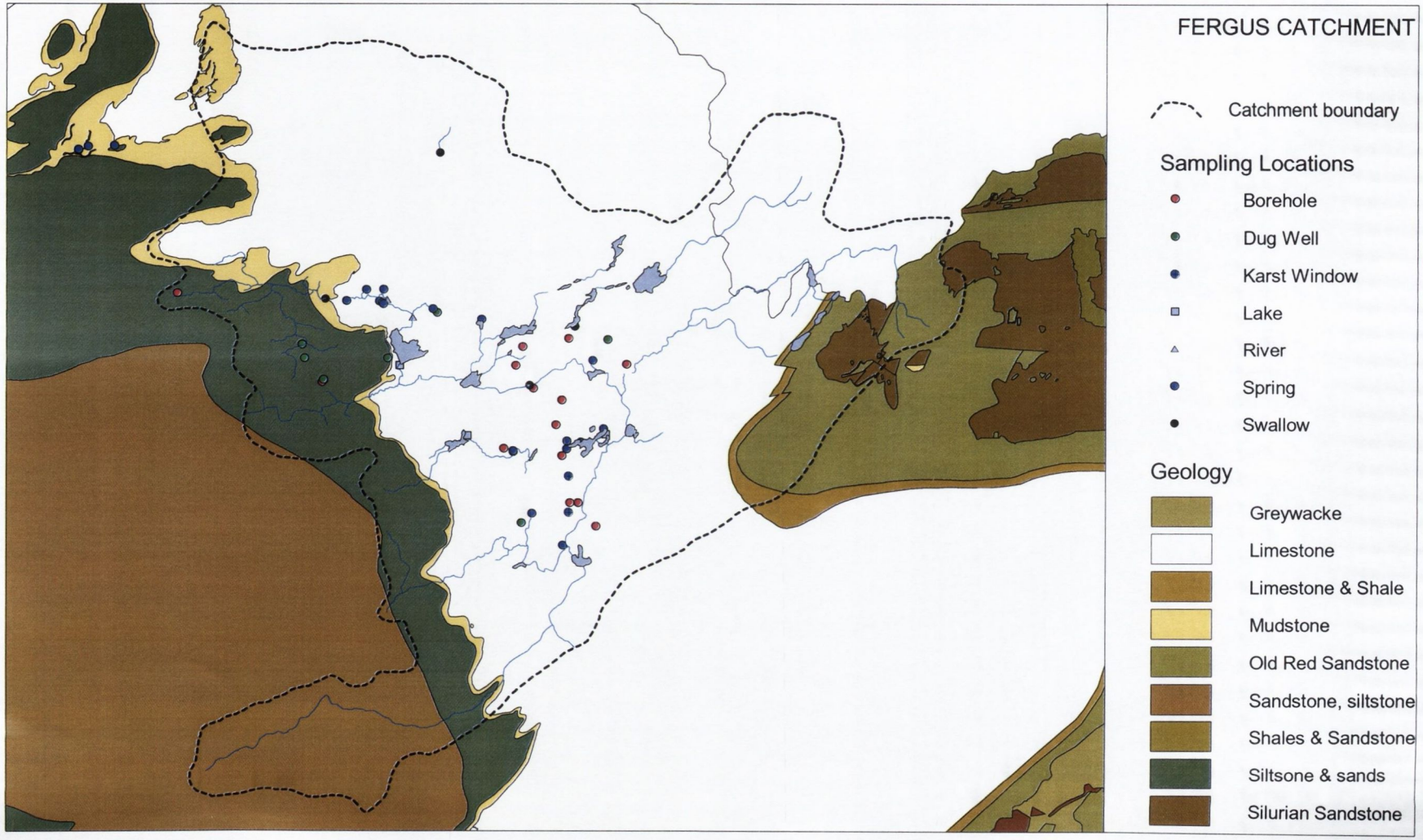
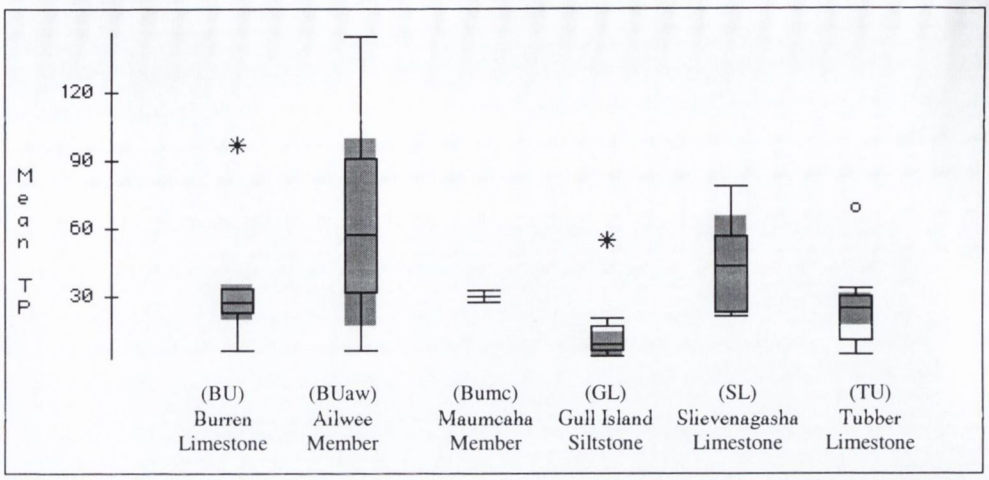


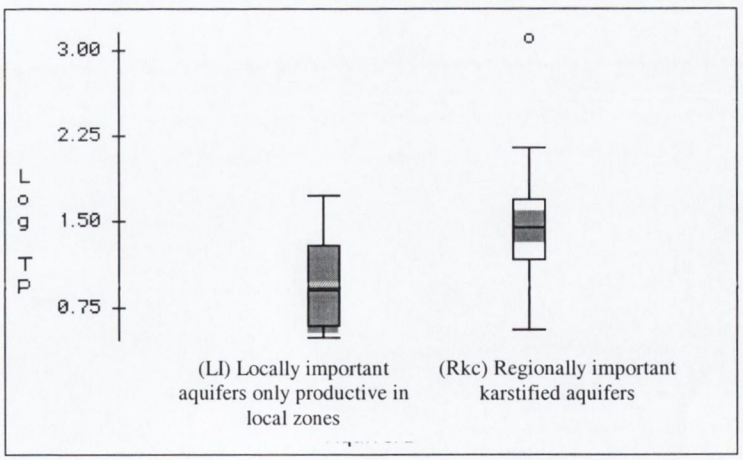
**Figure 5.16 Bedrock lithologies for the Fergus catchment.**




(ii) *Aquifer classification in the Fergus catchment*

The Fergus catchment sites are either located in locally important aquifers which are moderately productive only in local zones (LI) or in regionally important karst aquifers in which development potential is limited by concentrations of flow (RKc). The RKc sites have significantly higher mean TP levels than LI sites (p=0.0123). This is effectively a comparison between Namurian rocks and Lower Carboniferous limestones, since all aquifers with LI aquifer class are in the Gull Island Formation.

**Figure 5.17 Mean TP boxplots of Fergus sites. (See Table 5.3 for aquifer details).**




## 5.4.4 Geological phosphorus in the Fergus catchment

Several of the sites in the Fergus catchment were suspected of intercepting the apatite layers in the Namurian shales. In addition, some groundwater sites around Lisdoonvarna, near where apatite used to be mined, were also sampled (see Figure 3.3). Three boreholes,

FB15, FB17, FB11 and FB07 all may intercept the apatite layer. FD08 is a dug well, no longer used. FD04 is a shallow bore providing drinking water for summer cottages overlooking Lough Inchquin. The Lisdoonvarna sites were the (FS19) St Brendan's Well spring, the twin wells ((FS20; a magnesium rich source), FS21 and an Iron (FS15) and Magnesium (FS16) well in Lisdoonvarna village. Table 5.4 summarises TP data for these sites. The Fergus catchment sites all reported low P levels generally below 12 $\mu g\ l^{-1}$ TP, except for one sample for FB11 (140 $\mu g\ l^{-1}$ TP) and one sample for FD04 (31$\mu g\ l^{-1}$ TP). The Lisdoonvarna sites were also generally low except for FS19 and the FS21.

**Table 5.4 Sites on the Namurian Gull Island Formation, potentially intercepting groundwater from the apatite layer.**

| *Site Name* | *Range of Total P ($\mu g\ l^{-1}$)* | *Number of samples* |
|---|---|---|
| FB07 | 4 | 1 |
| FB11 | 19 - 140 | 4 |
| FD04 | 10 - 31 | 5 |
| FB15 | 4 - 12 | 3 |
| FB17 | 2 - 4 | 3 |
| FD08 | 3 - 11 | 5 |
| FS19 | 29 - 35 | 2 |
| FS20 | 6 | 2 |
| FS21 | 44 - 146 | 2 |
| FS15 | 23 | 1 |
| FS16 | 6 | 1 |

### 5.4.5 Robe catchment results

The STRIDE maps lack sufficient detail for any analysis of TP levels. All the sites are located in what is referred to as Pure Limestone, except RD02 which is classified as Muddy Limestone and Mudstone. All the Robe sites are located in a regionally important aquifer, except RD02 well which is located in a locally important aquifer.

### 5.4.6 Discussion

The 40 Limerick sites penetrated a wide variety of geologies. Sites located in Namurian and Silurian rocks, and the Waulsortian Limestone had lowest TP levels. Sites in the Knockroe Volcanics had significantly higher TP than the Waulsortian Limestone, the most common geology. All other geologies had either only one site or a wide scatter of TP values amongst sites.

In the Fergus catchment, sites located in the Gull Island Siltstone, the second most common geology, had significantly lower TP than most of the Lower Carboniferous Visean rocks. The Gull Island Siltstone is an Upper Carboniferous, Namurian rock type and is described as grey siltstones with sandstones at the base, decreasing towards the top, and 135 – 400m thick (Deakin and Daly, 2001). These rock types are classified as being a potentially locally important aquifer where the bedrock is moderately productive only in local zones. The Namurian tills overlying the Gull Island Siltstone, discussed above, together with a total absence of karst features contribute to less TP being found in sites in this bedrock.

There was a wide range of aquifer types in the Limerick sites. Statistically there was no difference between each type. In median terms the sites locally important aquifers which are generally moderately productive had the highest TP levels. There were only two major aquifer types in the Fergus catchment. The regionally important karst aquifer (RKc) had significantly higher TP than the locally important aquifers which are moderately productive only in local zones (LI). The RKc group of karst aquifers are classified with limited development potential due to concentrations of flow. Most flow through RKc aquifers occurs along particular conduits. Point recharge via sinks at rivers and lakes will also contribute to the nutrient load to groundwater (Coxon and Drew, 2000). Thus, pollution events within RKc aquifers can travel quickly away from the contamination source. These reasons may explain the significantly higher TP levels in RKc aquifers.

It is not clear whether any of the Fergus catchment sites on the Namurian shales derive groundwater from the phosphatic shale layer. All these sites, excluding 2 outliers, reported very low TP levels. Therefore, if the sites do intercept the apatite, this geological source of P does not appear to be providing any appreciable amount of mobile P. The Lisdoonvarna sites are less clear. Drew (1996a) suggests that the Phosphate Shale appears to act as a barrier to the vertical movement of groundwater, and thus lateral flow dominates above this stratum. Therefore the Lisdoonvarna springs are fed by groundwater above this layer which have limited groundwater circulation (effective porosity 1-2% at most) in joints and between laminae of the shale bands. Except for FS19 and FS21, TP levels were generally low. Overall therefore, the limited number of sites examined tend to indicate that the Phosphatic Shale is not resulting in elevated groundwater TP levels.

## 5.5 *Aquifer vulnerability*

### 5.5.1 Introduction and methods

The vulnerability of an aquifer to contamination is determined by the GSI primarily using the parameters: subsoil type (permeability) and thickness; recharge type (point or diffuse); and the thickness of the unsaturated zone. The Limerick and Clare groundwater protection schemes both provide vulnerability maps based on these parameters (see Appendix B). The vulnerability of each of the groundwater sites was obtained using these maps. In the case of the Limerick sites for which source reports were available (see Appendix B) preference was given to the vulnerability class in these reports because they were based on more site specific information. In the Robe catchment the STRIDE vulnerability map was used. The GSI have published guidelines for mapping vulnerability in Irish groundwaters (see Table 5.5).

**Table 5.5 Vulnerability mapping guidelines for Irish groundwaters.**

| Vunerability Rating | Hydrogeological Conditions | | | | |
|---|---|---|---|---|---|
| | Subsoil Permeability (Type) and Thickness | | | Unsaturated Zone | Karst Features |
| | High permeability (sand/gravel) | Moderate permeability (e.g. sandy subsoil) | Low permeability (e.g. clayey subsoil) | (Sand/gravel aquifers only) | (<30 m radius) |
| Extreme (E) | 0 – 3 m | 0 – 3 m | 0 – 3 m | 0 – 3 m | - |
| High (H) | > 3 m | 3 – 10 m | 3 – 5 m | >3 m | N/A |
| Moderate (M) | N/A | >10 m | 5 – 10 m | N/A | N/A |
| Low (L) | N/A | N/A | > 10 m | N/A | N/A |
| Notes: (1) N/A = not applicable (2) precise permeability values cannot be given at present (3) release of point contamination is assumed to be 1-2 m below ground surface. | | | | | |

(From DeLG *et al.*, 1999; Table 1)

### 5.5.2 Co. Limerick

Figure 5.18 presents the vulnerability of all the groundwater sites in Limerick. The majority of sites were classified with extreme vulnerability (21) followed by high (16) and low vulnerability (3). There was no significant difference between each vulnerability category. Greatest variability occurred in sites with extreme vulnerability. The nineteen sites with source reports were examined further (see Figure 5.19). Greater confidence in the vulnerability classes could be attributed to these sites because they had been subject to

site-specific hydrogeological assessment. Mean TP decreases as vulnerability decreases. However, these differences are not statistically significant.

**Figure 5.18 Vulnerability of all Limerick groundwater sites.**

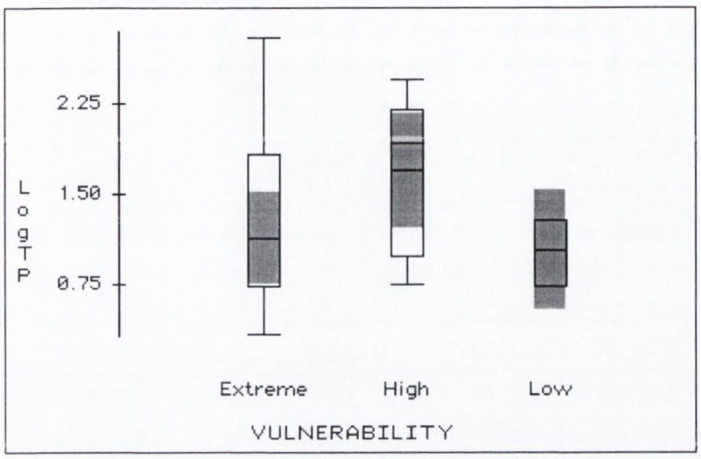
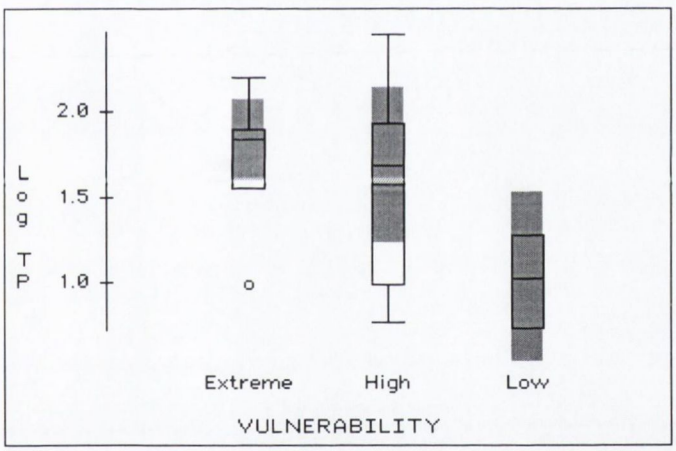


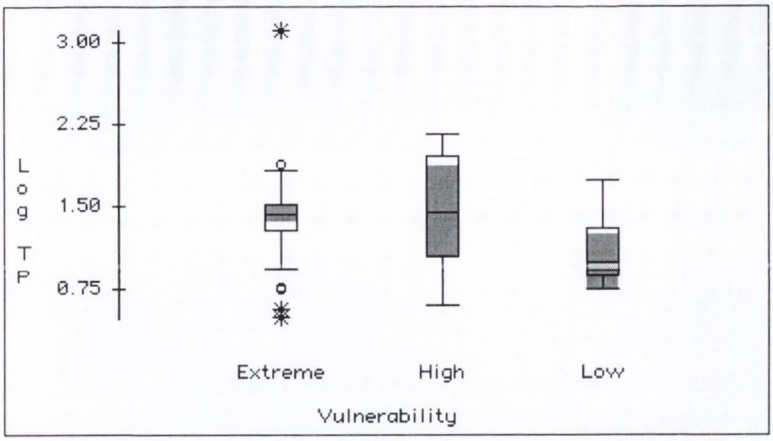

**Figure 5.19 Vulnerability of the 19 Limerick sites with source protection reports.**




### 5.5.3 Fergus catchment

In the Fergus catchment 25 of the sites were located in extreme vulnerability zones, 12 in high vulnerability and 7 in low vulnerability zones. Figure 5.20 presents boxplots of vulnerability for the Fergus catchment. Median TP levels of sites in high vulnerability zones were higher than low zones, but not statistically different. Median TP levels for high and extreme zones were similar.

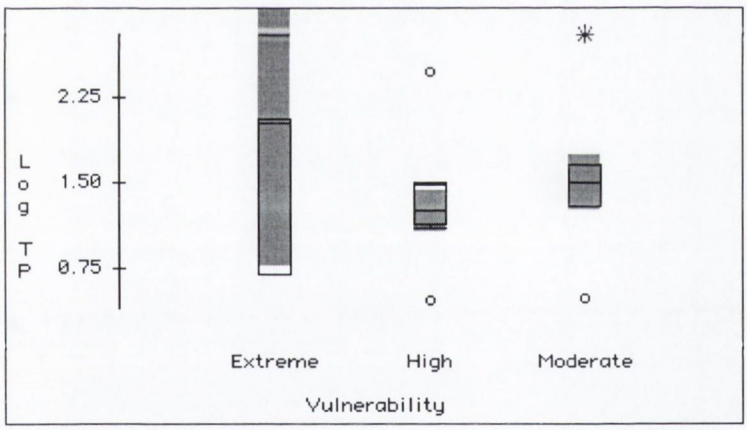
**Figure 5.20 Vulnerability of all Fergus groundwater sites.**




### 5.5.4 Robe catchment

In the Robe catchment 3 sites were located in extreme vulnerability zones, 9 in high vulnerability zones and 6 in moderate vulnerability zones. There was no significant difference between the means of each vulnerability class.

**Figure 5.21 Vulnerability of Robe groundwater sites.**




### 5.5.5 Discussion

The vulnerability of an aquifer to contamination is determined by the GSI primarily by combining depth to bedrock data, subsoil types (permeabilities) and identified karst features (Daly and Warren, 1998). Examination of boxplots for each catchment area yielded general trends of higher TP as vulnerability increased, however, this trend was not statistically significant. The boxplots of the 19 Limerick sites with source reports (Figure 5.19) is the best example of this trend, illustrating the benefit of site specific hydrogeological assessment over generalised derived data from large county maps.

### 5.6 Overall discussion

The Limerick source reports provide the most hydrogeological information for detailed analysis. They also confer much more confidence in classification of site characteristics because they have been subject to detailed site-specific hydrogeological assessment. Information on static water levels and abstraction rates for example yield some interesting trends. Total P levels generally increased with groundwater vulnerability as defined by the Geological Survey of Ireland, but lack of relationships between TP and depth to bedrock probably decreased the strength of this trend. In the Fergus catchment, despite the presence of phosphatic shales, geological P did not appear to be a potential source of groundwater P based on the sites sampled. In general terms, some hydrogeological factors emerged as potentially important controls on groundwater P levels:

- *Abstraction Rates:* Sites with greater abstraction rates had lower TP levels. This trend was also reflected in the EPA NGQMP data. This probably represents a dilution effect.
- *Depth to Standing Water:* Extreme TP levels were found where the depth to standing water was less than 10m below ground level. However, within the 10m unsaturated zone layer, there was no clear relationship with water table depth. It is likely that other non-hydrogeological factors become important in shallower water tables.
- *Quaternary Deposits:* Type and permeability of Quaternary Deposits were important factors. In the Limerick area, sites located in till with gravel, a high permeability subsoil, had the highest TP levels of that catchment. In contrast, sites in Namurian till, a low permeability subsoil, of the Fergus catchment had lowest TP levels.
- *Karstification:* Karstic groundwater tended to have higher P levels than other aquifer types. In the Fergus catchment, sites located in the regionally important aquifer which is conduit flow dominated had higher TP levels than sites located in the locally important aquifers. Sites in Namurian bedrock had lower TP levels than other bedrocks in the Fergus and Limerick catchments.

Overall, Quaternary deposits and karstification appears to be the main hydrogeological factors influencing groundwater P levels. This chapter attempted to examine the strictly hydrogeological controls of P in groundwater. Therefore, it does not take into account the source of P or P loading on land to the various sites. This may explain the difficulty in finding clear statistically significant relationships with hydrogeology.

# CHAPTER 6. TEMPORAL ANALYSIS

## *6.1 General Introduction*

This chapter is concerned with various temporal aspects of phosphorus in groundwater. Temporal changes in nutrient concentrations in groundwater will be determined by two major factors. Firstly, a source of the nutrients is required. This may take the form of natural levels within the soil and geological materials or anthropogenic inputs. In the latter case land-use regimes will determine temporal periods when the source of nutrients is greatest. For example, slurry spreading is most suitable in Ireland around March, but can occur all year round depending on slurry storage capacity (Tunney *et al.*, 1998). Silage production in Ireland generally occurs in the summer months, thus the impacts of silage effluent will be concentrated during this period. Secondly, the nutrients must be transported from the surface to the water table. Precipitation will generally drive this movement but nutrients will encounter several obstacles en route. Soils and subsoils will act to intercept these nutrients to varying degrees depending on their intrinsic properties. The Burren karst in Co. Clare is particularly vulnerable in this regard due its thin or sometimes absent soils (Drew, 1996b). Once nutrients reach groundwater, soluble forms will travel in groundwater by diffusion and advection, but dispersion and retardation factors (e.g. adsorption and precipitation in the case of P) will dilute and restrict their movement (Fetter, 1999). Again, the fissure and conduit flow nature of karst aquifers can effectively by-pass these attentuation properties, whilst also providing enough energy to facilitate particulate transport during high stage events.

Thus, temporal variation in land-use activities and climate combine to influence nutrient levels in groundwater. Precipitation in Ireland typically follow a certain cycle. After the winter rains, there is a steady decrease in rain volume and a subsequent increase in evapo-transpiration rates. This results in a increase in soil moisture deficit during the summer period. Early autumn sees the beginning of recharge and depletion of the soil moisture deficit. Deviations from this cycle are common, and indeed many peaks of P loss from soil to water have been attributed to summer storm events (Kurz, 2000). Lennox *et al.* (1997) studied the relationship between flow and DRP loss in two river catchments in Northern Ireland. The authors found that much of the temporal variation in annual loss rates was related to the interaction of short-term runoff events with slurry spreading or poaching of

land by animals in the winter. Therefore, in assessing temporal changes in groundwater nutrient levels an awareness of land-use patterns and variable climatic conditions is required. In addition different nutrients will behave differently. For example, in surface waters typically nitrate concentrations tend to be lower at high flows due to dilution (Roberts, 1987) whereas P concentrations tend to be higher at high flows due to greater P mobilisation (Heathwaite *et al.*, 1996). It will be of interest to see to what extent groundwater P follows behaviour patterns similar to P in surface waters.

The data collected during this research extends from July 1998 to March 2000. Seasonal, monthly, fortnightly, daily and 8 hourly sampling programs were carried out during this period. The seasonal sampling is dealt with in Section 1.2 and most of the sampling locations are incorporated into this analysis. Monthly and fortnightly samples were grouped together into Section 1.3 which deals with medium term changes. Four sites in the Robe catchment (RS03, RS04, RS01 and RS06) and four in the Fergus catchment (FS05, FS08, FS13 and FS18) were assessed in this way. Short term changes are dealt with in Section 1.4 and include the daily and 8 hourly samples. Only three locations, one in the Robe catchment (RS06) and two in the Fergus catchment (FS05 and FS13) were included in the short term analysis.

This chapter aims to assess whether Irish aquifers show broad seasonal variation in P and if so, which season is highest and therefore most likely to impact on surface waters. In surface waters, much of the temporal controls on P levels are both hydrological (storm events) and biological (P uptake by plants and algae). It is expected that groundwater will exhibit hydrological response to P, but this may be dampened by storage in the aquifer. The karst aquifers should exhibit responses closer to surface waters due to their high connectivity with the land and surface water.

Shorter timescales are examined to establish whether aquifers show rapid responses to meteorological changes and to see whether they are related to degree of karstification. Given the highly karstified nature of the Fergus catchment it is envisaged that more rapid responses will be seen here than in the Robe catchment.

Chapter Four indicated that DRP was by far the dominant fraction in the groundwaters studied. Allot (1990) found that DRP in lakes in the Fergus catchment were highest in

winter and decreased to almost below detection limits during the summer growing season. Therefore how groundwater fractions behave temporally, particularly during periods when algal growth is greatest, may have important repercussions for productivity in these lakes. Biweekly sampling at four Fergus springs and four Robe springs may shed some light on this issue.

## *6.2 Materials and Methods*

### 6.2.1 Sampling Procedures and analytical techniques

The P fractions analysed to examine temporal aspects were total P (TP), total dissolved P (TDP) and dissolved reactive P (DRP). All sites were analysed for TP and only the biweekly sampled springs were analysed for the TDP and DRP. The techniques used to analyse these parameters as well as the procedures used to collect samples and quality control issues are described in Chapter Four.

Not described elsewhere in detail is the SIGMA automatic samplers (autosampler) used here to assess short term changes (daily) in groundwater P. The autosampler comprises essentially two parts, a base section and an upper unit. A base section which contains twenty four 500ml plastic bottles. The upper unit consists of: a pump which aspirates a calibrated amount of water; a rotating arm with a line from the pump which fills each of the bottles; and a computer with battery pack which can be programmed to sample particular volumes and intervals. The upper unit sits on the base and is lockable and waterproof. PVC tubing of approximately 4m length was used to connect the pump to the springs. The intake point of the tubing was attached on top a submerged rock sitting proud of the spring bed, to prevent intake of suspended matter. Several trial pumps were carried out to ensure this did not occur and to calibrate the pump with the length of tubing used. Only 22 bottles were filled on each run. The 23$^{rd}$ and 24$^{th}$ bottles were respectively filled with deionised water (to act as a blank) and a QC standard (20 $\mu$g $l^{-1}$ P) to ensure that the procedure did not add or remove P from the sample. Samples were recovered weekly. Dramatic changes in concentration of DRP can occur after collection (Ryden *et al.*, 1973; Kotlash and Chessman, 1998) and therefore it was felt that TP was the only valid P parameter that could be analysed.

### 6.2.2 Rainfall in the Study Catchments

Rainfall data were obtained from the Irish Meteorological Service. Table 6.1 lists the stations used in this study and their associated details. Daily potential evapotranspiration was only available for Shannon airport. This data was used to calculate effective rainfall (ER) at Shannon airport.

**Table 6.1 Meteorological Stations used in this study**

| *Station Name* | *Catchments covered* | *Height (m)* | *Grid Ref.* | *Daily data obtained* |
|---|---|---|---|---|
| Knock Airport | Robe, Co. Mayo | 203 | M 463 955 | Potential Evapotranspiration |
| Claremorris | Robe, Co. Mayo | 65 | M 342 751 | Rainfall |
| Corofin | Fergus, Co. Clare | 29 | R 287 887 | Rainfall |
| Shannon Airport | Co. Limerick | 6 | R 379 603 | Rainfall & Potential Evapotranspiration |

Figure 6.1 - Figure 6.3 presents monthly rainfall and long term monthly averages for the period May 1998 through to April 2000 for the three meteorological stations used for rainfall. Generally the trends at each station during the study period are consistent with the 30 year monthly averages. However, there were some peculiarities. The summer of 1998 was very wet, especially for June. September 1999 was an exceptionally wet month at all three stations. The wettest month during the study period was December 1999. These particular months contrast with the corresponding 30 year monthly averages.

**Figure 6.1 Monthly rainfall and 30 year average for Claremorris, Co. Mayo.**

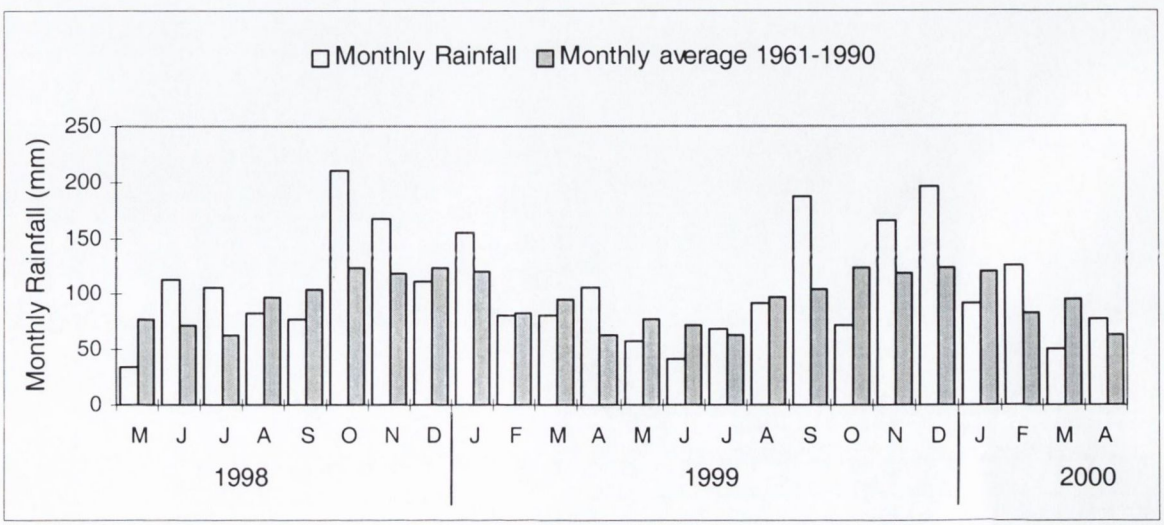


**Figure 6.2 Monthly rainfall and 30 year average for Corofin, Co. Clare.**

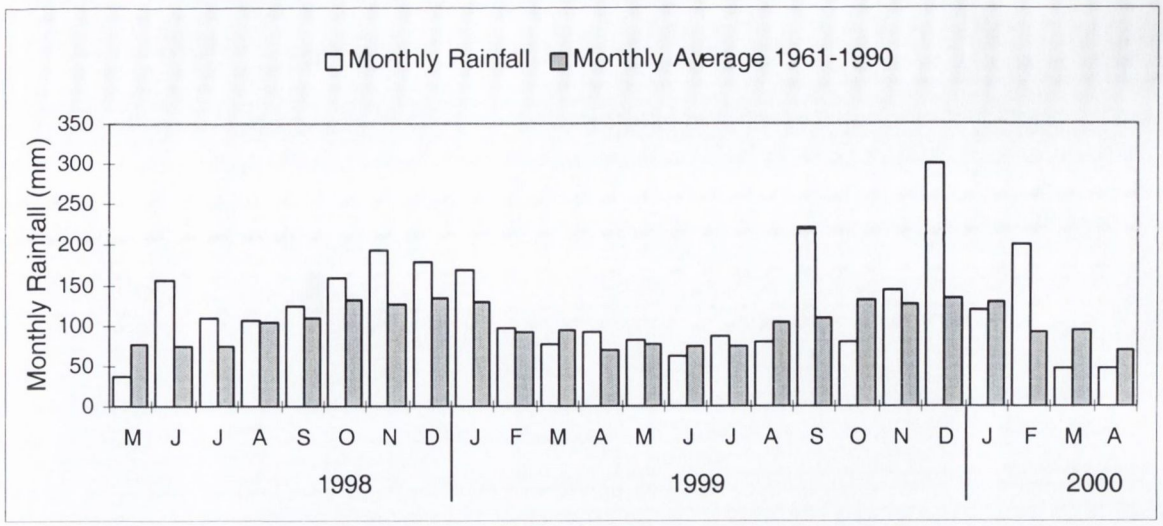
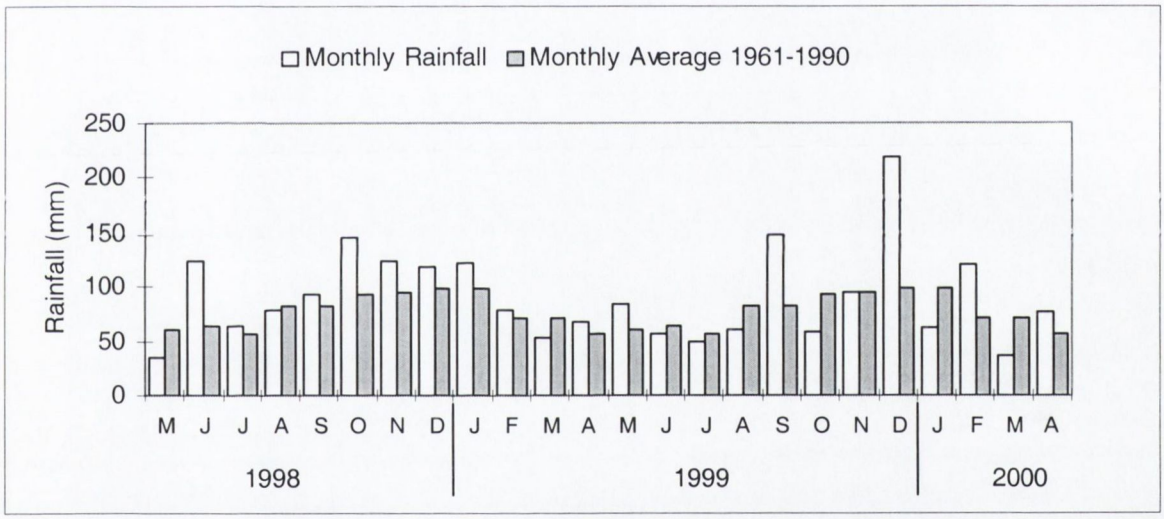


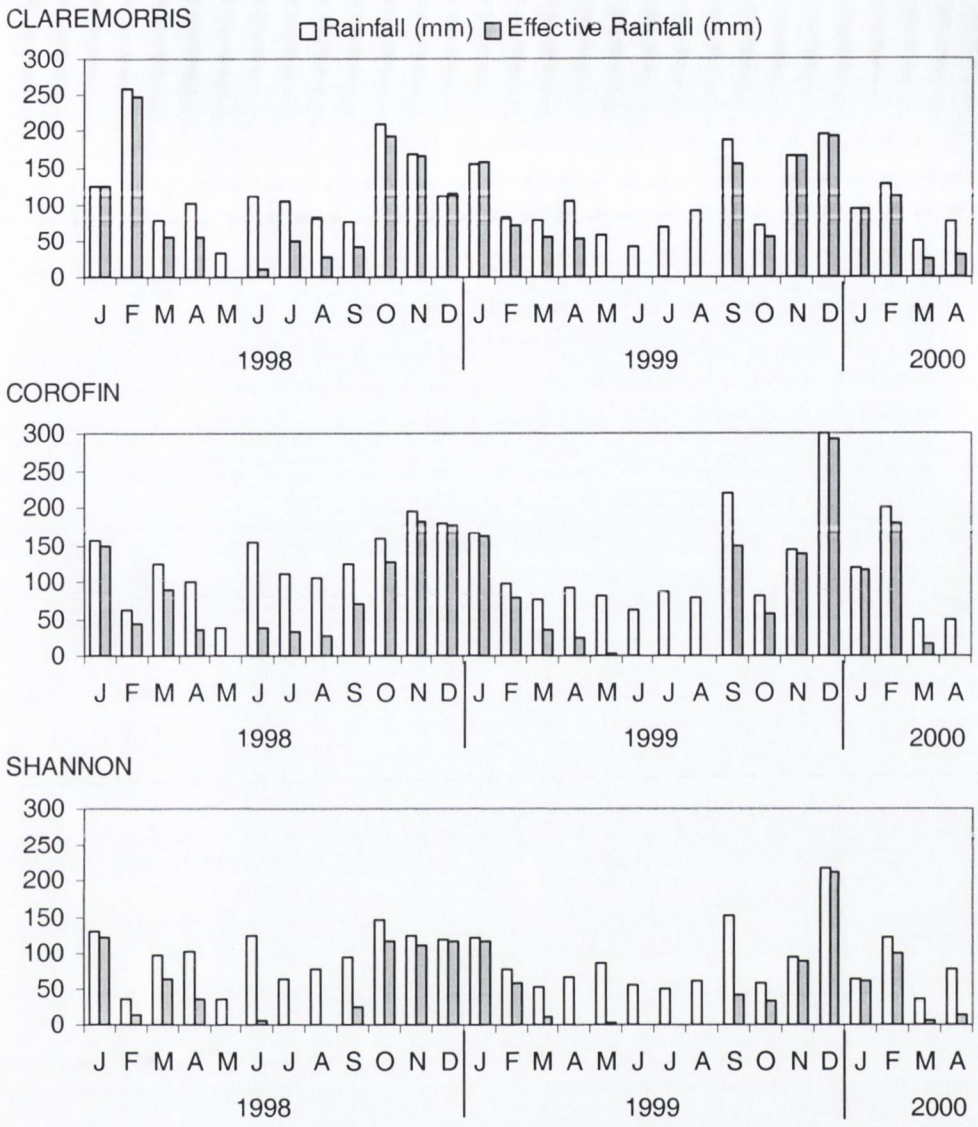

**Figure 6.3 Monthly rainfall and 30 year average for Shannon Airport, Co. Clare**




### 6.2.3 Effective rainfall and soil moisture deficits

Monthly potential evapotranspiration (PE) data was used to calculate effective rainfall (ER). Rainfall and ER are for each of the rainfall stations is presented in Figure 6.4. Unfortunately PE data is only available for the main synoptic stations in Ireland. Therefore the Shannon PE data was used to calculate ER for Corofin and Shannon. For Claremorris, PE data at Knock airport, located 10 km to the north, was used to calculate ER. In each case rainfall data at Claremorris and Corofin was used.

**Figure 6.4 Rainfall and effective rainfall at Claremorris, Corofin and Shannon..**




Consistent at all three stations was a period of no effective rainfall in the summer of 1999. In particular the months of June, July and August 1999 show a prolonged period where the soil moisture deficit is so great that all rainfall is either taken up by the soil or evapotranspired. This extended soil moisture deficit period was not replicated in the previous summer of 1999.

## *6.3 Long Term Changes in Groundwater P*

### 6.3.1 Introduction

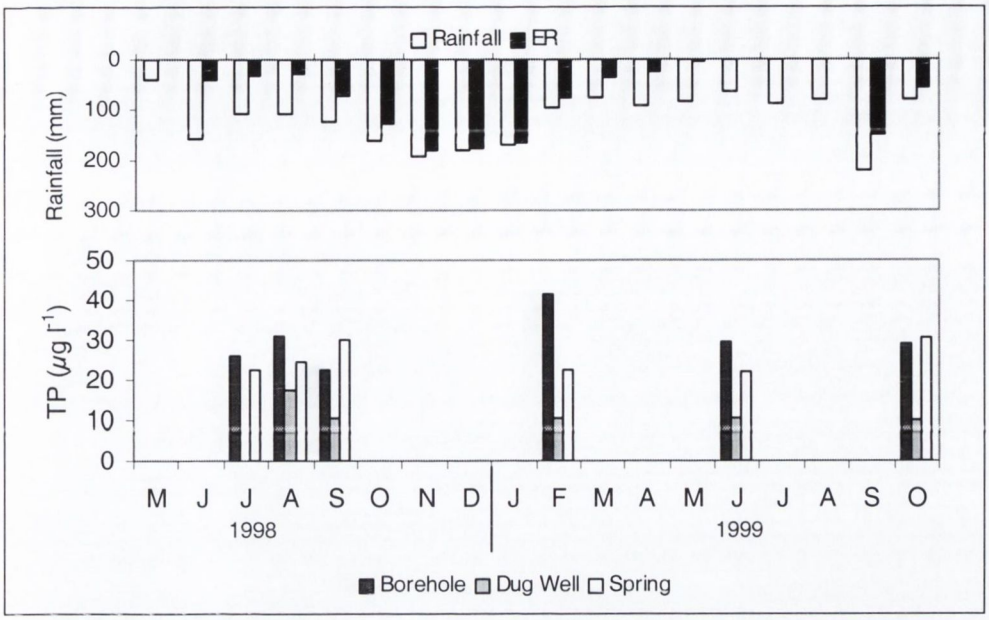
The assessment of long term changes was based on an examination of temporal changes in TP at various site types over the duration of the project. TP was used for this assessment because it comprised the largest dataset. All groundwater sites were included in this analysis, except in situations where the TP levels were of gross proportion, (see Section 6.3.5). Temporal changes in measured surface water TP are not described here (see Chapter Eight).

### 6.3.2 Fergus catchment

The Fergus catchment results are presented in Figure 6.5. Boreholes, springs, dug wells, and lakes were grouped by median for each month sampled. Overall, the TP in groundwater remains relatively stable over the 15 month period. Boreholes and springs between July and September 1998 exhibit a trend of slight increase, which may reflect the beginning of autumnal recharge. However, it should be noted that June 1998 was an exceptionally wet month and July and August 1998 were also wetter than the long term monthly averages which may obscure recharge inferences.

Borehole TP levels increase after the January 1999 rains, exhibiting a slight decrease from February to June 1999. This may reflect the increasing soil moisture deficit as the effects of the winter recharge recedes. However, spring TP in June 1999 remained stable despite been in the middle of a high soil moisture deficit period. There is a rise in median spring TP levels in October 1999. This follows the extreme rainfall reported for September 1999 (100% above the long term mean) which was large enough to negate the large moisture deficit which built up in the soil. The dug wells remained fairly stable with the lowest mean TP levels. This may reflect their isolation from the main body of groundwater, and a limited contributing area of surficial recharge.

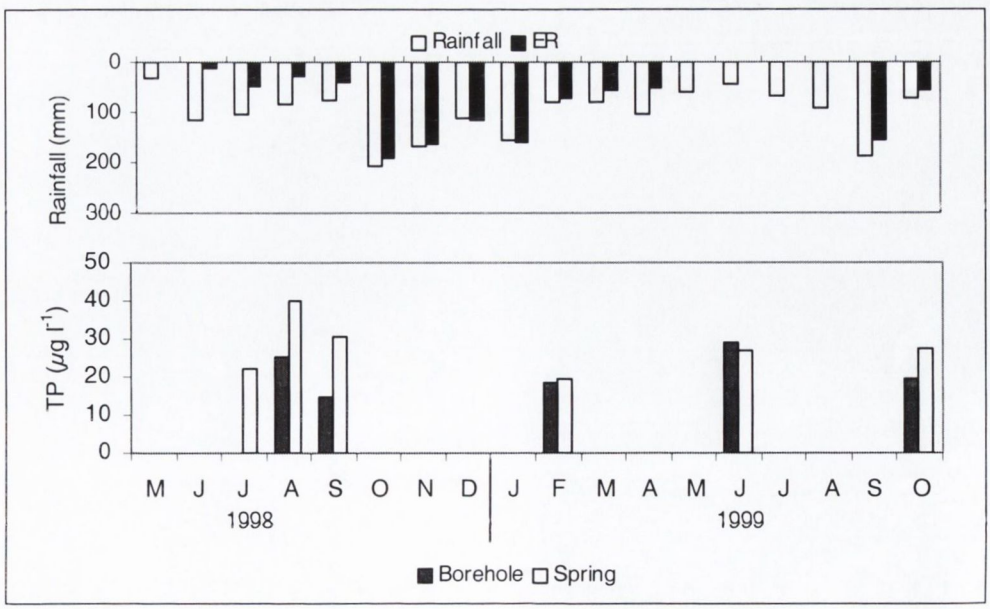
**Figure 6.5 Seasonal changes in median TP in groundwater of the Fergus catchment.**




### 6.3.3 Robe catchment

Figure 6.6 presents long term changes in mean TP in the Robe catchment for boreholes and springs. Between August and September 1998 median borehole and spring TP decrease with reduced monthly rainfall. The remaining data shows no clear relationship with rainfall. The February and October 1999 median groundwater TP appears unaffected by high effective rainfall in January and the exceptionally wet September 1999. The July data increases from Feburary despite a lack of effective rainfall.

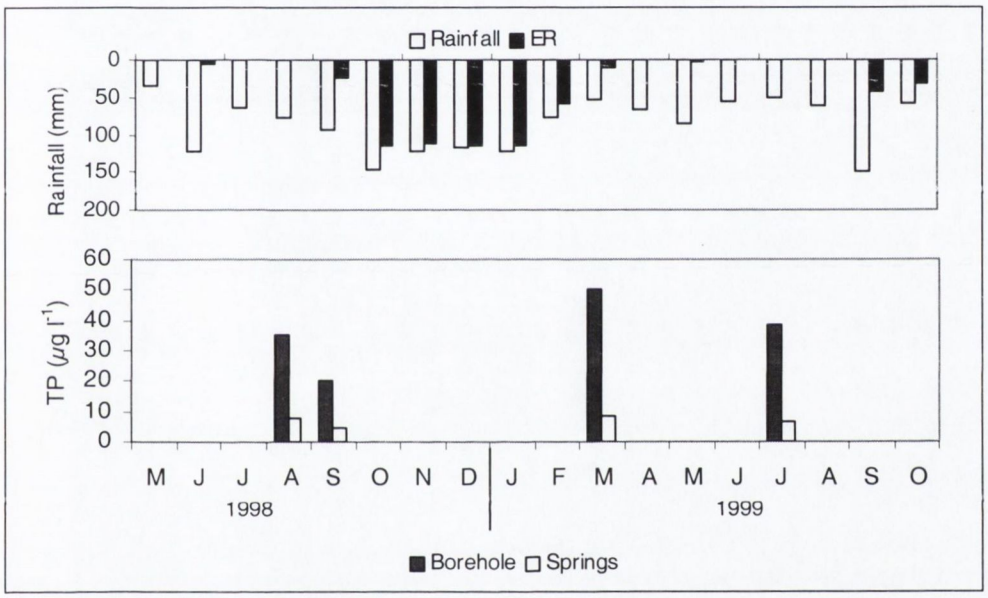
**Figure 6.6 Seasonal changes in median TP in groundwater of the Robe catchment.**



### 6.3.4 Limerick sites

Figure 6.7 presents long term changes in mean groundwater TP in Co. Limerick. Only public supply boreholes and springs were included in this analysis because the group schemes were only sampled in summer 1998 and summer 1999. The boreholes are consistently higher in TP than the springs, which are extremely low in TP (<10 $\mu g\ l^{-1}$). Both springs and boreholes exhibit little response to recharge. An exception is the March 1999 borehole median, the slight increase may reflect a delayed response to the winter rains.

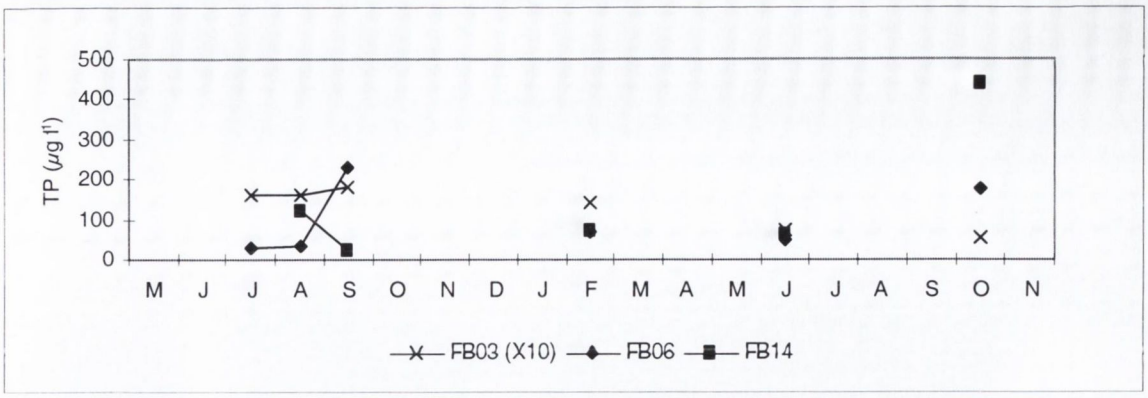
**Figure 6.7 Seasonal changes in median TP in Limerick groundwater.**




### 6.3.5 Boreholes with gross levels of TP

Several of the boreholes in each catchment were not included in the long term analysis due to gross levels of TP reported on at least one occasion. Levels greater than two standard deviations from the mean borehole level in a catchment were identified as gross. Generally gross levels constituted TP concentrations greater than 100 $\mu g\ l^{-1}$. Figure 6.8 to Figure 6.10 present these boreholes for the Fergus and Robe catchment, and Co. Limerick.

**Figure 6.8 Fergus boreholes with gross TP levels.**




It can be seen from Figure 6.8 that of these three boreholes in the Fergus catchment only FB03 and FB06 exhibit any trends that be explained in terms of recharge. FB03 was the borehole with highest TP levels recorded in the whole project. Note, values for FB03 have been presented with a dilution factor of times 10 (i.e. FB03 X10). The borehole was situated in the farmyard, and although reasonably protected at the well-head, the farm was very intensively farmed, with shallow soils. It is likely that either farmyard washing or a nearby septic tank was the cause of the contamination. A slight increase occurs between July and September 1999 (maximum 1814 $\mu g\ l^{-1}$) with the onset of autumnal recharge. The TP levels steadily recede, irrespective of recharge, to an October level of 515 $\mu g\ l^{-1}$. This could reflect adoption of mitigating measures by the landowner, since this borehole was also used for drinking water supply and was also experiencing elevated bacterial levels. The borehole FB06 also shows a response to recharge both after an increase in rainfall in September 1998 and 1999. This domestic well, may have a nearby source of phosphorus (e.g. septic tank), which only impacts the well after periods of heavy rainfall. Trends at the FB14 are unclear. Only the October 1999 result, 441 $\mu g\ l^{-1}$ TP, may be a response to September 1999 rainfall. This borehole is completely unprotected from stock and casing is flush with ground level. Therefore, it is likely that during heavy rainfall, both P from dung patches and landspreaded material (the borehole is situated on a grazing field) is washed either down the side of the casing or directly into the well.

**Figure 6.9 Robe boreholes with gross TP levels.**

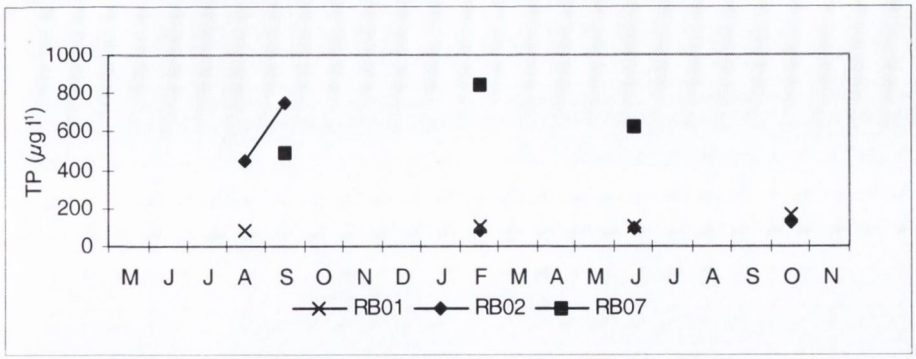
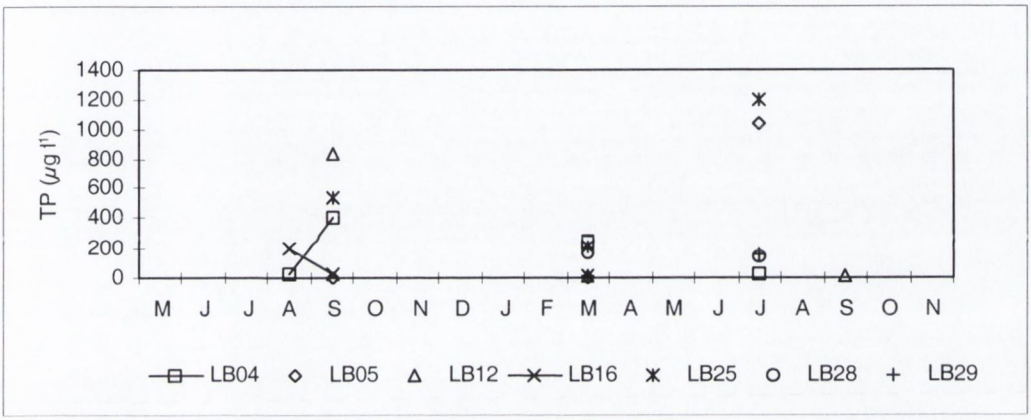



Figure 6.9 presents data for three boreholes in the Robe catchment. RB07 is located within an old farmyard that is poorly maintained. The elevated TP levels could easily be sourced to the farmyard. The fact that an adjacent borehole (RB06 approx. 100m away) has very low levels of TP (16 - 50 $\mu g\ l^{-1}$) may indicate that the groundwater contributing to RB07 has spatially restricted karst openings. Disparate water quality characteristics also tends to confirm that RB06 and RB07 are fed by separate groundwater. For example, in February 1999 pH, DO and EC for RB07 was 7.55 pH units, 3.07 mg $l^{-1}$ and 905 $\mu S\ cm^{-1}$, versus for RB06 8.08 pH units, 10.23 mg $l^{-1}$ and 670 $\mu S\ cm^{-1}$. RB02 is a borehole which is situated in a grazing field, and prior to the February 1999 sampling was not protected from stock. However, by February the landowner had joined the REPS scheme and the borehole was fenced off from grazing cattle. This action coincides with elevated TP levels of 449 and 748 $\mu g\ l^{-1}$ before February, with reduced concentrations of 86 - 130 $\mu g\ l^{-1}$ thereafter. The protection measures around the well may have aided in this reduction. However, it should be noted that the summer of 1998 was exceptionally wet, thus any slurry or effluent spread (commonly spread at that time) on the land may also have impacted the well. RB01 probably does not represent a grossly polluted well. Rather, it represents the upper bound of normal TP levels in Robe boreholes. This is reflected in the consistency and level of the results. TP ranges from 82 $\mu g\ l^{-1}$ in August 1998 to 167$\mu g\ l^{-1}$ October 1999. The borehole is also a drinking well located within the farmyard which is meticulously maintained. Therefore, the likely source of elevated P is not clear, but may be a nearby septic tank.

Figure 6.10 presents data for several boreholes in County Limerick. Seven boreholes were excluded from the long term analysis. It is difficult to infer trends from so few data points. LB25 is consistently high, but the others have samples which are both very high and very low. Two good examples are LB12 and LB05. LB12 begins the period with 839 $\mu g\ l^{-1}$ TP

in September 1998, but subsequent samples are 13 and 17 $\mu g\ l^{-1}$. The LB05 borehole begins with two samples in September 1998 and March 1999 both below 10 $\mu g\ l^{-1}$, but July 1999 yielded 1039 $\mu g\ l^{-1}$. Cases where there is a large disparity between results can only be explained by either short-lived pollution events or by sampling error. This latter point cannot be assessed for the August and September 1998 samples because these samples were taken by Limerick County Council staff.

**Figure 6.10 Limerick boreholes with gross TP levels.**




## *6.4 Medium Term Changes in Groundwater P*

### 6.4.1 Introduction

Four springs from the Robe catchment catchment (RS03, RS04, RS01 and RS06) and four in the Fergus catchment (FS05, FS08, FS13 and FS18) were chosen for regular monitoring. These springs have been subject to previous hydrogeological studies, thus making them ideal candidates for detailed analysis. A combination of fortnightly and monthly sampling was carried out between June 1999 and March 2000. Fortnightly sampling was concentrated on the period June to October, when the plant and algal growth in lakes and rivers in greatest. Monthly sampling was then continued from November to March.

### 6.4.2 Robe Catchment

Figure 6.11 presents the P fractions DRP, DOP and PP for each of the four springs sampled intensively in the Robe catchment. Included in the figure are daily rainfall data to pick out individual rainfall events and monthly rainfall/effective rainfall data to compare periods of

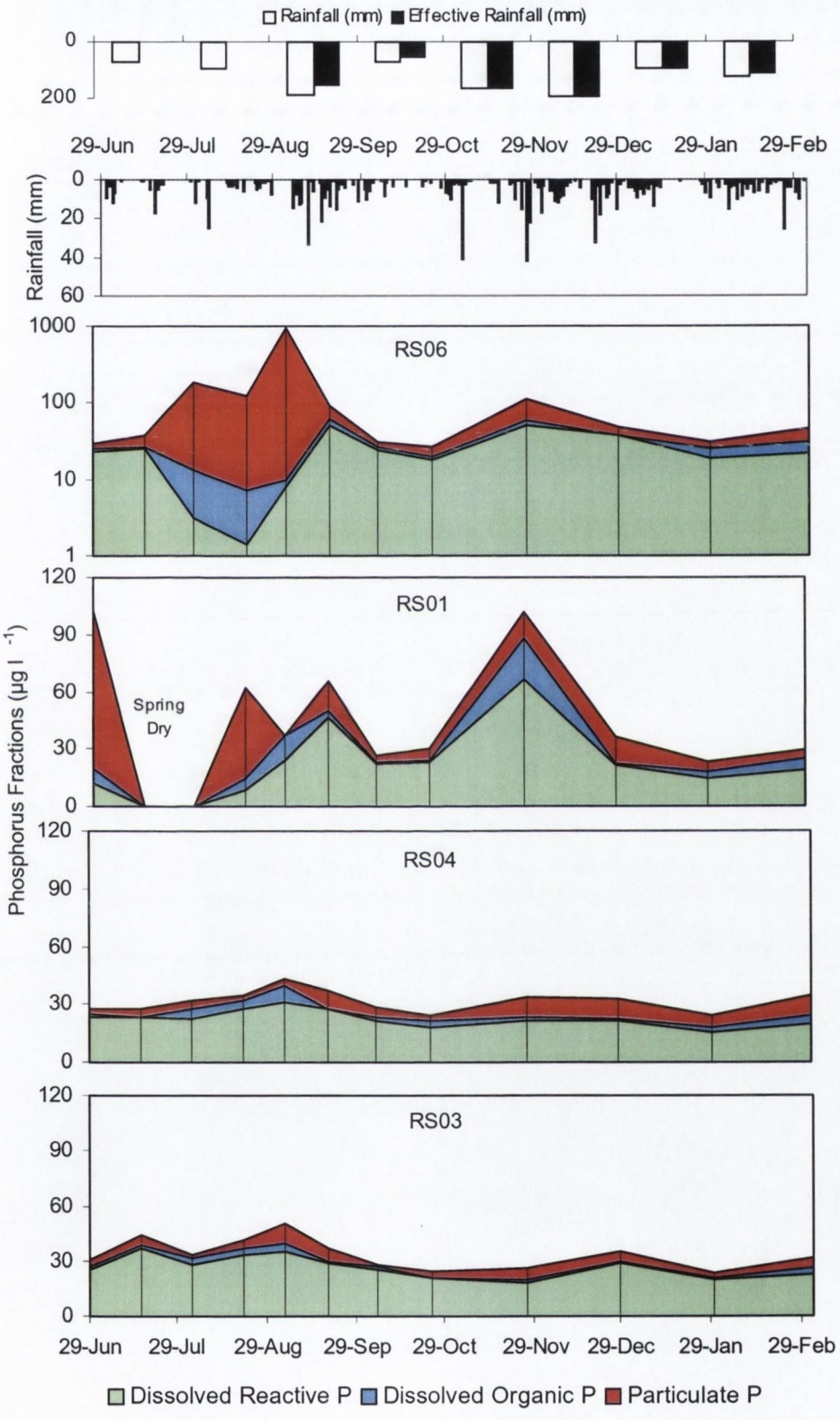
varying soil moisture deficit. The RS03 and RS04 springs are assessed together due to their similarities in P concentration and temporal behaviour. RS06 and RS01 are also taken together for the same reasons.

The two largest springs sampled in the Robe catchment were the RS03 and RS04 springs. Both springs exhibit similar trends in regard to general P changes over the sample period. The fortnightly sampling period between June and October 1999 illustrate a strong hydrological control on spring P levels. The first effective rainfall in September which ends the soil moisture deficit couples well with phosphorus peak for both RS03 and RS04. The monthly sampling period between November and March shows stable P elvels despite heavy rains. The two springs also compare when examining the different P fractions. DRP is the dominant fraction in both with marginally more PP in RS03. It is not unreasonable that both RS03 and RS04 should exhibit such similarities, since water has been traced to both springs from a sink in an up gradient turlough (see Figure 3.6; and Coxon, 1986).

The springs at RS06 and RS01 are also comparable since it is likely that both are fed by similar contributing areas (see Section 6.5.2). RS06 was subject to a pollution event around the 20$^{th}$ July 1999. It is likely that RS01 also was impacted by this event. The RS06 spring became polluted in late July. The exact date is not known but it is likely to be somewhere between the sampling dates 17$^{th}$ and 26$^{th}$ July when the TP concentration jumped from a background level of 38 $\mu$g l$^{-1}$ to 122 $\mu$g l$^{-1}$. It should be noted that the Y-axis in is plotted on a logarithmic scale to account for the large magnitude of TP values after the event.

A detailed appraisal of the effects this event had on RS06 is discussed in Section 6.5.2, which looks at TP concentrations in the spring during 8 hourly and daily sampling. In summary, the pollution event has been attributed to a leaking silage clamp up gradient of the spring. Before the event the measured dissolved fractions (DRP and TDP) were very close to the measured TP fraction. However, once the effluent comes through the spring, DRP becomes minimal and DOP and PP dominate. This reflects the nature of the effluent which is highly organic and would also readily adsorb any free phosphate ions in solution. The phosphorus peaks on the 4$^{th}$ September with a TP value of 956 $\mu$g l$^{-1}$. After this date the TP values decrease to background levels as rainfall recedes.

**Figure 6.11 P fractions and rainfall events at Robe springs.**



This relates with the clear drop in effective rainfall between September and October 1999. The dissolved fractions once again reassert their dominance as the particulate-rich P effluent is removed from the spring. There is smaller peak (112 $\mu g\ l^{-1}$ TP) on the 27th November which coincides with a storm event and probably represents residual effluent being flushed from the conduits feeding the spring.

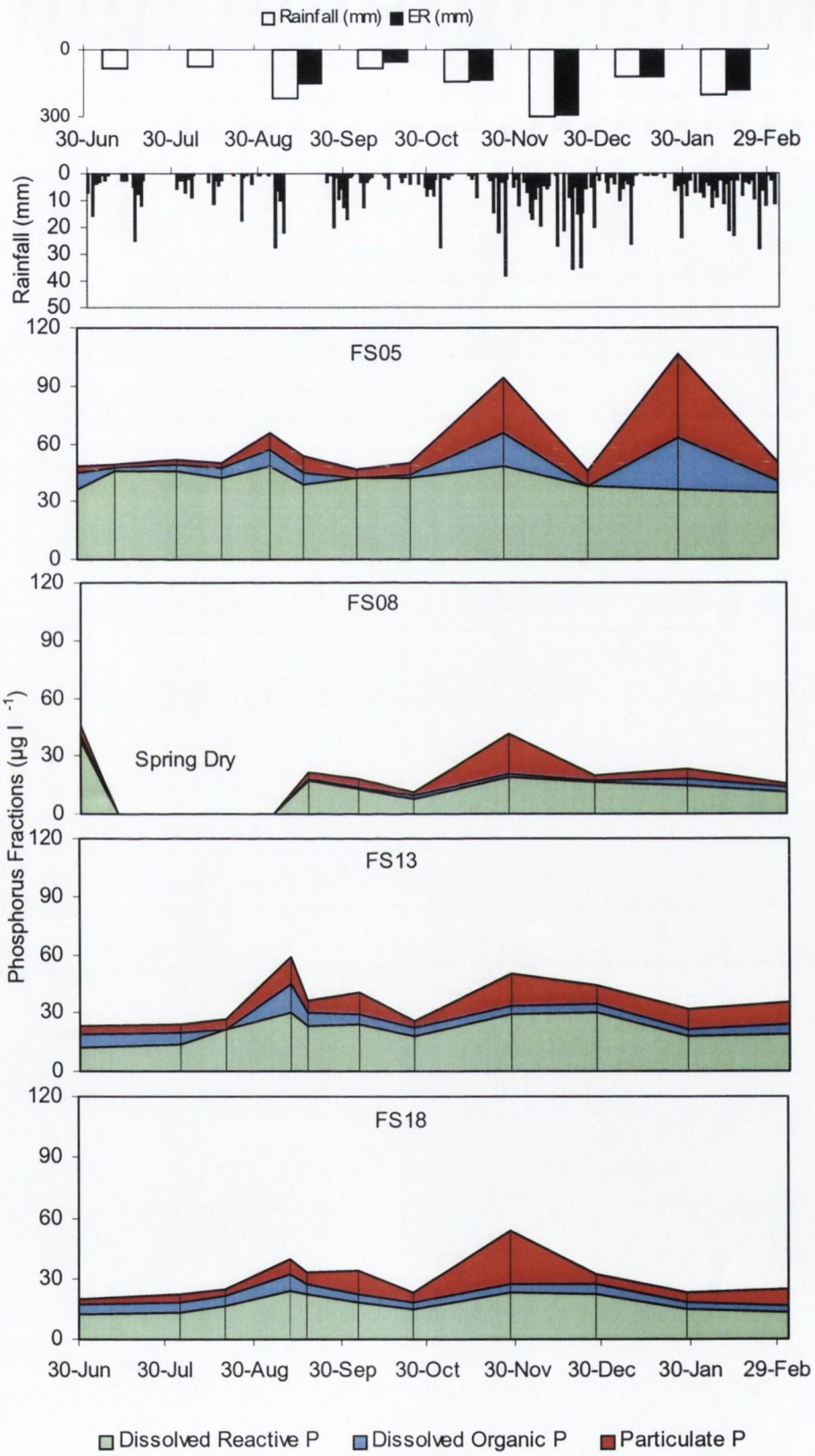
Trends at RS01 are less clear. For a period of approximately 7 weeks, between July 17th and August 21st, the spring was either not flowing (a stagnant pool) or dry. Before this dry period there is an particulate-rich peak which may be attributed to nearby stock (the spring is not fenced off). Thus, as the flow in the spring falls off the impact of the stock may be accentuated due to a reduced dilution effect. Once the flow is restored in the spring there is a similar particulate P rich peak. This again may be due to stock or it may be associated to the pollution event at RS06 which is situated 2.5 km up-gradient of RS01. Like RS06, RS01 exhibits a peak in all P forms on the 27th November which follows the increase in rainfall. This is followed by a decrease in P after December as rainfall falls off.

### 6.4.3 Fergus Catchment

Figure 6.12 presents the P fractions DRP, DOP and PP for each of the four springs sampled intensively in the Robe catchment. As for the Robe figure, are daily rainfall data are included to pick out individual rainfall events and monthly rainfall/effective rainfall data allow comparison between periods of varying soil moisture deficit.

In the Fergus catchment FS05 and FS08 are the two largest springs sampled in terms of maximum flow (Drew, 1988). However, FS08 is very flashy and, like RS01 spring in the Robe catchment, was dry for a period. FS05 in contrast, is reasonably stable in terms of flow. Drew (1988) reported that 39 mm of rain falling over a 72 hour period caused a tenfold increase in discharge in most springs of the upper Fergus catchment, but FS05 only experienced a twofold increase.

**Figure 6.12 P fractions and rainfall events at the Fergus springs.**



FS05 exhibits similar responses to recharge as described for the Robe springs but perhaps more clearly. There is an increase in P concentrations with increasing recharge, predominantly particulate P, but also DOP. Thus, recharge increases the load and relative proportion of particulate P to the spring. The three peaks coincide with three storm events and also match the three greatest effective rainfall months. Otherwise, the P levels are stable with inorganic P being the dominant fraction, background levels averaging 50 $\mu g\ l^{-1}$ DRP. After each rainfall peak, P levels at FS05 decrease to background levels with DRP once again constituting the major component.

FS08, like RS01 spring in the Robe catchment, presents a more complicated pattern. Prior to FS08 going dry there was a peak in P, which, like RS01, may be due to nearby stock and reduced dilution effect. Similar to FS05, phosphorus peaks with increased particulate proportions, especially during the November 28$^{th}$ storm event. DRP is once again the stable parameter.

FS13 and FS18 again exhibit the hydrological controls discussed for FS05 and FS08. Both springs increase in DOP and PP in response to storm events, particularly at November 28$^{th}$. DRP also responds but is more muted. Overall the general P trend appears to be a stable DRP component combined hydrologically controlled peaks of particulate P. Overall FS13 and FS18 have similar trends in TP temporal trends. This is expected given that Coxon (1995) has established a common sink at Lough Keogh (see Figure 3.4) which feeds both springs.

## *6.5 Short Term Changes in Groundwater P*

### 6.5.1 Introduction

This section is concerned with the responses of the groundwater springs to short term temporal events. Three springs were assessed in this way: RS06 spring in the Robe catchment; and FS05 and FS13 springs in the Fergus catchment. A 24-bottle automatic sampler was used to obtain either 8 hourly or daily samples. Since the samples were left in the sampler for up to one week only TP could confidently be analysed.

### 6.5.2 RS06 spring: Robe catchment short term changes

As mentioned in section 6.4.2 above, RS06 was subject to a pollution event commencing around the 20th July. Anecdotal evidence strongly suggests that the source of the pollution was a leaking silage clamp located up-gradient of the spring. Results from the autosampling corroborate this suggested source. Figure 6.13 presents the data obtained using the auto sampler at RS06 spring.

A background TP value of 38 $\mu g\ l^{-1}$ was recorded on July 17th, and when the auto sampler was installed on July 26th a TP value of 122 $\mu g\ l^{-1}$ was reported. Therefore, whilst the pollution event could have occurred before July 17th, its arrival at the spring was after this date. For the first two weeks, as indicated on the graph, samples were recovered every 8 hours, and thereafter on a daily basis. Once the pulse of effluent is recorded at the spring (26th July), a sustained level of TP is maintained around 170 $\mu g\ l^{-1}$ for about two weeks. The extreme peaks in TP do appear to follow extreme rainfall peaks. This is particularly true of the TP peak of 878 $\mu g\ l^{-1}$ on 7/8/99 which was preceded with 22 and 27 mm of daily rainfall on the 5/8/99 and6/8/99 respectively. Similarly, the TP peak of 1814 $\mu g\ l^{-1}$ on 27/8/99 is preceded by 21 mm of daily rainfall on the 25/8/99. These timings would indicate a 24 to 48 hr response at the spring to rainfall events. Local climatic variations may dictate a slightly shorter or longer response time. July and August 1999 were both months with nil monthly effective rainfall (see Figure 6.4). Therefore, the spring is responding to rainfall and producing contamination even where calculations suggest that there is a soil moisture deficit.

Figure 6.14 plots the same graph but as a reduced TP scale to facilitate clearer viewing of the smaller TP peaks (although still circa 100 $\mu g\ l^{-1}$, so important in algal production terms). Between August 12th and August 26th TP follows a saw tooth effect. Between these dates there are also a series of rainfall events. Whilst these TP peaks do not coincide consistently with the storm events, their regularity suggest hydrological control. An explanation of this pattern could be that some effluent in the initial two week pulse did not come through to the spring but got caught up in some dead-end karstic fissures. These trapped pockets of effluent only rejoin the main flow path to the spring during storm events which acts to flush them out.

**Figure 6.13 Autosampler TP data and daily rainfall for RS06 spring, Robe catchment.**

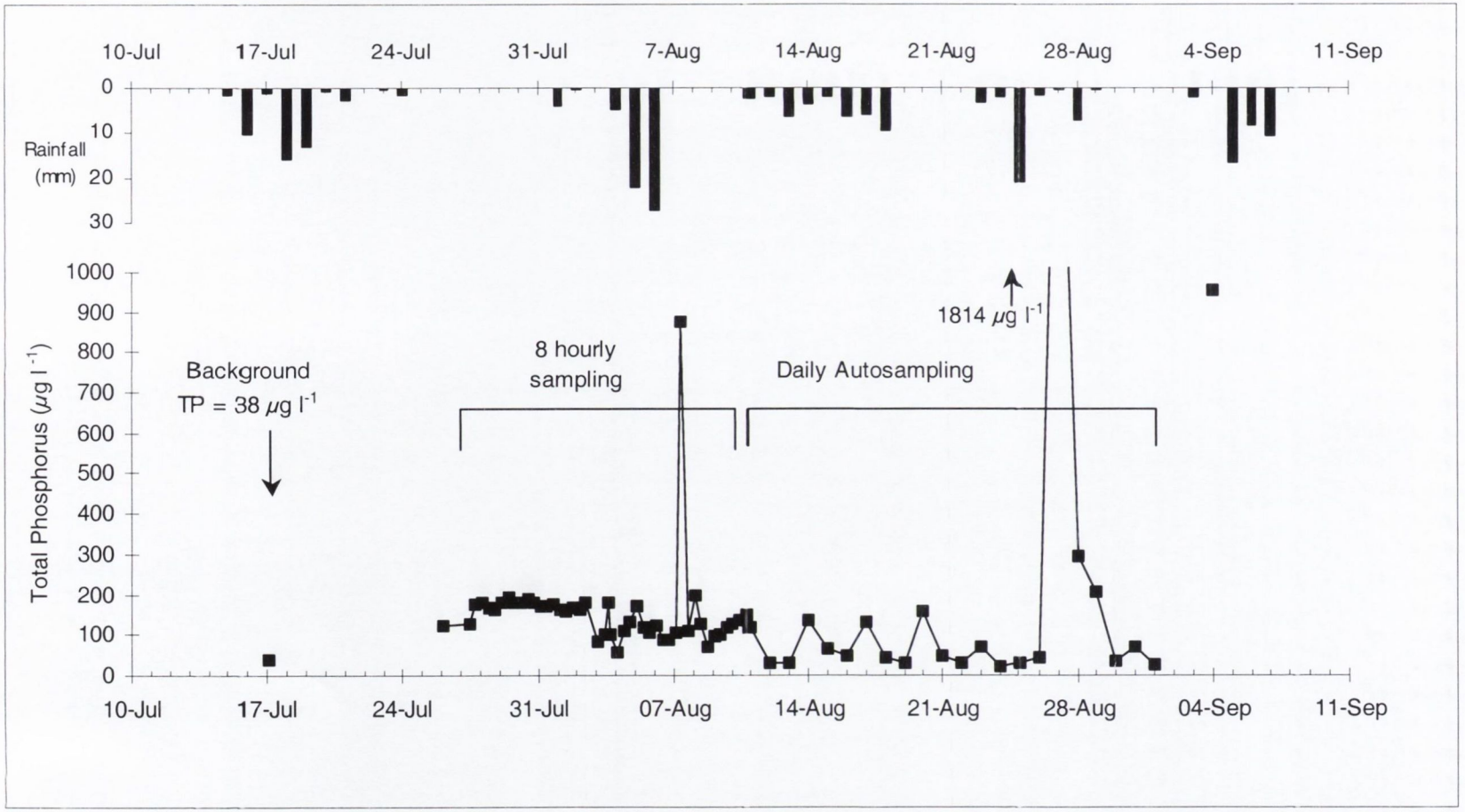
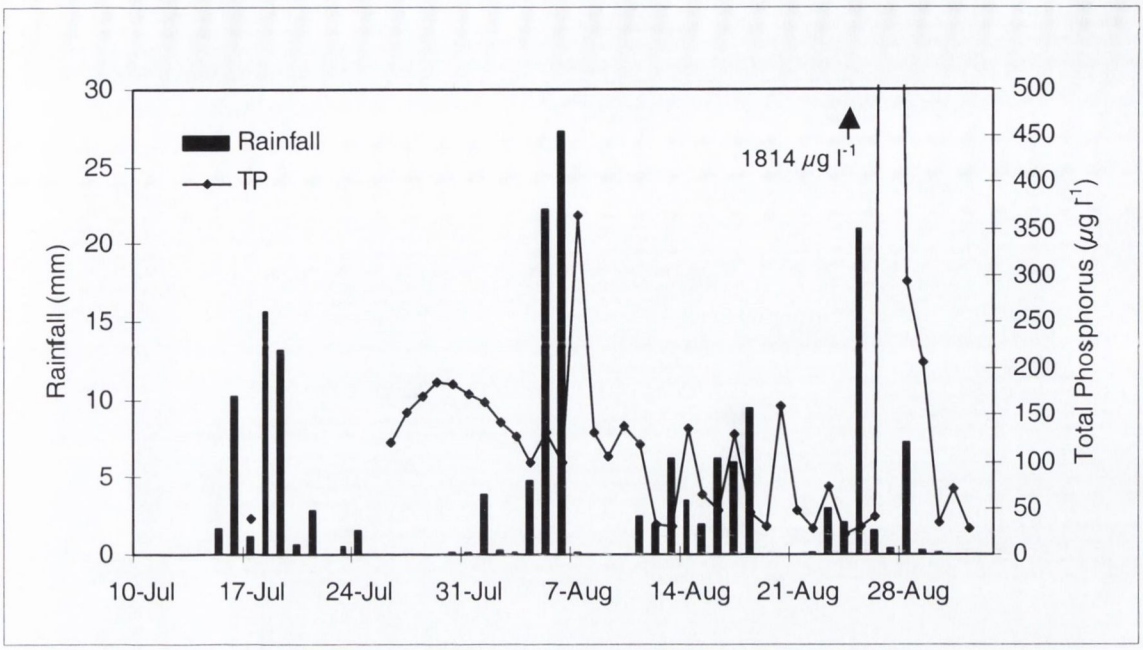


**Figure 6.14 RS06 Daily TP: reduced TP scale, 8 hourly samples averaged.**



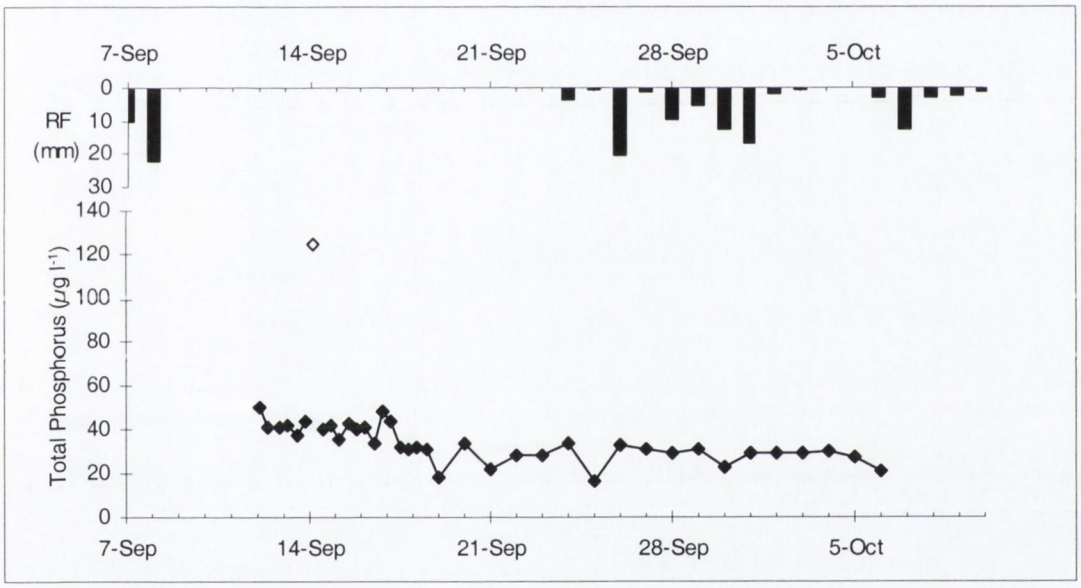

The timing of this pollution event and the sustained pulse for the first two weeks strongly indicate that silage effluent was the cause. Several authors have reported that most of the effluent from a silage clamp is produced within the first two weeks of ensiling (Bastiman, 1976, O'Kiely, 1985, Morgan and O'Toole, 1992). July and August are common months for silage production and a similar contamination event happened at RS06 the following year in August 2000. All this evidence points towards silage effluent contamination. However, this could only be validity through detailed site-specific assessment of potential sources.

### 6.5.3 RS13 spring: Fergus catchment short term changes

FS13, in the Fergus catchment is one of several springs that feed Lough Dromore. It was also subject to automatic sampling. Samples were taken by the autosampler between 12/9/99 and the 6/10/99. An eight hourly sampling program was carried out until 18/9/99. Thereafter, samples were taken daily until 6/10/99. Figure 6.15 presents the data obtained using the auto sampler at FS13spring. In stark contrast to the RS06 autosampler data, FS13 exhibits no response to daily rainfall. There is one extreme TP value of 124 $\mu g\ l^{-1}$ from a sample taken at 4:15 a.m. on the 14/9/99. However, it does not coincide with any rainfall peak, and possibly represents an erroneous result caused by sampling error (e.g. the intake tube may have sucked in some sediment). Overall, both the 8 hourly and daily sampling

display a decreasing TP trend with time. A potential quality control issue associated with using autosamplers is that of P loss (or gain) due to sample storage time (Kotlash and Chessman, 1998). However, the results from the blanks and spike samples tend to indicate that for TP storage time did not impact greatly on the data. Therefore this outlier may represent a local thunderstorm not picked up by the rain gauge at Corofin. After the long soil moisture deficit built up over June, July and August 1999, it only in September that the first effective rains reach groundwater (see Figure 6.4). However, due to the build up in soil moisture deficit, only 68% of the total rainfall in this month is effective rainfall. Perhaps the lack of response represents this 32% of total rainfall which did not reach groundwater.

**Figure 6.15 Autosampler TP data and daily rainfall for FS13 Spring. Clear diamond represents possible erroneous TP value.**

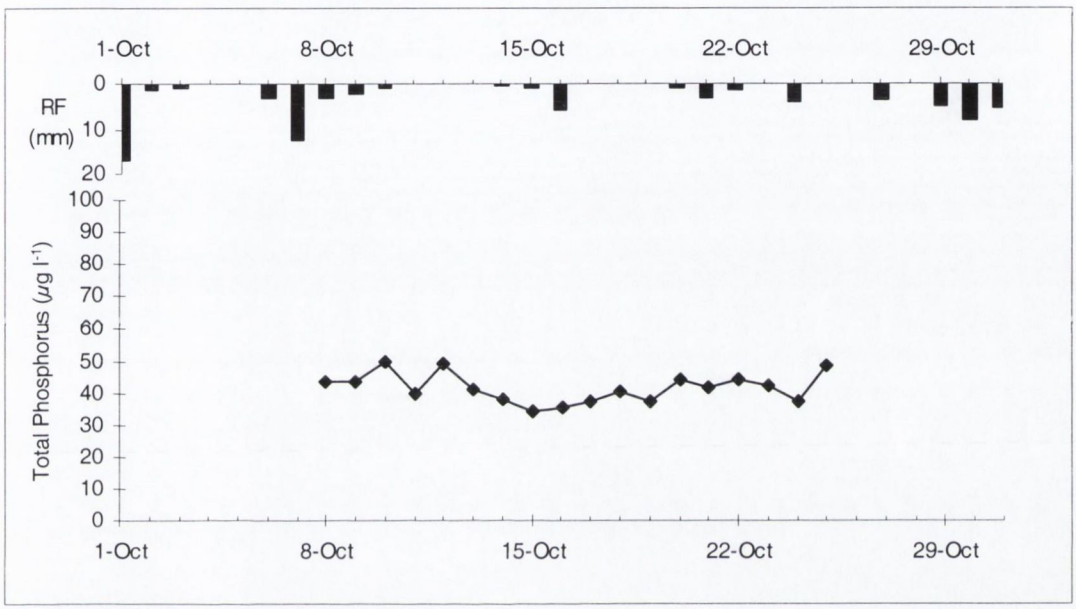



### 6.5.4 FS05 spring: Fergus catchment short term changes

The FS05 spring was sampled between 8th and 25th of October 1999. Due to an initial mechanical failure, only daily samples were taken between these dates. Figure 6.16 presents the TP data and daily rainfall data for this period at FS05. FS05 is the largest spring sampled in the Fergus catchment and unlike many of the other flashier springs has quite a stable flow, reflecting the more diffuse nature of its recharge. This stability in terms of flow is paralleled with a stability in TP concentration during this two and half week period. It is clear from Figure 1.1 that rainfall events are not influencing TP levels at FS05. However, few rainfall events occurred during the autosampling period and the maximum

was only 5.9 mm on October 16th. The long period without effective rainfall in the three months prior to September built up a large moisture deficit in the soil. While September was an exceptionally wet month (twice the long term average), effective rainfall was still only 68% of the total. Even into October effective rainfall is at 69% of the total and only by November has the deficit being completely eroded (see Figure 6.4).

**Figure 6.16 Autosampler TP data and daily rainfall for FS05 Spring.**




## *6.6 Discussion*

Groundwater quality is often considered more stable than surface waters primarily due to greater residence times. Temporal trends will therefore tend to evolve far quicker in surface waters than in groundwater (Loftis, 1996). There are exceptions, karstic aquifers being an especially relevant case for the Fergus and Robe catchments of this study. Whilst carrying out tracing experiments at sinks up-gradient of the RS04 spring, Coxon and Drew (1986) measured travel times greater than 100 m $hr^{-1}$ under high flow conditions. Drew (1988) reports travel times of 110 m $hr^{-1}$ under medium stage conditions between a sink at Carran Turlough (FL07) and FS08 spring. Thus, in karstic systems, conduit flow and point recharge can result in rapid responses at springs to rainfall events.

The long term data generally indicate an overall stability for each of the site types. However, there were some exceptions. Boreholes and springs in the Fergus catchment

exhibit slight increases in the September 1998 and October 1999 sampling events. This could reflect a mobilisation of soil P and flushing through the aquifer after the first autumnal rains. P accumulated in the aquifer interstices and fissures may only become mobilised after substantial rains following the drier summer period. This phenomenon has been reported for loss of P from soils via overland flow. Dils' (1997) study of a grassland catchment in Leicestershire reported greatest TP concentrations during storm events, particularly in response to the first autumnal rains. Similarly, Kurz's (2000) study of overland flow in a high soil P plot in Co. Wexford reported highest P loadings during August 1997, the first major rains after the summer. However, given the often wet nature of Irish summers, and in this case a particularly wet June 1998, such an explanation may only be partially true. The September 1998/October 1999 peaks, may also reflect the timing of land-use activities (e.g., the landspreading of silage effluent described above), which is subsequently flushed through to the aquifer after substantial rains.

Boreholes and springs in the Robe catchment, in contrast to the Fergus catchment, exhibited little response to the exceptionally wet September 1999. Although overburden in the Robe catchment is at least 20 m thick in places, it is variable, and patches of limestone pavement do occur (Coxon and Drew, 1986). Therefore, whilst a thicker subsoil could the delay or eliminate a response to substantial rains the likelihood is that groundwater in the Robe simply responded earlier to the high September 1999 rains, and the October 1999 sampling missed this episode. This fact is brought out when examining the medium and short term changes (see below).

Several of the boreholes sampled had TP at levels way beyond the normal distribution in each catchment area. Daly (2000) identifies several reasons why boreholes get contaminated when a source of pollution exists: vulnerability of groundwater; poor management of pollution sources; inappropriate location of pollution source and boreholes, and; poor borehole construction and sanitary protection. The vulnerability of the groundwater, as determined by subsoil thickness and permeability (DELG *et al.*, 1999), will determine the likelihood of contaminants passing through the soil and subsoil to the groundwater. This factor is dealt with in more detail in Chapter Five. Poor management of pollution sources includes ineffective containment of wastes (e.g. slurry and silage pits, and septic tanks). Many of the boreholes with gross TP levels are located close to or within the farmyard. Thus, a pollution source is placed within the ZOC of the borehole. Daly (2000)

indicates that one of the pathways for contaminant to reach groundwater is where surface water or shallow groundwater has direct access to the borehole either down the outside of the well casing and some time inside the well casing. A suitable concrete collar and protective casing system is required to minimise such contamination (Fetter, 1999). It is likely that one or a combination of these reasons has resulted in these boreholes having elevated TP levels.

Both the Robe and Fergus catchment springs exhibited some hydrological control of P fraction levels. All eight springs particularly responded to the extreme rainfall in September 1999. However, subsequent rainfall events peaks in December 1999 and February 2000, generally appeared to have a lesser impact on P levels. The impact of the first major autumnal rains could have driven this trend, with subsequent rainfall peaks having a lesser impact on spring P as most of the mobile P is used up, or as land-use activities cease. It should be noted that the frequency of sampling after the end of October 1999 was monthly, which could have result in loss of resolution.

All P fractions tended to increase to varying degrees after periods of heavy effective rainfall. Pionke *et al.* (1999) studied a agricultural catchment in Pennsylvania over a 12-year period and found that dissolved P concentrations in streamflow were highest in storm events during all seasons, but especially during the summer when the flow was least. The springs are therefore exhibiting similar trends to those reported in surface water and artificial subsurface drainage. Several of the peaks in P coincided with individual rainfall events. This highlights the inextricable link between surface water and groundwater in karstic systems. Whilst DRP remained the dominant and most stable fraction in all cases, PP and DOP tended to increase to a far greater degree than DRP during periods of high rainfall. This would indicate that during these periods a greater proportion of DOP and PP are being transported through the aquifer to the springs. Kronvang (1992) found strong positive relationships between particulate P concentrations and discharge in the Lyngbygaards River in Denmark. Grant *et al.* (1996) also reported high PP concentrations in subsurface drains during storm events from arable catchments in Denmark. In the case of the studied springs, the increased volume and speed of water travelling along flow paths to the springs is providing sufficient energy to transport particles either flushed through the soil or present in the aquifer, which under normal stage conditions would not be mobilised.

The daily sampling illustrated contrasting responses of karst springs to storm events. RS06 spring in the Robe catchment offered a unique example to examine the behaviour of a spring in terms of TP during extreme pollution stress. The spring appeared to respond to rainfall and produced contamination even where calculations suggest that there is a soil moisture deficit. FS13 and FS05 were not so perturbed by such pollution and exhibited relatively stable TP concentrations. It is only when we examine these springs at a larger time scale that we see some degree of hydrological control. The fact that the likely source of the pollution at RS06 was close to a swallow hole would mean that there is a direct link to the aquifer. Therefore, even a high soil moisture deficit will have no effect, the soil being by-passed. The benefits of high frequency autosampling was demonstrated.

The pollution event at RS06 highlights the notoriously effective ability of karst aquifers to transmit rather than treat pollutants (Ford & Williams, 1989). It is only because the spring was supplying drinking water that the event was noted. The vast majority of the effluent had passed through the spring in almost 10 weeks, thus quarterly sampling could have missed this episode. In a karst spring in Sligo, Coxon and Thorn (1989) noted marked changes in calcium and faecal coliforms over a month period as a result of changing flow conditions. They highlighted the need to adopt storm event driven sampling rather than discrete sampling in karstic springs showing rapid changes.

These events are particularly important when considering their contribution to surface water quality. In the Fergus catchment Coxon and Drew (1998) report north - south underground linkages of 100 - 200 m/hr, indicating a high degree of karstification, and rapid transfer potential of contaminants from sink to spring. Short term pollution events will be of particular concern during the summer months, during low stage conditions when in-river P concentrations are typically low due to plant uptake. Even small volumes of P rich contamination being transmitted via springs could have a dramatic effect on surface water productivity and ecology. Identification and management of sinks and springs in karstic areas presents an urgent and demanding challenge.

# CHAPTER 7. LAND COVER

## *7.1 General introduction*

This chapter examines to what degree land cover characteristics influence phosphorus levels in groundwater. Land cover characteristics have been used widely in the assessment and modelling of phosphorus in surface waters (Johnes, 1996; McGuckin *et al.*, 1999; Johnson *et al.*, 1997). Their use in the assessment of groundwater contaminants is also common, but generally associated with the assessment of bacteria (Boyer and Pasquarell, 1999) or nitrates (Hopstaken and Ruijgh, 1994). Less common are studies that have used land cover data to assess groundwater phosphorus. Groenenberg *et al.* (1996) used land use data, and soil characteristics among other datasets to model P leaching to groundwater in phosphate-saturated soils in the Netherlands. Dreischer and Gelbrecht (1993) in their study of the lower River Spree, Germany, reported highest TP levels (1-10 mg $l^{-1}$) in groundwater under sewage fields. However, over all such assessments appear infrequent. This may reflect the general neglect of phosphorus in groundwater studies discussed in Chapter One.

This chapter examines groundwater P with three land characteristics: soil classification in each of the catchment areas was provided using published hard copy soil maps; land cover data using the CORINE Land cover database; and agricultural statistics by district electoral division using data from the Central Statistics Office.

## *7.2 Soil Cover*

### 7.2.1 Introduction

For phosphorus to enter the groundwater it must be leached from the surface layers, and be transported through the vadose zone to the saturated zone. Leaching of phosphorus from soils has been identified in areas which have the following characteristics: coarse textured soils (Eghball, 1996) and sandy soils (Zhu *et al.*, 1994; Breeuwsma *et al.*, 1992) with high permeability (Chen *et al.*, 1996), shallow water tables (Abrams *et al.*, 1995; Grant *et al.*, 1996), low soil-calcium concentrations, (Zhu *et al.*, 1994), soils with low P sorption

capacity (Breeuwsma *et al.*, 1995; Chen *et al.*, 1996), and in phosphorus saturated soils (Breeuwsma *et al.*, 1992).

Three principal soil-forming processes take place in Ireland (Gardiner and Radford, 1980); leaching, gleisation and calcification. Most free-draining soils in Ireland are influenced by leaching and therefore require continuous renewal of nutrients. Gleisation is the soil-forming process caused by water-logging which may be due to a high water table or to the impermeable nature of the soil itself. Calcification results in a redistribution of calcium carbonate in the soil and is an important process for Rendzinas and high base Brown Earths. The most common parent material in Irish soils is glacial drift. Glacial drift varies considerably in constitution and in geological composition giving rise to many different soils.

Soil hydrology has been identified as a key factor controlling P movement in soils (Pionke *et al.*, 1997; Dils and Heathwaite, 1996). In an earlier study Ryden *et al.* (1973) noted that "the concentration of dissolved inorganic P in subsurface and groundwater runoff will depend on the nature and amounts of P-retaining components in the profile, the surface area exposed to percolating waters, and the ease of percolation which affects the contact time of dissolved inorganic P with the retaining components".

Sims *et al.* (1998) carried out a review of P loss in agricultural drainage. Among their conclusions, they identified two hydrological pathways in the subsurface movement from the soil to water. The first is a gradual downward movement of P in percolating waters through the soil eventually reaching the water table or tile drainage. The second is bypass flow, the rapid movement of P via macropores (biological and physical) from the soil surface to the water table of tile drains. In Ireland, Ryan (1998) has identified that the movement through cracks in the soil, worm burrows and other macropores reduces the contact time between percolating water and soil, thus decreasing the natural attenuating capability of the soil.

Daly *et al.*'s (2000) study of agricultural grassland soil types in Ireland reports that soils vulnerable to P loss by desorption were identified as those with elevated soil P status and low P sorption capacity. Daly *et al.*' (2000) attempted to model riverine P loads in Irish catchments using a variety of variables including soil P levels, soil desorption, land-use,

fertiliser and manure. She concluded that catchments with poorly drained soils had higher river P loads than catchments with well-drained soils. The corollary is expected for groundwater, i.e. well drained soils should allow more P to reach groundwater.

Therefore, soil type in terms of physical and chemical properties and drainage behaviour have been seen to influence the downward movement of P through the soil profile. This section examines soil types at each of the groundwater sites in each catchment area.

### 7.2.2 Methods

The primary objective of the methodology was to ascertain the soil classification at each groundwater sampling location in each catchment area. An Foras Talúntais (the National Soil Survey of Ireland) was established in 1959 to carry out a National Soil Survey Programme. During the course of this survey some eight county soil maps were published; the remaining counties were either partially survey or were only subject to a preliminary reconnaissance. This body of work formed the basis of the soil classifications for the majority of groundwater sites. Complete soil maps (Scale 1:126,720) and accompanying bulletins are available for Counties Clare (Finch, 1971) and Limerick (Finch and Ryan, 1966). Additional soils information was available for nineteen of the Limerick public supply sites from source protection reports from the GSI (Appendix B). Whilst a detailed soil map is available for West Mayo, unfortunately only a preliminary soil reconnaissance has been carried out for East Mayo, which includes the Robe catchment (Walsh and Burke, 1980). A report Walsh (1975) on the Corrib-mask drainage scheme provides some additional preliminary soils information for the Robe.

The locations of the Limerick and Fergus sites were identified on the soil map and the soil series classification noted. Characteristics of the derived soil series classification were obtained from the Soil Survey Bulletins. Analysis of groundwater phosphorus and soil characteristics was then carried out. Due the coarse nature of the preliminary soil reconnaissance of East Mayo, only a qualitative assessment of the influence of soil type on groundwater P levels was possible in the Robe catchment.

Mean total P was used as a measure of P concentration so as to maximise the number of sites available for analysis. As discussed previously (see Section 2.3.2) the TP data were

log-transformed to allow for parametric statistical analysis. Boxplots were used to compare medians. One-way ANOVA (ANalysis Of VAriance) was used to compare groups statistically.

### 7.2.3 Limerick Catchments Results

A general map of the soils of Co. Limerick is presented in Figure 7.2. The Soil Series and Great Soil Group classifications of the Limerick groundwater sites are listed in Table 7.1. As can be seen from this table the three major groups represented by the groundwater locations are the Brown Earths, the Gleys and the Grey-Brown Podzolics. The Grey-Brown Podzolics are represented solely by the Elton Soil Series, which occupies the largest area in Co. Limerick (28%). The Gleys are represented primarily by the Howardstown Soil Series, which occupies the second largest area in Co. Limerick (18%). Figure 7.1 indicates that the Grey-Brown Podzolics (Elton Soil Series) constitutes the majority of the Maigue catchment sites (twelve of eighteen). The Deel Catchment, in contrast, has a more complex mix of soils, Gleys being the most common group.

**Figure 7.1 Major Great Soil Groups at groundwater sampling locations in the Maigue and Deel catchments (soil data from Finch and Ryan, 1966).**

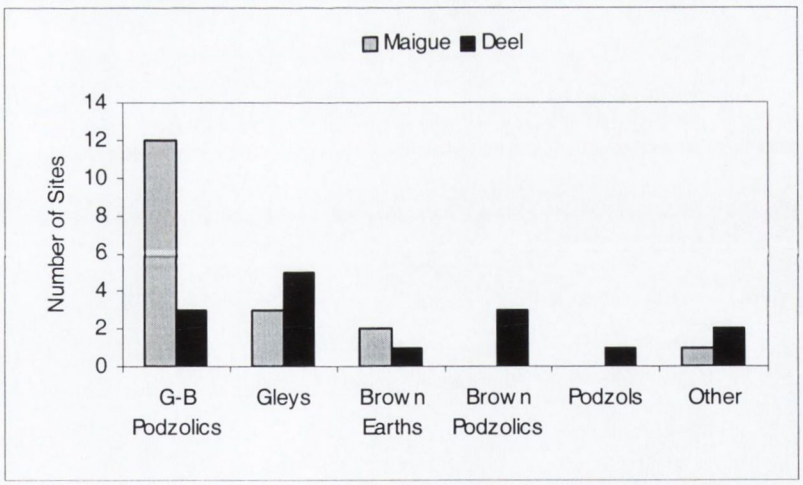
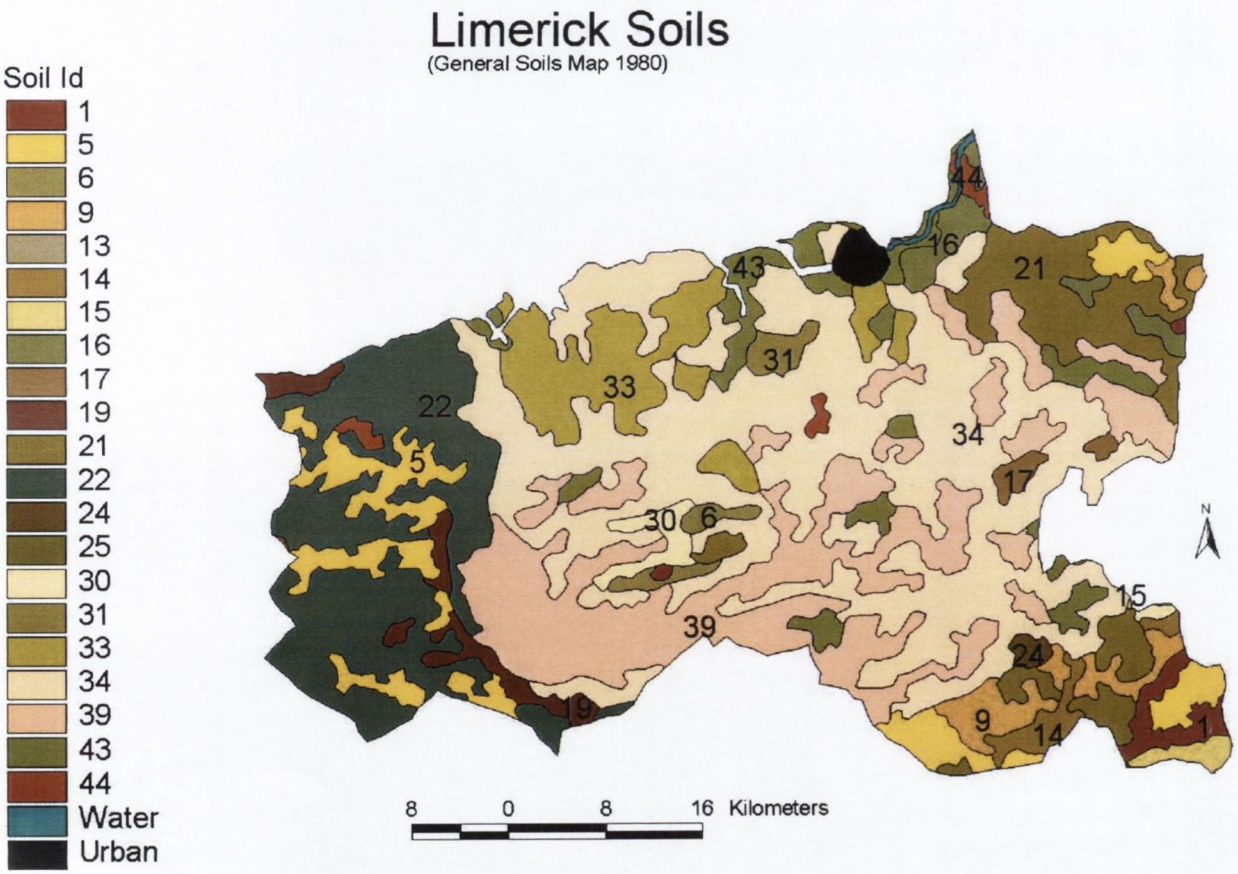



Table 7.2 lists the parent material associated with each Soil Series. Finch and Ryan (1966) point out that a single Great Soil Group is not confined to a particular geological parent material since the basic criteria for classifying the soils are the characteristics of the profile.

**Figure 7.2 General soil map of the Co. Limerick.**




| *Soil ID* | *Soil Type (after Gardiner and Radford, 1980).* |
|---|---|
| 1 | Peaty Podzols |
| 5 | Blanket Peat – High level |
| 6 | Brown Podzolics – Mostly sandstone |
| 9 | Brown Podzolics – shale and mica schist |
| 13 | Acid Brown Earths – Mixed sandstone, limestone glacial till |
| 14 | Acid Brown Earths – shale glacial till |
| 15 | Brown Podzolics – shale glacial till |
| 16 | Acid Brown Earths – Moranic sands and gravels and blown sands |
| 17 | Acid Brown Earths – Basalt glacial till |
| 19 | Acid Brown Earths – shale and sandstone glacial till |
| 21 | Gleys – Sandstone glacial till |
| 22 | Gleys – shale glacial till |
| 24 | Blanket Peat – Low level |
| 25 | Gleys – shale sandstone glacial till |
| 30 | Grey Brown Podzolics |
| 31 | Minimal Grey Brown Podzolics |
| 33 | Shallow Brown Earths and Rendzinas |
| 34 | Minimal Grey Brown Podzolics |
| 39 | Gleys – Limestone glacial till |
| 43 | Gleys – Alluvium |
| 44 | Basin Peat |

**Table 7.1 Soil Series and Great Soil Group for each groundwater site in County Limerick (soil data from Finch and Ryan, 1966).**

| *Site Name* | *Site Type* | *Catchment* | *Soil Series* | *Great Soil Group* | *Soil Series Drainage* |
|---|---|---|---|---|---|
| LB26 | Borehole | Maigue | Derk/Elton | B-Earths/G-B Podzolics | Well |
| LB13 | Borehole | Deel | Baggotstown | Brown Earths | W-E |
| LD02 | Dug Well | Maigue | Baggotstown | Brown Earths | W-E |
| LS03 | Spring | Mulkear | Ballyanders | Brown Earths | Well |
| LB28 | Borehole | Mulkear | Ballyvorheen | Brown Earths | W-E |
| LS05 | Spring | Mulkear | Ballyvorheen | Brown Earths | W-E |
| LB19 | Borehole | Shannon | Kilfergus | Brown Earths | Well |
| LB03 | Borehole | Deel | Mountcollins | Brown Podzolics | Well |
| LB18 | Borehole | Deel | Mountcollins | Brown Podzolics | Well |
| LS01 | Spring | Deel | Mountcollins | Brown Podzolics | Well |
| LB07 | Borehole | Deel | Abbeyfeale | Gleys | Poor |
| LB29 | Borehole | Mulkear | Cluggin/Darkisland | Gleys | Poor |
| LB08 | Borehole | Maigue | Howardstown | Gleys | Poor |
| LB09 | Borehole | Maigue | Howardstown | Gleys | Poor |
| LB15 | Borehole | Maigue | Howardstown | Gleys | Poor |
| LS04 | Spring | Deel | Howardstown | Gleys | Poor |
| LS07 | Spring | Deel | Howardstown | Gleys | Poor |
| LS08 | Spring | Deel | Howardstown | Gleys | Poor |
| LB02 | Borehole | Deel | Kilrush/Howardstown | Gleys | Poor |
| LB05 | Borehole | Aherlow | Puckane | Gleys | Poor |
| LB01 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LB04 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LB06 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LB10 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LB11 | Borehole | Deel | Elton | Grey-brown Podzolics | Well |
| LB14 | Borehole | Deel | Elton | Grey-brown Podzolics | Well |
| LB16 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LB17 | Borehole | Aherlow | Elton | Grey-brown Podzolics | Well |
| LB20 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LB21 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LB22 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LB24 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LB27 | Borehole | Maigue | Elton | Grey-brown Podzolics | Well |
| LS06 | Spring | Mulkear | Elton | Grey-brown Podzolics | Well |
| LS02 | Spring | Feale | Blanket Peat | NA | |
| LB23 | Borehole | Maigue | Rineanna Complex | NA | Variable |
| LB30 | Borehole | Deel | Rineanna Complex | NA | Variable |
| LD01 | Dug Well | Deel | Ashgr. Compex/Elton | NA/G-B Podzolics | Variable |
| LB35 | Borehole | Maigue | Rin. Complex/Elton | NA/G-B Podzolics | Var/Well |
| LB12 | Borehole | Deel | Knockanimpaha | Podzols | Variable |

**Table 7.2 Parent Material of each soil series derived for each groundwater site in County Limerick (after Finch and Ryan, 1966).**

| *Great Soil Group* | *Soil Series* | *Parent Material* |
|---|---|---|
| Brown Earths | Derk | Glacial drift composed of over 60 per cent volcanics with some limestone, shale and sandstone mixture. The volcanics are predom-inantly from pyroclastic feldspar rocks. Drift is of Weichsel Age. |
| | Baggotstown | Glacial gravels and sands predominantly of limestone composition with sandstone-shale admixture and a low proportion of volcanic materials; of Weichel Age. |
| | Ballyanders | Solifluction deposits predominantly of Silurian Shale composition (with some Old Red Sandstone influence); overlying a Saale Age Drift. |
| | Ballyvorheen | Fluvio-glacial and out-wash materials mainly of Old Red Sandstone origin with some shale and limestone admixture; of Weichsel Age. |
| | Kilfergus | Glacial Drift (containing many boulders) of Upper Carboniferous shale-sandstone origin; mainly of Weichsel Age. |
| Brown Podzolics | Mountcollins | Colluvium predominantly of Coal Measure Shale origin with some glacial drift admixture of Millstone Grit origin; of Saale Age. |
| Gleys | Abbeyfeale | Glacial drift and soliflucted material of Upper Carboniferous shale and sandstone composition; mainly of Saale Age. |
| | Cluggin | Glacial drift composed of almost equal proportions of limestone and sandstone with some shale admixture; of Weichsel Age |
| | Darkisland | River Alluvium (fine textured, base rich). |
| | Howardstown | Glacial drift predominantly of limestone composition with admixture of shale, sandstone and volcanics; of Weichsel Age. |
| | Kilrush | Glacial drift of Upper Carboniferous shale-sandstone origin and mainly of Weichsel Age |
| | Puckane | Glacial drift mainly of mixed sandstone-shale composition, with a little limestone; of Saale Age. |
| Grey-brown Podzolics | Elton | Glacial drift predominantly of Limestone composition but with a small proportion of sandstone, shale and volcanics; of Weichsel Age. |
| Podzols | Knockanimpaha | Upper Carboniferous shale and grit bedrock and associated colluvium. |
| Other Soils | Blanket Peat | N/A |
| | Rineanna Complex | Includes three soil series; Rineanna, Ballincurra and Elton Series. |
| | Ashgrove Compex | Includes five soil series; Ashgrove, Rooskagh, Abbeyfeale, Howardstown and Kilrush. |

Deakin (1994) further summarised the more typical parent material and their associated soils. A modified version of her assessment to focus only on the groundwater sampling locations in Co. Limerick is presented in Table 7.3.

**Table 7.3 Typical parent material of Limerick groundwater sites and associated soil classification (after Deakin, 1994).**

| *Parent material* | *Typical Soil Series* | *Great Soil Group* |
|---|---|---|
| Limestone till (well drained) | Elton | Grey Brown Podzolic |
| Limestone till (poorly drained) | Howardstown | Gley |
| Limestone sands and gravels | Baggotstown | Brown Earth |
| Limestone-sandstone till | Cluggin | Gley |
| Limestone bedrock | N/A | Rineanna Complex |
| Shale-sandstone till | Mountcollins | Brown Podzolics |
| Silurian till | Ballyanders | Brown Earth |

*GREAT SOIL GROUP*

Analysis of mean TP levels at the groundwater sampling sites was carried out against the Great Soil Group classes and the drainage classification associated with each soil series. Figure 7.3 presents a boxplot of mean groundwater TP for each soil group. Untransformed and log-transformed are both presented to better facilitate group comparison. LB05 and LB25 are two obvious outliers with total P greater than 300 $\mu g\ l^{-1}$. Table 7.4 list the summary statistics for Figure 7.3. Sites located in Gleys have lowest median TP levels, but the Brown Earths have lowest standard errors.

**Figure 7.3 Groundwater total P (A) and log total P (B) for the major Great Soil Groups in Limerick. The two outliers (starbursts) are LB05 and LB25.**

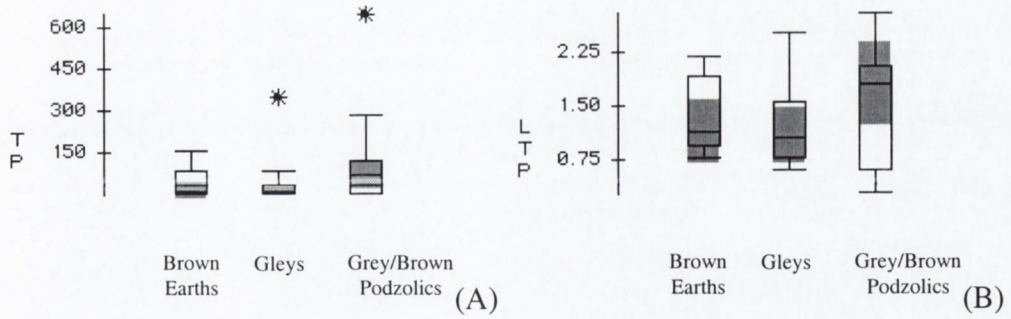



**Table 7.4 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.3.**

| *Great Soil Group* | *n* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|
| Gleys | 10 | 56 | 12 | 34 | 106 | 350 |
| Brown Earths | 11 | 49 | 14 | 18 | 60 | 162 |
| Grey-brown Podzolics | 16 | 106 | 65 | 41 | 164 | 651 |

In Figure 7.4, the two outliers of LB05 and LB25 have been removed to allow for better examination of differences between the Great Soil Groups. Table 7.5 list the summary statistics for Figure 7.4. Once the two outliers are removed the mean and standard error of the Gleys is dramatically reduced.

**Figure 7.4 Groundwater total P (A) and log total P (B) for the major Great Soil Groups in Limerick after removing the two outliers in Figure 7.3.**

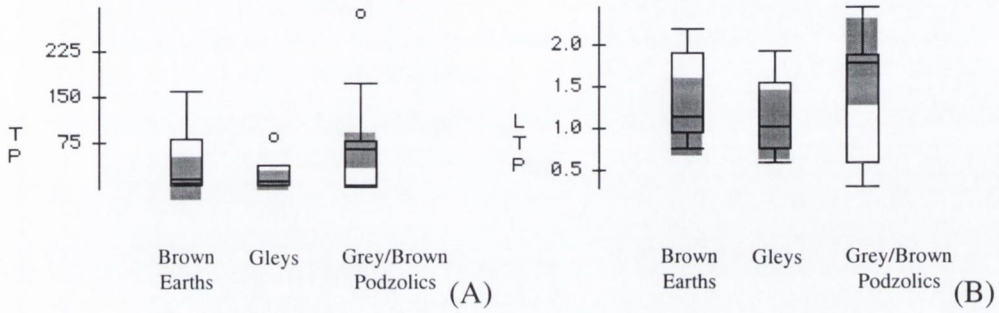


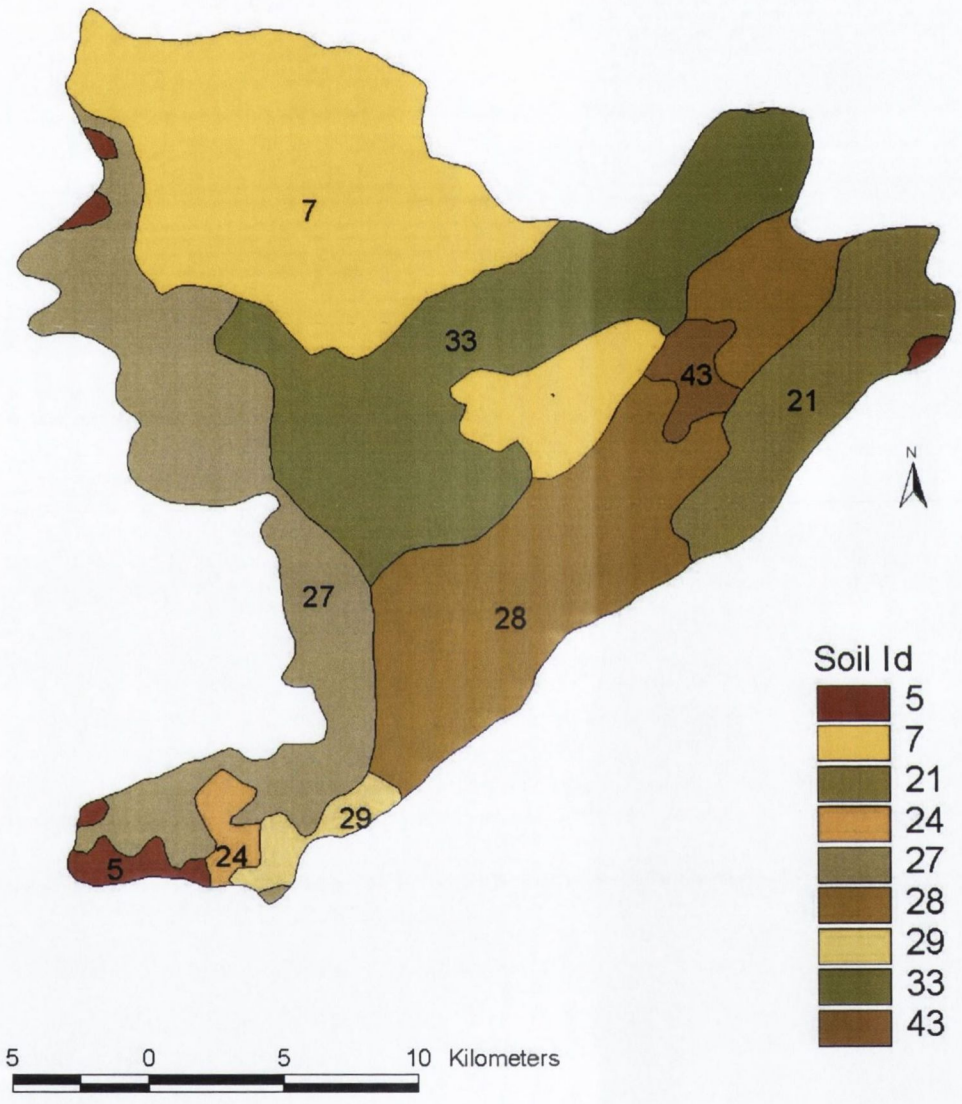

**Table 7.5 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.4.**

| *Great Soil Group* | *n* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|
| Gleys | 9 | 23 | 11 | 9 | 27 | 85 |
| Brown Earths | 11 | 49 | 14 | 18 | 60 | 162 |
| Grey-brown Podzolics | 15 | 70 | 63 | 20 | 78 | 289 |

*SOIL DRAINAGE*

In Figure 7.5 the soil drainage classes attributed by Finch and Ryan (1966) to each Soil Series are compared using mean groundwater total P. The two outliers of LB05 and LB25 are also evident. Table 6 lists summary statistics for Figure 7.5. These two outliers are again removed in Figure 7.6 and Table 7.7. In both cases, the poorly drained soils have lowest mean and median TP. Soils with well to excessive drainage had the largest standard errors.

**Figure 7.7 General soil map of the Fergus catchment.**




| *Soil ID* | *Soil Type (after Gardiner and Radford, 1980).* |
|---|---|
| 5 | Blanket Peat – high level |
| 7 | Rendzinas – with outcropping rocks |
| 21 | Gleys – with some peaty gleys |
| 24 | Blanket Peat – low level |
| 27 | Gleys – with some interdrumlin peat and peaty gleys |
| 28 | Grey Brown Podzolics |
| 29 | Acid Brown Earths |
| 33 | Shallow Brown Earths and Rendzinas |
| 43 | Gleys – with some brown earths and peaty gleys |

These problems are particularly acute in the case of springs fed by a significant proportion of conduit flow originating from considerable distance away. Therefore, the soil type identified where a spring emerges may not have any resemblance on the soils in the found in the principal contributing areas of such a spring. Nonetheless, it was felt that the polygons of the soil map were large enough that a significant proportion of the recharge to the spring would be influenced by the soil type at the spring. Table 7.8 lists the soil classification details for groundwater sampling locations in the Fergus catchment. Table 7.9 lists the parent material for which the major soil groups are derived.

As is evident from Figure 7.8, there are four major Great Soil Groups at the groundwater locations of the Fergus catchment. Map 1 presents the Great Soil Groups of the Fergus catchment. The Gleys are common in the west of the catchment where the Namurian Shales dominate.

**Figure 7.8 Frequency histogram of Great Soil Groups at the Fergus catchment groundwater sampling locations.**

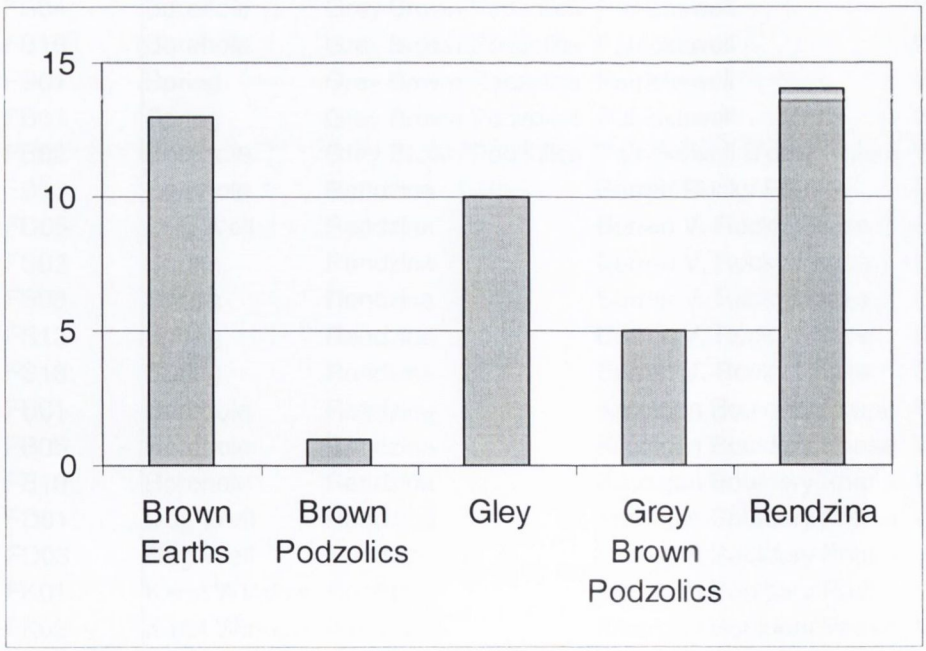


**Table 7.8 Soil classification for Fergus catchment groundwater locations (soil data from Finch, 1971).**

| *Site Name* | *Site Type* | *Great Soil Group* | *Soil Series* | *Drainage* |
|---|---|---|---|---|
| FB03 | Borehole | Brown Earths | Kinvarra | Well |
| FB06 | Borehole | Brown Earths | Kinvarra | Well |
| FB08 | Borehole | Brown Earths | Kinvarra | Well |
| FB09 | Borehole | Brown Earths | Kinvarra | Well |
| FB12 | Borehole | Brown Earths | Kinvarra | Well |
| FB14 | Borehole | Brown Earths | Kinvarra | Well |
| FD02 | Dug Well | Brown Earths | Kinvarra | Well |
| FS02 | Spring | Brown Earths | Kinvarra | Well |
| FS04 | Spring | Brown Earths | Kinvarra | Well |
| FS09 | Spring | Brown Earths | Kinvarra | Well |
| FS10 | Spring | Brown Earths | Kinvarra | Well |
| FS12 | Spring | Brown Earths | Kinvarra | Well |
| FS14 | Spring | Brown Earths | Kinvarra | Well |
| FD04 | Dug Well | Brown Podzolics | Mountcollins | Well |
| FS11 | Spring | Gley | Drombanny | Poor |
| FS05 | Spring | Gley | Feale | Poor |
| FS06 | Spring | Gley | Feale | Poor |
| FB07 | Borehole | Gley | Kilrush | Poor |
| FB11 | Borehole | Gley | Kilrush | Poor |
| FB15 | Borehole | Gley | Kilrush | Poor |
| FB17 | Borehole | Gley | Kilrush | Poor |
| FD06 | Dug Well | Gley | Kilrush | Poor |
| FD07 | Dug Well | Gley | Kilrush | Poor |
| FD08 | Dug Well | Gley | Kilrush | Poor |
| FB04 | Borehole | Grey Brown Podzolics | Patrickswell | Well |
| FB16 | Borehole | Grey Brown Podzolics | Patrickswell | Well |
| FS01 | Spring | Grey Brown Podzolics | Patrickswell | Well |
| FB01 | Spring | Grey Brown Podzolics | Patrickswell | Well |
| FB02 | Borehole | Grey Brown Podzolics | Patrickswell B'dery Phase | Well |
| FB13 | Borehole | Rendzina | Burren Rocky Phase | Excessive |
| FD05 | Dug Well | Rendzina | Burren V. Rocky Phase | Excessive |
| FS03 | Spring | Rendzina | Burren V. Rocky Phase | Excessive |
| FS08 | Spring | Rendzina | Burren V. Rocky Phase | Excessive |
| FS13 | Spring | Rendzina | Burren V. Rocky Phase | Excessive |
| FS18 | Spring | Rendzina | Burren V. Rocky Phase | Excessive |
| FB01 | Borehole | Rendzina | Kilcolgan Bouldery Phase | Well |
| FB05 | Borehole | Rendzina | Kilcolgan Bouldery Phase | Well |
| FB10 | Borehole | Rendzina | Kilcolgan Bouldery Phase | Well |
| FD01 | Dug Well | Rendzina | Kilcolgan Bouldery Phase | Well |
| FD03 | Dug Well | Rendzina | Kilcolgan Bouldery Phase | Well |
| FK01 | Karst Window | Rendzina | Kilcolgan Bouldery Phase | Well |
| FK02 | Karst Window | Rendzina | Kilcolgan Bouldery Phase | Well |
| FS17 | Spring | Rendzina | Kilcolgan Bouldery Phase | Well |

**Table 7.9 Description of soil parent material at the Fergus groundwater sites (soil data from Finch, 1971).**

| *Great Soil Group* | *Soil Series* | *Parent Material* |
|---|---|---|
| Brown Earths | Kinvarra | Drift of limestone origin with some granite, of Weichsel age |
| Brown Podzolics | Mountcollins | Drift of Weichsel age composed mostly of Upper Carboniferous sandstone with some shale |
| Gley | Drombanny | Alluvium derived from limestone drift with some Upper Carboniferous shales and sandstones |
| | Feale | Alluvium derived from Upper Carboniferous shales and sandstones with some limestone |
| | Kilrush | Drift of Weichsel age of Upper Carboniferous shale composition over the Clare Shales |
| Grey Brown Podzolics | Patrickswell | Drift of Weichsel age composed of limestone with a small proportion of granite |
| | Patrickswell Bouldery Phase | As for the Patrickswell series except for the presence of many boulders. |
| Rendzina | Burren Rocky Phase | Carboniferous limestone bedrock |
| | Burren V. Rocky Phase | As above |
| | Kilcolgan Bouldery Phase | As for the Kilcolgan Series (Drift of limestone origin, of Weichsel age) except for the presence of many boulders |

*GREAT SOIL GROUP*

Figure 7.9 presents boxplots of the relationships between Great Soil Groups and groundwater P in the Fergus catchment. There was no statistical difference between the groups. However, it can be seen from Table 7.10 that the groundwater sites overlain by Gleys have the lowest median total P levels. It should be noted that two of the Soil Series in the Gley group, Feale and Drombanny, are actually alluvial soils (see Table 7.8). These soil series include three sites, FS05, FS06 and FS10. When these three sites are removed groundwater sites overlain by the Gley group are significantly lower in P than Brown Earths ($p=0.0443$) and Rendzinas ($p=0.0152$).

**Figure 7.9 Groundwater log TP for the Great Soil Groups in the Fergus catchment. Outlier in the Brown Earth Group is FB03 (circle).**

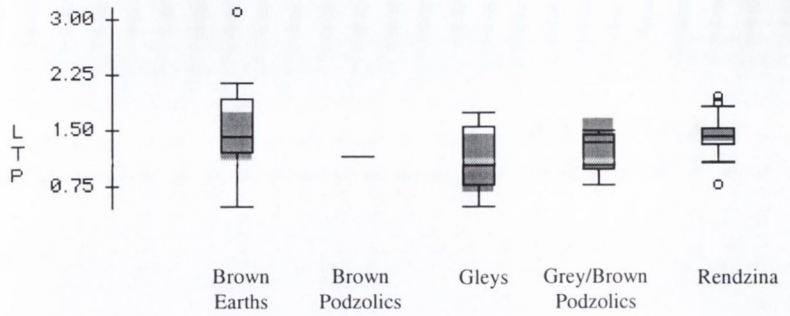



**Table 7.10 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.9.**

| *Group* | *Count* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|
| Gley | 10 | 22 | 12 | 7 | 21 | 57 |
| Brown Podzolics | 1 | 15 | 15 | na | na | 15 |
| Grey Brown Podzolics | 5 | 20 | 22 | 5 | 11 | 32 |
| Brown Earths | 13 | 138 | 27 | 97 | 349 | 1290 |
| Rendzina | 14 | 34 | 28 | 7 | 26 | 91 |

*SOIL SERIES*

The soils present at each groundwater sampling location are examined in more detail here using the soils series classification (see Table 7.8) The significance of combining Feale and Drombany with the other Gley soil series, Kilrush, can be seen clearly in Figure 7.10 and Table 7.11 (Drombany is omitted because only represents one site). Groundwater sites with Kilrush (Gley) soils have the lowest median TP levels and have significantly different TP to that of the Kinvarra (Brown Earth) soils (p=0.0443); as expected given all the Brown Earths are Kinvarra. Sites on the Kilrush Series also have significantly lower groundwater TP than those on Kilcolgan Bouldery Phase (Rendzina) soils (p=0.0089). The Feale and Drombanny soils had the highest median TP levels.

**Figure 7.10 Log total P for the major Soil Series in the Fergus Catchment. Outlier in Kinvarra Series is FB03 (circle) (soil series data from Finch, 1971, see Table 7.8).**

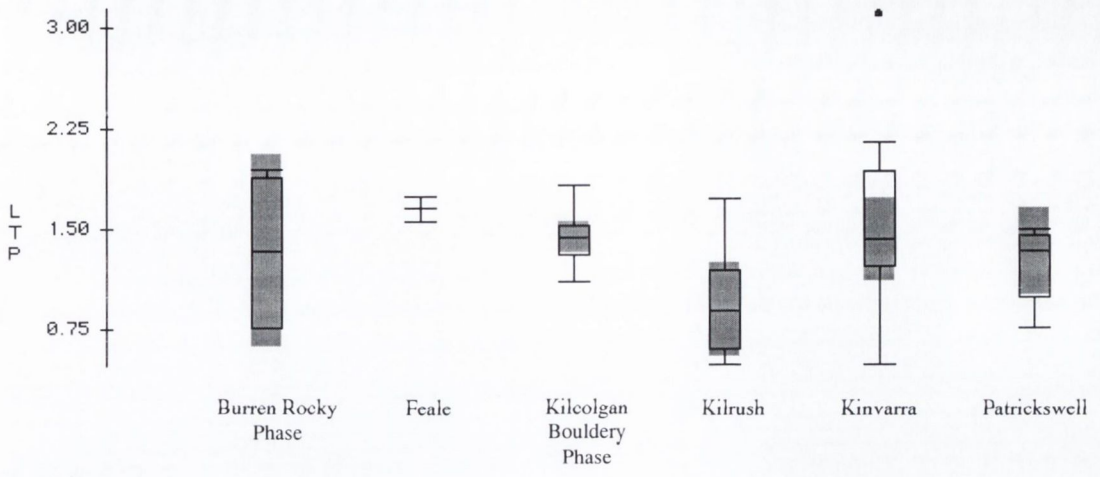



**Table 7.11 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.10.**

| *Soil Series* | *Count* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|
| Kilrush | 7 | 14 | 8 | 7 | 18 | 55 |
| Mountcollins | 1 | 15 | 15 | na | na | 15 |
| Burren v. Rocky Phase | 6 | 38 | 22 | 15 | 38 | 91 |
| Patrickswell | 5 | 20 | 22 | 5 | 11 | 32 |
| Kinvarra | 13 | 138 | 27 | 97 | 349 | 1290 |
| Kilcolgan Bouldery Phase | 8 | 32 | 29 | 6 | 16 | 69 |
| Drombanny | 1 | 30 | 30 | na | na | 30 |
| Feale | 2 | 47 | 47 | 10 | 14 | 57 |

*SOIL DRAINAGE*

Soils classified with poor drainage (Gleys) had lowest Median TP levels (see Table 7.12 and Figure 7.11). Soils with excessive drainage (Burren Rocky Phase) had large 95% confidence intervals due to small sample size and high variability. The groundwater P values from sites with poorly drained soils were not significantly different from those at sites with well drained soils. However, when the three sites from the Feale and Drombanny Soil Series were removed, the poorly drained soils were statistically different to the well drained soils (p=0.0152).

**Figure 7.11 (A) Groundwater log TP and soil drainage classification in the Fergus catchment. Outlier is FB03 (starburst). (B) excluding Feale and Drombanny Series.**

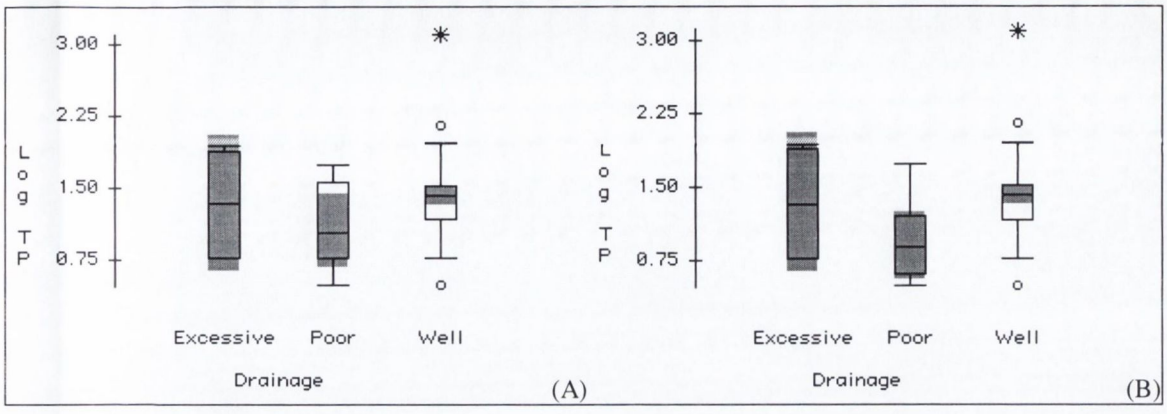



**Table 7.12 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Figure 7.11.**

| *Group* | *Count* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|
| Poor | 10 | 22 | 12 | 7 | 21 | 57 |
| Excessive | 6 | 38 | 22 | 15 | 38 | 91 |
| Well | 27 | 80 | 27 | 47 | 244 | 1290 |

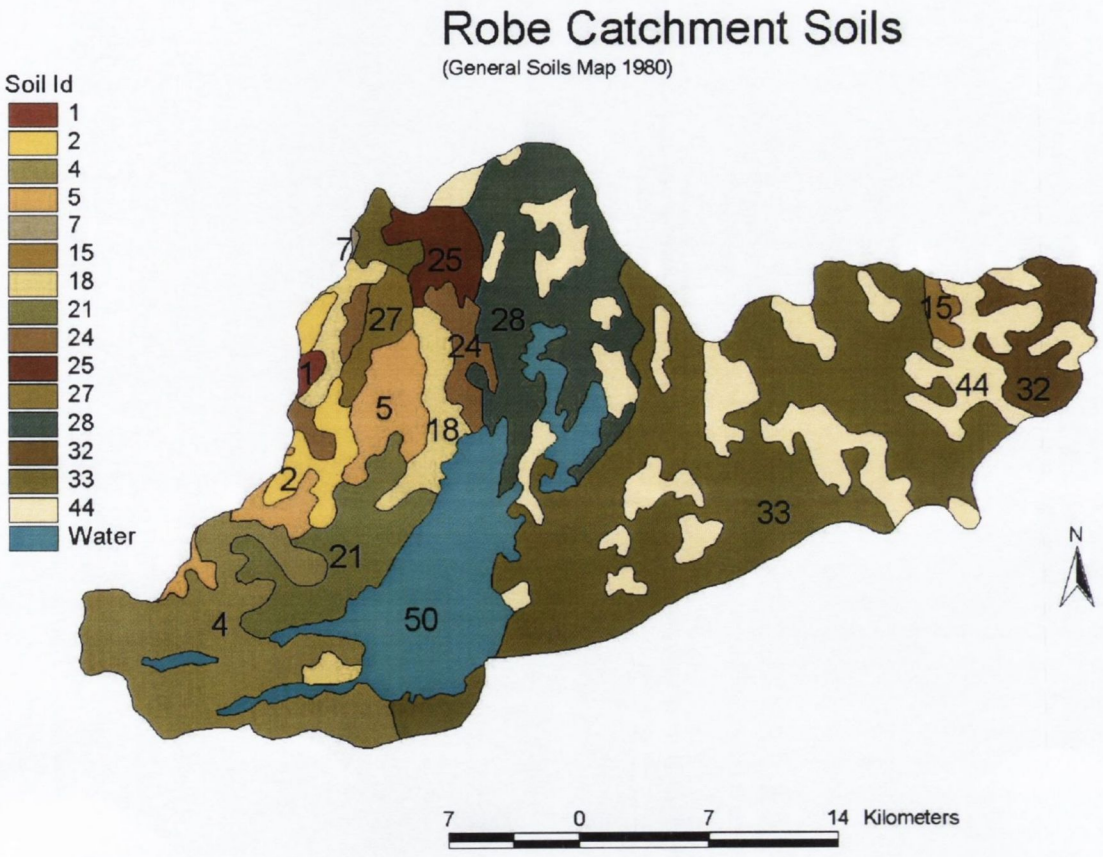
### 7.2.5 Robe Catchment Results

A general soils map of the Lough Mask (Robe) catchment is presented in Figure 7.12. As discussed above, there is no detailed soil map available for east Mayo including the Robe catchment. The only available published soil map is a preliminary soil survey carried out by Walsh and Burke (1980). Only three soil divisions are classified in the Robe catchment in this map: Grey Brown Podzolics, Shallow Brown Earths and Basin Peat. A summary of the characteristics of these three soils is presented in Table 7.13. Glacial drift of Weichsel age (i.e. last glaciation) comprises most of the subsoils in the catchment. In the east of the catchment between Ballinrobe and Lough Mask, the soils are 5 to 15 cm deep, generally well drained with sandy loam to loam textures (Walsh, 1975).

**Table 7.13 Summary characteristics of the Robe catchment soils (after Walsh and Burke, 1980).**

| *Soil Divisions* | *Description* | *Parent Material* | *Drainage* |
|---|---|---|---|
| Grey Brown Podzolics | 50-100cm depth. Loamy with a marked increase in clay content in the subsoil | Limestone till | Good natural drainage |
| Brown Earths | Shallow, 30cm depth. Loamy with skeletal soils | Limestone till | Not given, but presumed to be good |
| Basin Peat | Deep, cut-over for fuel. | N/A | Frequent flooding, but arterial drainage has improved the situation |

Figure 7.12 General soil map of the Robe catchment.




| *Soil ID* | *Soil Type (after Gardiner and Radford, 1980).* |
|---|---|
| 1 | Peaty Podzols |
| 2 | Peaty Gleys |
| 4 | Lithosols – Outcropping Rock |
| 5 | Blanket Peat – High level |
| 7 | Rendzinas – with Outcropping Rock |
| 15 | Brown Podzolics |
| 18 | Podzols |
| 21 | Gleys – Acid Brown Earths and Peat |
| 24 | Blanket Peat – Low level |
| 25 | Gleys – Acid Brown Earths Interdrumlin Peat and Peaty Gleys |
| 27 | Gleys – Interdrumlin Peat and Peaty Gleys |
| 28 | Grey Brown Podzolics |
| 32 | Degraded Grey Brown Podzolics |
| 33 | Shallow Brown Earths and Rendzinas |
| 44 | Basin Peat |

Due to the large scale of the soil map (1 inch to 8 miles) accurate identification of the groundwater sites' soil divisions is not possible. Therefore, only an indicative assessment of the influence of soil type on groundwater P levels can be made.

Least likely to impact the groundwater would be areas of Basin Peat where water logging may favour overland flow. The Grey Brown Podzolics and Brown Earths may facilitate more P movement to groundwater due to their good drainage and shallow nature.

### 7.2.6 Discussion

Haygarth and Jarvis (1999) reviewed many aspects concerning the transfer of P from agricultural soils. They recognized that while the term leaching is often used to describe movement down a soil profile, it does not accurately describe the pathway involved. They identify two major hydrological pathways down a soil profile. The first is a saturated/piston flow that is most common in sandy soils. The second is a preferential/macropore flow, which can be prevalent in clay soils vulnerable to cracking. It is likely that the soils from the studied catchments are subject to a combination of these two hydrological processes. The primary free-draining soils in each catchment are the Grey Brown Podzolics and Brown Earths in all three areas, with the Rendzinas specifically in the Fergus catchment. In these soils saturated/piston flow may be the dominant pathway of P to groundwater. The primary poorly drained soils in each catchment are the Gleys. The two primary gleys are the Howardstown Soil Series in Co. Limerick and the Kilrush Soil Series in the Fergus. The Howardstown soils are poorly drained due to flat relief, causing slow runoff, and because of the poor permeability of the soils themselves (Finch and Ryan, 1966). The Kilrush soils are poorly drained because of their heavy texture and weak structure (Finch, 1971). In these soils, preferential flow may provide a pathway to groundwater.

Irrespective of transfer mechanism, it is clear from the data that areas with poorly drained soils have far lower groundwater P levels than areas with well drained soils. In the Maigue catchment of Co. Limerick Grey Brown Podzolics (Elton series) was the dominant soil type. The adjacent Deel catchment had a more complex mix of soil types. The Maigue catchment had higher overall TP than the Deel catchment, which could reflect the influence of the dominant, well drained, Elton series.

In the Fergus catchment these differences were more strongly emphasised statistically possibly due to the more concentrated distribution of sites and smaller study area. Lowest P levels were reported at groundwater sampling sites underlain by the Kilrush Gleys. These sites were predominantly located in the west of the catchment and reflect the low hydraulic conductivity of the Namurian bedrock and Quaternary deposits derived from the Namurian rocks. In this part of the catchment overland flow is probably the dominant P transfer mechanism. Groundwater underlying the Rendzina group had highest median TP levels of all Great Soil Groups in the Fergus catchment. This is expected given that Rendzinas are shallow soils usually not more than 50 cm deep and drainage is always free to excessive (Finch, 1971). The northern part of the Fergus catchment is dominated by Rendzina soils and the groundwater in this area has been identified as particularly vulnerable to agricultural contamination (Drew, 1995; 1996b). The Brown Earth and Grey Brown Podzolics are dispersed in pockets around the central and southern portion of the catchment. The data indicated that these areas also offer less protection to groundwater than the gleys, but are less vulnerable than the Rendzinas.

The Robe catchment comprises of three major soil types: Grey Brown Podzolics, Shallow Brown Earths and Basin Peat. Water logging in the peat may reduce the impact to groundwater. However, peat may not be completely benign regarding P transfer. Kløve (2001) reported mean groundwater levels of 400 $\mu g\ l^{-1}$ TP in a peat mining facility in Central Finland. He also noted peak P concentrations occurred during dry periods when old groundwater dominated runoff. However, he noted a 10-fold reduction in P levels in nearby drain water highlighting the importance of drains to attenuate P in milled peat operations. The other two soil groups and particularly the Shallow Brown Earths may be more important in P transfer to groundwater. These soils are very thin and free draining. These factors, augmented by the moderately karstic nature of the Robe aquifer, may pose a particular threat to groundwater particularly in the west of the catchment where the soils (Walsh, 1975) and Quaternary deposits (Coxon and Drew, 1986) are thinner and areas of bare rock occur.

Overall soil type does appear to be an important consideration in either retarding or facilitating P movement to groundwater. Often these trends mirror underlying parent material such as the case of the Gleys and Namurian rocks in the Fergus catchment. In other situations, such as the shallow brown earths of the Robe catchment and Rendzinas of

the Fergus, soil cover may represent the only attenuating layer before groundwater is reached.

## *7.3 CORINE Landcover Classes*

### 7.3.1 Introduction

This chapter examines the relationships between groundwater P concentrations and the land cover classification that overlies each sampling location. It is envisaged that groundwater P will be higher in agricultural land classes than for forested or natural vegetation land cover classes. In addition, within the agricultural it is expected that areas with more intensive practices such as high productivity pasture are most likely to have highest groundwater P levels.

CORINE (Co-Ordination of INformation on the Enviroment) is a Europe-wide land cover database established by the European Union in the late 1980s and early 1990s to assemble data on the environment of Europe (McGuckin *et al.*, 1999). Production of the CORINE land cover database is based on visual interpretation of satellite imagery and the allocation of land cover types. In 1991 89% of all Irish farms were pasture. Ireland has carried out a further sub-division of this class into three subclasses: high productivity grassland, low productivity grassland, and an intimate mix of the two previous classes (O'Sullivan, 1994). High productivity grassland is defined as grasslands that are sown and have a uniform sward. Low productivity grassland as defined as grassland where sown grass dominates but there could be significant rushes, thistles, nettles, ragwort, etc. The intimate mix class is defined as areas with an intimate mix (at least 25%) of the above two classes. The Peat Bog class was also considered to broad for Ireland was further subdivided into Unexploited Bog and Exploited Bog.

Several studies have adopted the use of such land cover databases to examine impacts on surface waters. Satellite derived land cover data was used by Tufford *et al.* (1998) in South Carolina to examine in-stream nonpoint source nutrient levels with land use proximity. Tufford *et al.* reported highest P levels in areas with high proportions of agricultural and urban land. Forest and wetland areas were associated with lower P levels. Sharpley *et al.* (1995) cite Omernik (1977) whose study of 928 non-point source catchments found that

the P export to surface waters increased as the proportion of forested land decreased and as agricultural land increased. Johnson *et al.* (1997) caution that P is more difficult to relate to land use than N because of the strong relationship to particulate dynamics and the temporal scale of transport dynamics. Fewer studies examine groundwater in this context. However, Close and Davies-Colley (1990) reported higher yields of N and P to river baseflow in New Zealand from pasture compared to forested catchments.

Sharpley and Rekolainen (1997) cite several studies that indicate that P losses from agricultural land are higher than from forested land. Miztal *et al.* (1992) examined groundwater nutrient input to a Lake in Poland from different land cover types and reported greatest N and P loadings from groundwater in the agricultural area. McGarrigle *et al.* (1993) examined the causes of eutrophication in L. Conn, north Mayo, and attributed agricultural land use as the greatest contributor of P load to the lake. Agricultural land use has been identified as a key factor in P loss from land to surface water.

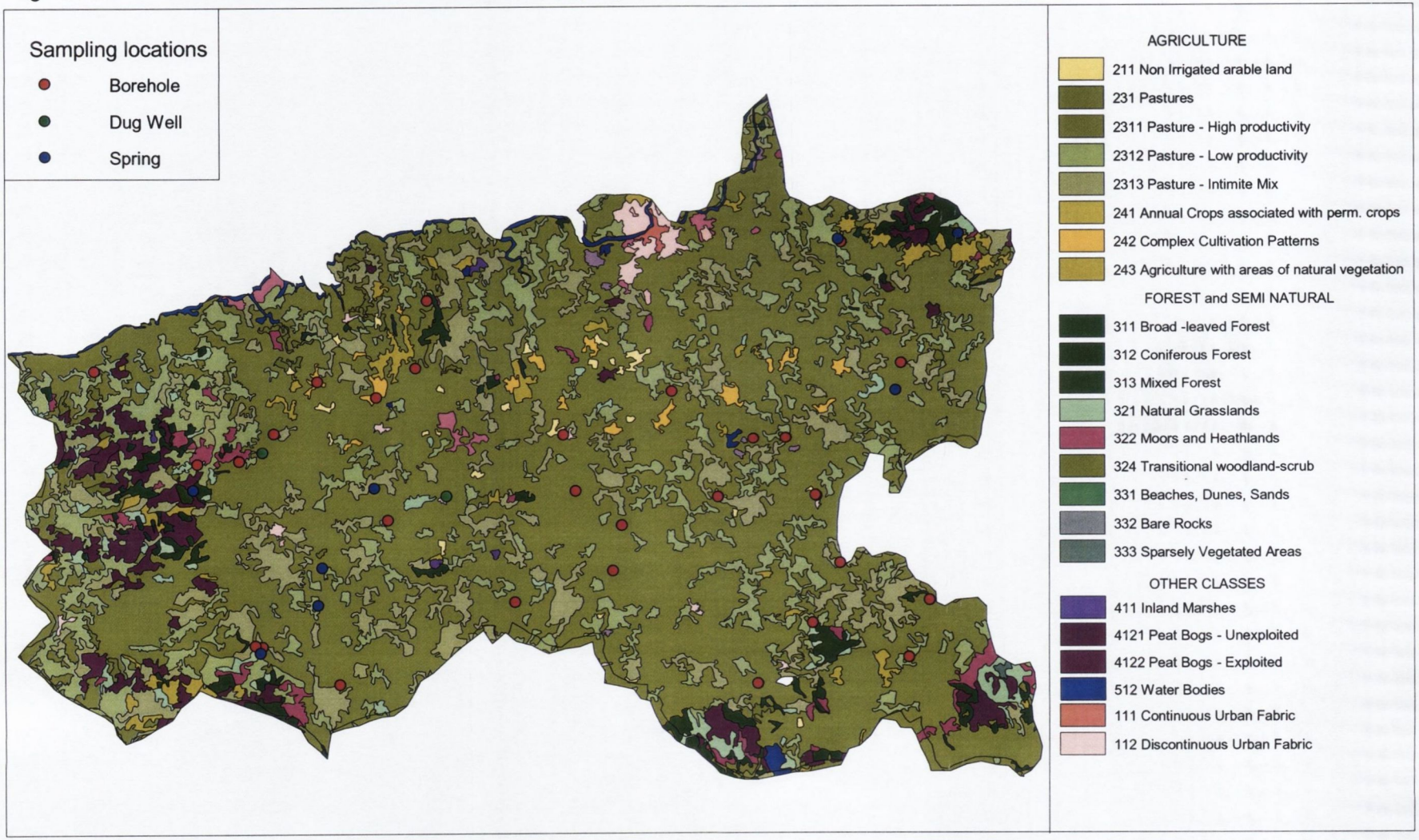
### 7.3.2 Methods

The CORINE land cover data were available in Arcview format and could therefore be interrogated spatially using GIS techniques. A point-in-polygon assessment was carried out to identify what CORINE class was present at the co-ordinates of each groundwater sampling location. Specifically, a spatial join was carried out between the attribute table of the groundwater location point data and the attribute table of the CORINE polygon data. The derived table was then exported to Excel for formatting and then exported to Datadesk for statistical analysis. The data were log-transformed to allow for parametric analysis. Boxplots and one way ANOVA were used to compare land cover classes.

### 7.3.3 Limerick Catchments Results

Figure 7.13 presents the CORINE land cover classes for Co. Limerick. Pasture, and specifically high productivity pasture is clearly the primary land cover class in Co. Limerick. This fact is also borne out in the land cover classes which each of the groundwater locations intercept.

Figure 7.13 Limerick CORINE land cover classes and sampling locations.



Approximately 60% of the sites are located in high productivity pasture (see Table 7.14). Figure 7.14 presents a boxplots of each of the land cover class. While higher median TP levels are located in agricultural land cover classes than for sites with coniferous forest, urban areas and unexploited peat bogs, the small number of samples in non-agricultural classes (three) negates the significance of this comparison. Within agricultural land cover classes there were no significant differences. Non-irrigated arable land and high productivity pasture had highest median TP levels.

**Figure 7.14 CORINE land cover classes for Limerick Groundwater sites. See Table 7.14 for explanation of class codes.**

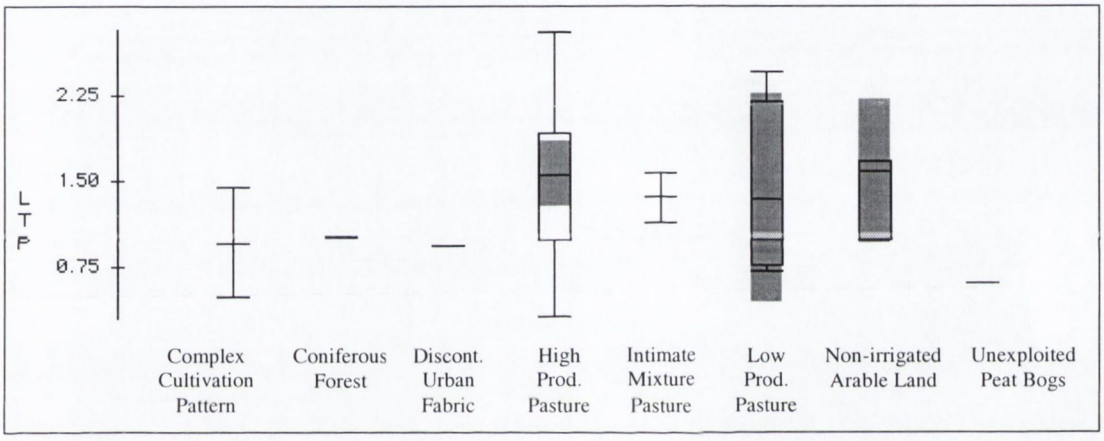



**Table 7.14 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Limerick CORINE data (see Figure 7.14).**

| *Group* | *Count* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|
| Peat Bogs - Unexploited | 1 | 4 | 4 | na | na | 4 |
| Discontinuous Urban Fabric | 1 | 9 | 9 | na | na | 9 |
| Coniferous Forest | 1 | 11 | 11 | na | na | 11 |
| Complex Cultivation Pattern | 2 | 16 | 16 | 13 | 18 | 29 |
| Intimate Mixture Pasture | 2 | 26 | 26 | 12 | 17 | 38 |
| Low Productivity Pasture | 6 | 87 | 31 | 47 | 116 | 289 |
| High Productivity Pasture | 25 | 85 | 37 | 28 | 141 | 651 |
| Non Irrigated Arable Land | 3 | 33 | 40 | 12 | 20 | 49 |

### 7.3.4 Fergus Catchment Results

Figure 7.16 presents the CORINE land cover classes for the Fergus catchment. Unlike Co. Limerick there is a more heterogeneous mixture of land cover types in the Fergus catchment. This is well illustrated in the more even distribution of sites between the nine land cover classes intercepted (see Table 7.15). The Intimate Mix Pasture class, which

represents an intermediate between high and low productivity pasture, is the most common class comprising approximately 25% of the sites (Figure 7.15). The distinction between agricultural and non-agricultural classes evident in the Limerick sites is unclear. The highest median TP levels are found in the class "agriculture with areas natural vegetation". This classification comprises areas that are principally occupied by agriculture but include areas of natural vegetation. For example, around upland margins there may be small patches of heath intermixed with the predominant pasture (O'Sullivan, 1994). However, sites located in woodland-scrub also had quite high median TP levels.

Variability was highest in the high productivity pasture sites, however, this is largely due to the FB03 boreholes which had excessively high TP values. If FB03 is removed from the group the standard error drops to 3.4 $\mu g\ l^{-1}$ TP. The agriculture with natural vegetation class was significantly different in TP than low productivity pasture (p=0.039) and almost significantly different to high productivity grassland (p=0.0575). The sites located in the agriculture with natural vegetation class were the boreholes FB04 and FB02, and the springs FS03, FS05, FS06, FS07 and FS17. The latter four springs had highest mean TP levels (37-79 $\mu g\ l^{-1}$).

**Figure 7.15 Groundwater log total P ($\mu g\ l^{-1}$) CORINE land cover classes for Fergus catchment groundwater sites.**

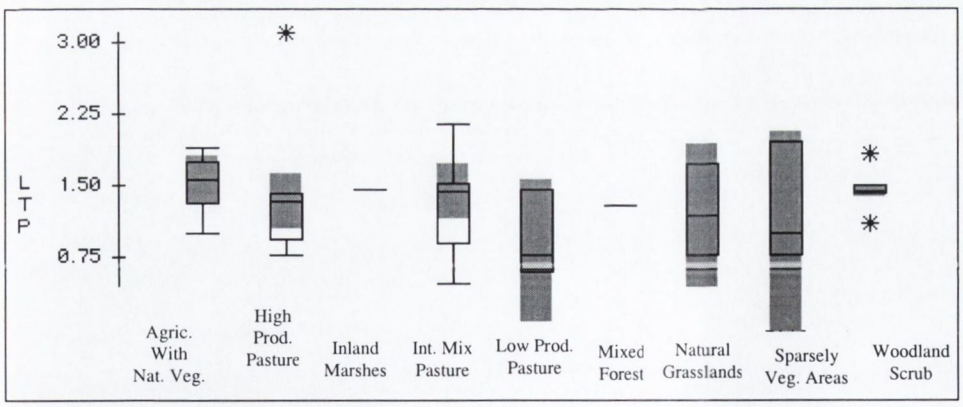


Figure 7.16 Fergus catchment CORINE land cover classes and sampling locations.

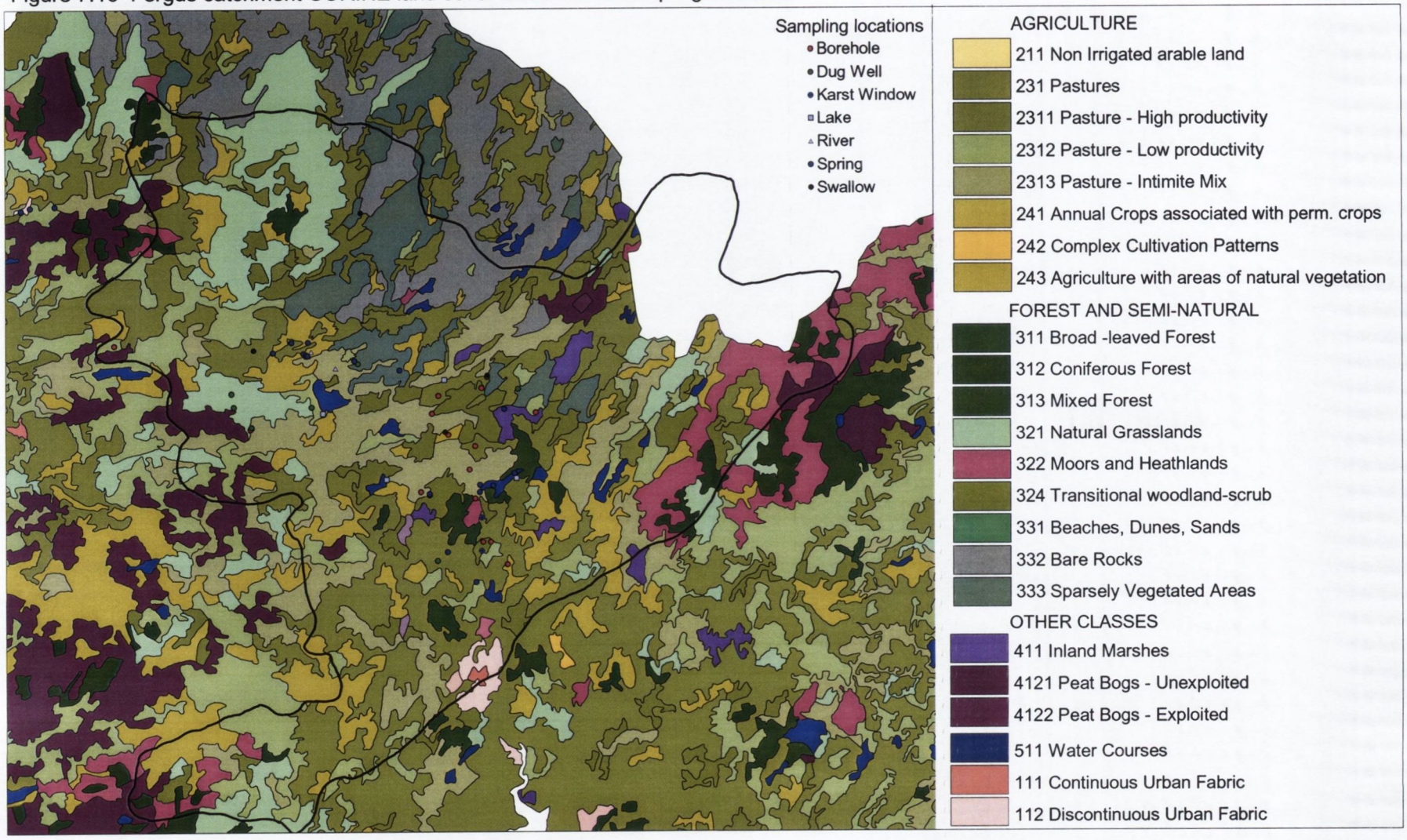


**Table 7.15 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Fergus catchment CORINE data (see Figure 7.15).**

| *Group* | *Count* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|
| Low Productivity Pasture | 3 | 13 | 6 | 8 | 14 | 29 |
| Sparsely Vegetated Areas | 3 | 36 | 10 | 28 | 48 | 91 |
| Natural Grasslands | 4 | 23 | 16 | 11 | 22 | 55 |
| Mixed Forest | 1 | 20 | 20 | na | na | 20 |
| High Productivity Pasture | 7 | 200 | 22 | 182 | 481 | 1290 |
| Intimate Mix Pasture | 11 | 37 | 28 | 13 | 45 | 145 |
| Woodland-Scrub | 6 | 33 | 28 | 8 | 19 | 69 |
| Inland Marshes | 1 | 30 | 30 | na | na | 30 |
| Agriculture with Natural Vegetation | 7 | 41 | 37 | 9 | 23 | 79 |

### 7.3.5 Robe Catchment Results

Figure 7.18 presents the CORINE land cover classes for the Robe catchment. High productivity pasture and agriculture with natural vegetation are the most extensive classes in the catchment. Moors and heath land are commonest towards the shores of Lough Mask. There are also several pockets of unexploited peat bogs. Figure 7.17 presents boxplots of the four CORINE classes intercepted by the Robe groundwater sites. There were four classes intercepted and as can be seen from Table 7.16 the sites are evenly distributed among these classes. Intimate mix pasture and woodland scrub had lowest median TP. The outlier in the woodland-scrub class is the borehole RB07 that, as discussed in Chapter. Four, may be tapping isolated groundwater. As can be seen from Table 7.16 removal of RB07 decreases the standard error from 127 to 6.

**Figure 7.17 CORINE land cover classes for Robe catchment groundwater sites. The starburst is borehole RB07.**

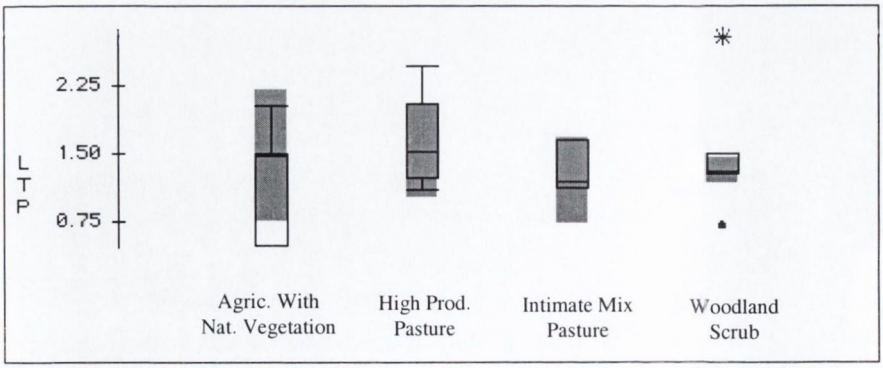


Figure 7.18 Robe catchment CORINE land cover classes and sampling locations.

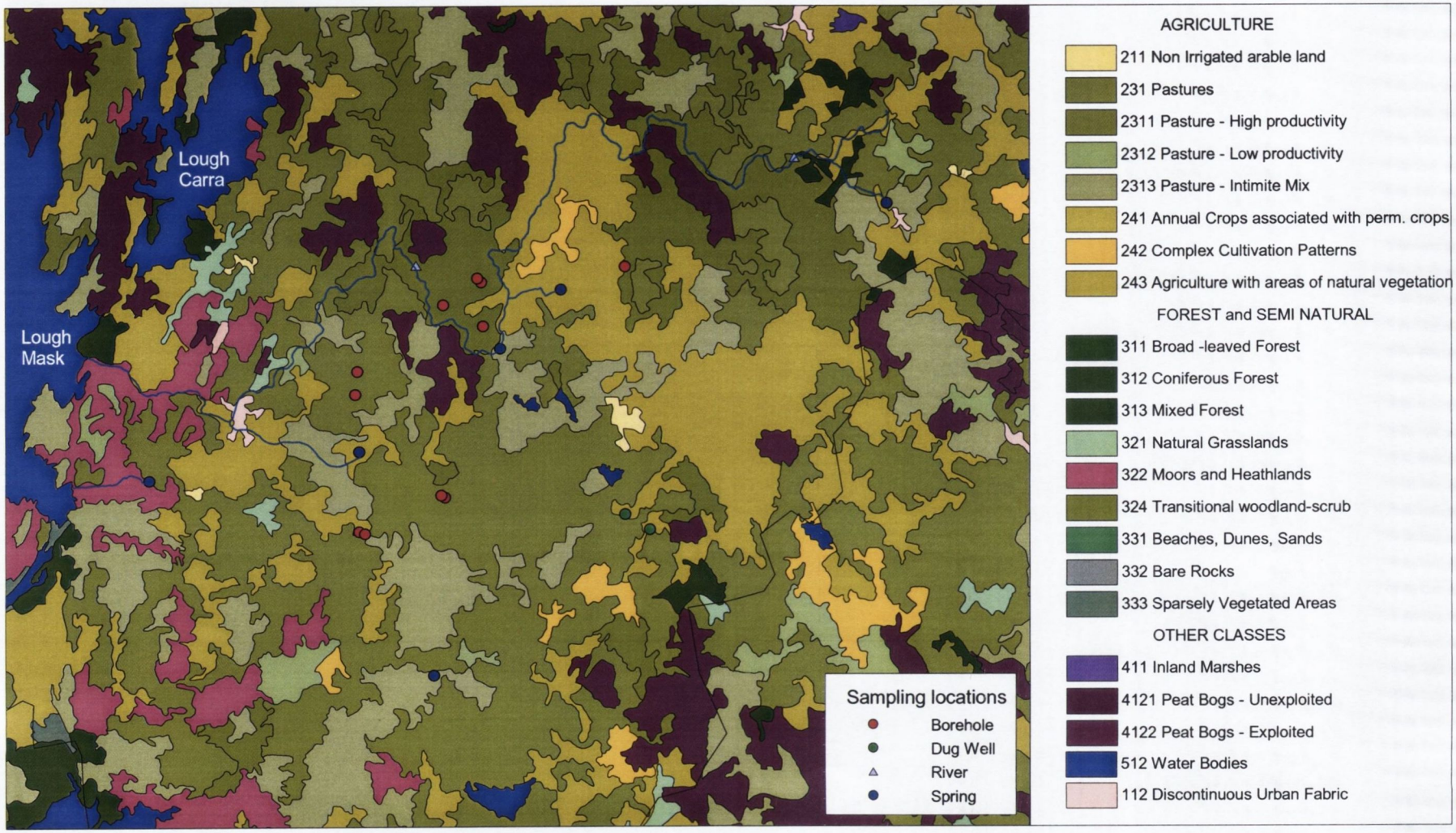


**Table 7.16 Groundwater total P ($\mu g\ l^{-1}$) summary statistics for Robe catchment CORINE data (see Figure 7.17).**

| *Group* | *Count* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|
| Intimate Mix Pasture | 3 | 26 | 16 | 11 | 19 | 47 |
| Woodland-Scrub | 5 | 146 | 21 | 127 | 283 | 652 |
| Woodland-Scrub (excluding RB07) | 4 | 20 | 21 | 6 | 11 | 32 |
| Agriculture with Natural Vegetation | 5 | 36 | 31 | 19 | 43 | 108 |
| High Productivity Pasture | 6 | 86 | 35 | 45 | 111 | 300 |

### 7.3.6 Discussion

In each of the three catchment areas studied, sites with agricultural land cover classes did not conclusively yield highest groundwater TP levels. However, in Co. Limerick this county's land cover had a strong bias towards high productivity pasture. This class also yielded highest median groundwater TP levels in the Robe catchment. Allott *et al.* (1998) reported a positive relationship between TP and percentage of lake catchment area with high productivity pasture. Daly *et al.* (2000) found highest annual river MRP correlated positively with percentage high productivity pasture.

Relationships in the Fergus catchment was less clear. The karstic nature of the Fergus aquifer poses several problems with adopting a point-in-polygon assessment of land cover. This can be seen in the high median TP values for the agricultural with natural vegetation classes (Table 7.15). The FS03, FS05 and FS17 springs derive much of their recharge from the Burren Plateau in the north and at sinks along the shale-limestone interface to the northwest (Drew, 1988). Therefore, the land cover class at these springs may not represent the land cover areas actually contributing recharge to the springs. A similar pattern may be occurring in the Woodland-Scrub land cover class in the Fergus catchment. The six sites in this land cover class are situated along the north-south karstic flow system (between L. Keogh sink (FL06) and FS18) where underground velocities range between 100-200 m $hr^{-1}$ (Coxon and Drew, 2000). Whilst the land cover class of Woodland-Scrub yielded the third highest median TP levels, the actual land cover class to the north in the L. Keogh and Upper Fergus catchment is probably more relevant to the groundwater at these sites. The problems associated with designating contributing areas for groundwater protection at the FS18 spring is examined in detail by Deakin (2000).

## 7.4 Agricultural Statistics

### 7.4.1 Introduction

Agricultural statistics were obtained from the Central Statistics Office (CSO, 1991) and are based on 1991 census information. This information is used here to examine relationships between groundwater P concentrations and agricultural activity. Census data is collected by the Government of Ireland every ten years. Included in the brief of the Census is the collection of agricultural statistics.

### 7.4.2 Methods

The smallest spatial area that these statistics cover is district electoral division (DED). Using the nearest townland names of each site the specific DED was identified and relevant statistics obtained from the CSO. A wide range of agricultural variables are available in the Census data. Only variables which relate to stocking density or agricultural intensity were used for this study. These statistics are listed and described in Table 7.17.

**Table 7.17 Definition of CSO statistics used in the analysis of groundwater P.**

| *Statistic* | *Description* |
|---|---|
| Cattle per hectare of DED total area | All types of cattle present in the DED |
| Sheep per hectare of DED total area | All types of sheep present in the DED |
| Percentage of area Farmed | Total percentage of DED area used for:<br>*Crops & horticulture, silage, hay, pasture and rough grazing land in use.*<br>*Excludes commonage & rough grazing land not in use.* |
| Percentage of area under silage | Percentage of DED area used to ensile grass. |
| Percentage of area under pasture | Percentage of DED area used as:<br>Permanent pasture and pasture in rotation under five years<br>*Excludes all rough grazing, silage and hay* |

The size of these DEDs varies, for example in Co. Limerick the average size was 2078 ha, with a maximum and minimum of 1253 and 3312 ha respectively. For the Limerick sites generally each site was attributed a single DED. For DEDs that contained more than one site, the mean TP value of the combined sites were averaged. This occurred rarely in Co. Limerick, but the Fergus and Robe catchments, which covered a much smaller area, incorporated fewer DEDs. The limerick, Fergus and Robe sites intercepted 33, 9 and 6 DEDs respectively. Mean groundwater TP levels were then used to examine relationships with the statistics listed in Table 7.17.

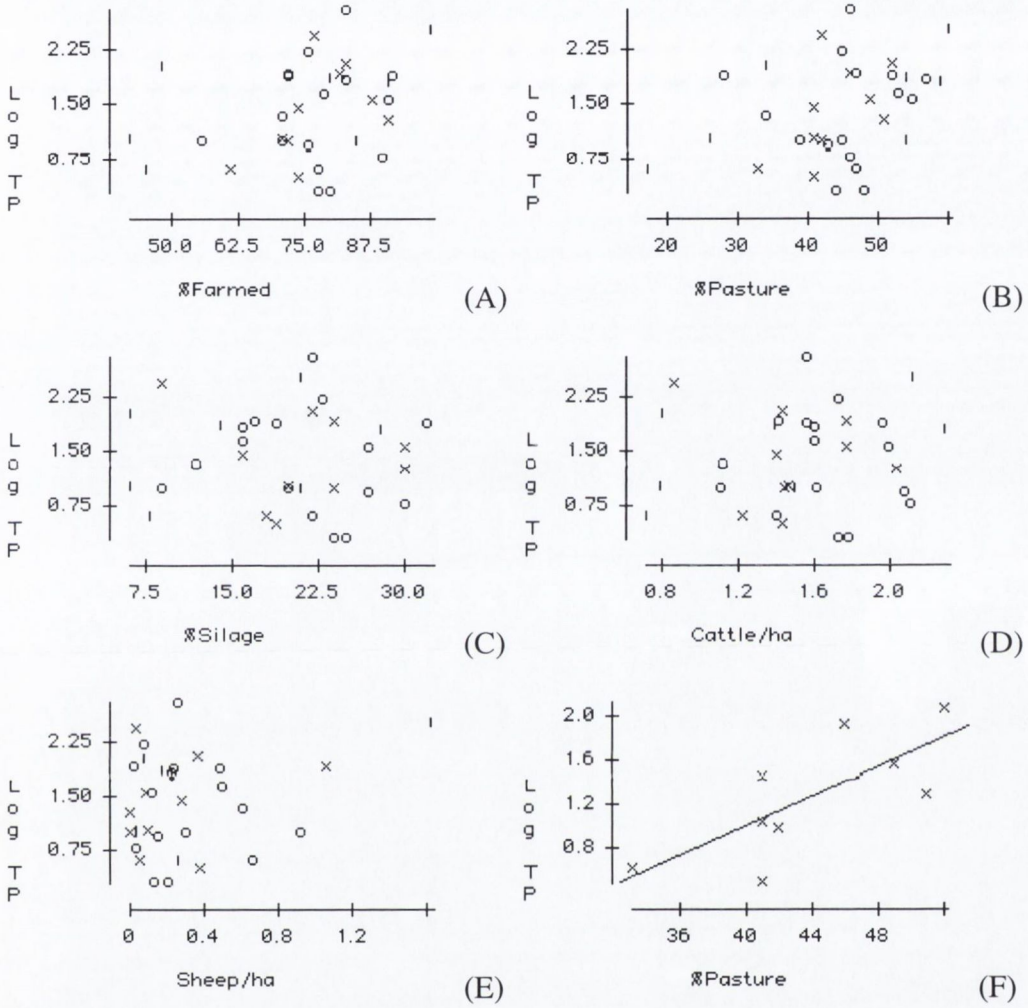
### 7.4.3 Limerick Catchments Results

In Co. Limerick the following groups were combined because they intercepted the same DED: LB02/LB03/LS01; LB29/LS06; LB28/LS05; and, LD01/LB18. Figure 7.19 (A) to (F) presents scatterplots between mean groundwater TP and DED agricultural characteristics. There were no strong statistical relationships, but several general trends emerged. Groundwater TP generally increased with percentage of area farmed and area used for pasture. TP tended to decrease as sheep density increases. Percentage silage and cattle density showed no clear trends. Table 7.18 presents a Pearson-Product Moment correlation matrix of Limerick DEDs. There are strong correlations between percentage pasture, silage and cattle density highlighting the relationships between cattle production and silage/pasture. Sheep density was least correlated with all the variables. Groundwater Total P was best correlated to percentage of land farmed and percentage of land devoted to pasture. This is brought out in Figure 7.19 (F) which plots Deel sites excluding one outlier (LB12, mean TP = 289 $\mu g\ l^{-1}$) against percentage pasture. A significant regression was observed is this plot ($R^2$ = 56%, p=0.0208).

**Table 7.18 Pearson-product moment correlation matrix of Limerick groundwater log TP and DED statistics. 5% significance limit = 0.344, 1% significance limit = 0.442.**

| | *Log TP* | *%Farmed* | *%Pasture* | *%Silage* | *Cattle/ha* | *Sheep/ha* |
|---|---|---|---|---|---|---|
| Log TP | 1 | | | | | |
| %Farmed | 0.313 | 1 | | | | |
| %Pasture | 0.337 | 0.857 | 1 | | | |
| %Silage | -0.051 | 0.782 | 0.573 | 1 | | |
| Cattle/ha | 0.09 | 0.842 | 0.715 | 0.891 | 1 | |
| Sheep/ha | 0.215 | 0.26 | 0.234 | 0.031 | 0.214 | 1 |

**Figure 7.19 Scatterplots between Limerick groundwater log TP and DED agricultural characteristics. O = Maigue catchment sites, x = Deel catchment sites, and | = other catchments. (F) examines the Deel sites excluding LB12.**




## 7.4.4 Fergus Catchment Results

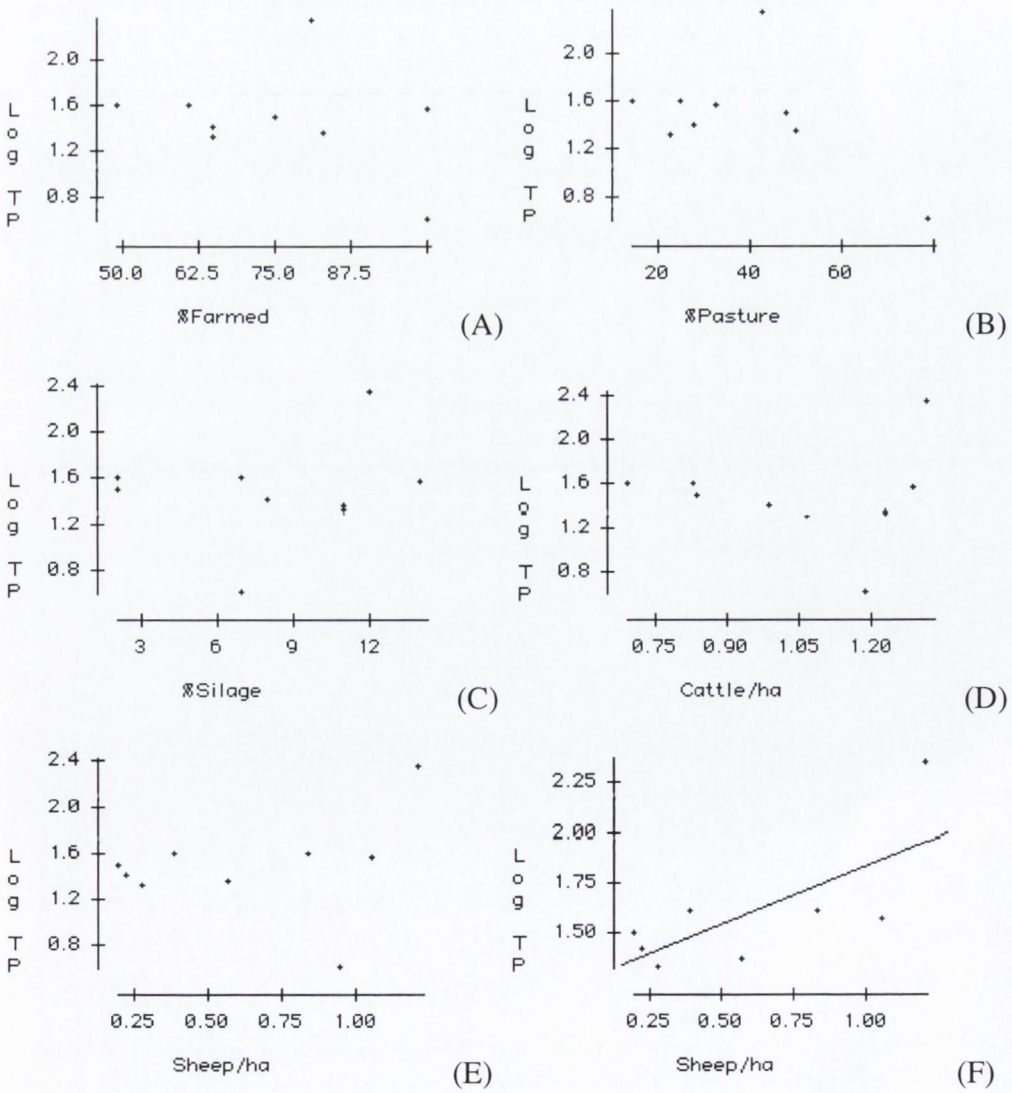
Forty seven groundwater sites were grouped into 9 DEDs. Five springs near Lisdoonvarna, outside the Fergus catchment, were included in this analysis. The characteristics of these DEDs are presented in Table 7.19. Kilfenora has the lowest TP but highest percentage area under pasture. However, this DED comprises only one site, FB07, in the far west of the catchment.

**Table 7.19 Summary statistics of Fergus DEDs.**

| *DED* | *No. of Sites* | *Mean TP* | *Median TP* | *StdErr* | *Pasture (%)* | *Silage (%)* | *Farmed (%)* | *Cattle (No./ha)* | *Sheep (No./ha)* |
|---|---|---|---|---|---|---|---|---|---|
| KILFENORA | 1 | 4 | 4 | na | 79 | 7 | 100 | 1.19 | 0.95 |
| RATH | 6 | 21 | 12 | 9 | 23 | 11 | 65 | 1.07 | 0.28 |
| KILTORAGHT | 3 | 26 | 16 | 15 | 28 | 8 | 65 | 0.99 | 0.22 |
| COROFIN | 3 | 38 | 17 | 27 | 33 | 14 | 100 | 1.29 | 1.06 |
| MUCKANAGH | 6 | 229 | 19 | 212 | 43 | 12 | 81 | 1.32 | 1.21 |
| LISDOONVARNA | 5 | 32 | 23 | 16 | 48 | 2 | 75 | 0.84 | 0.19 |
| KILLINABOY | 3 | 41 | 23 | 19 | 14 | 2 | 49 | 0.69 | 0.39 |
| TEMPLEMALEY | 6 | 23 | 25 | 3 | 50 | 11 | 83 | 1.23 | 0.57 |
| RUAN | 14 | 41 | 31 | 10 | 25 | 7 | 61 | 0.83 | 0.84 |

Log transformed mean groundwater TP was used to examine the nine DEDs agricultural characteristics. Resulting scatterplots are presented in Figure 7.20. There are no clear trends in the scatterplots.

**Figure 7.20 Scatterplots of between Fergus groundwater Log TP and DED agricultural characteristics. (F) Log TP versus sheep/ha with Kilfenora DED (one site) removed.**



In Figure 7.20 (F) the Kilfenora DED, which has only one site and very low TP, was removed. This results in a significant positive correlation between groundwater log TP and sheep per hectare ($R^2 = 52.3$, $p = 0.0425$).

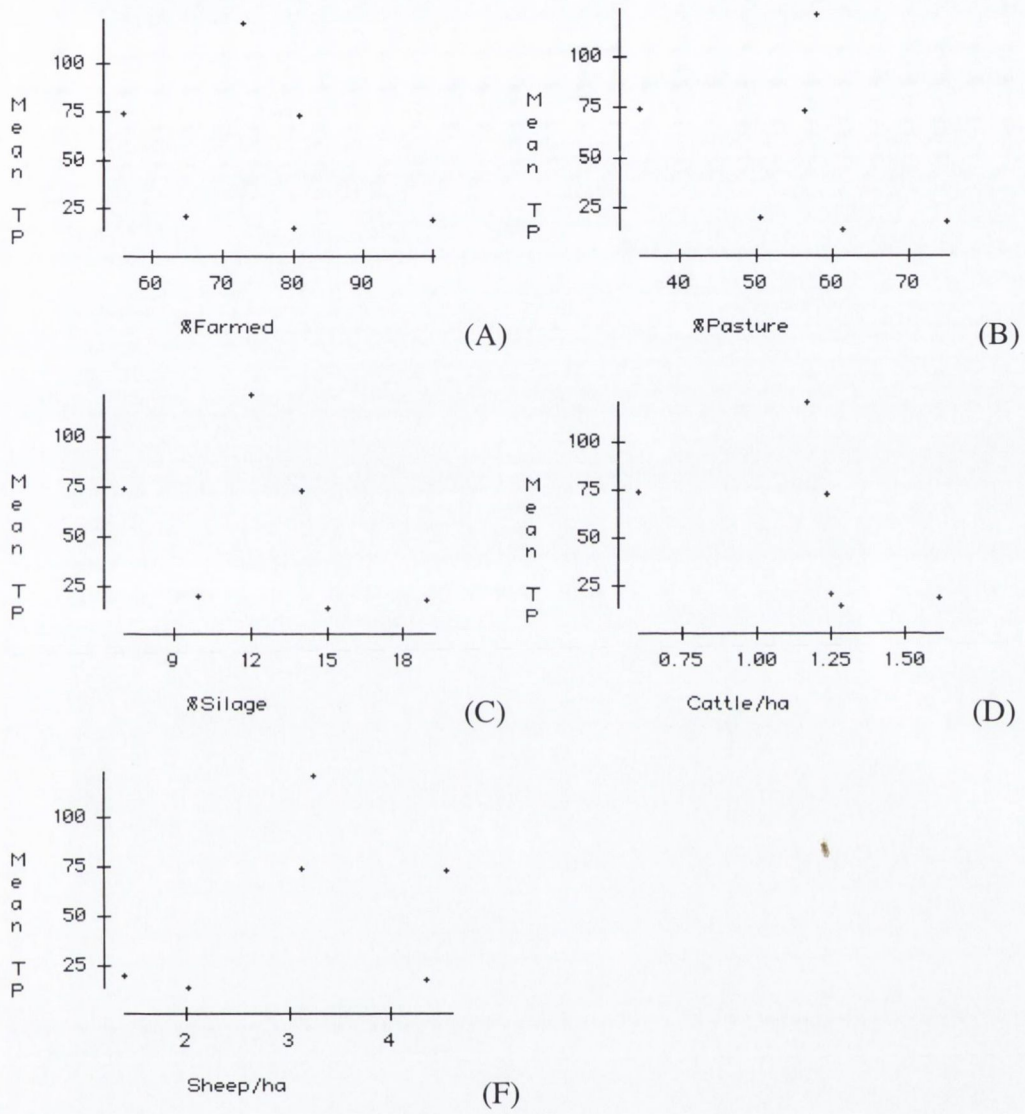
### 7.4.5 Robe Catchment Results

The Robe suffered from small sample size and small number of DED. As can be seen from the summary statistics in Table 7.20 some 68% of the sites are located in only two DEDs Hollymount and Kilmaine. What are striking in the DED statistics for the Robe catchment in comparison to the other two areas are the low percentage of pasture and the high densities of grazing sheep. This may reflect the large amount of rough grazing in these DEDs. Figure 7.21 plots groundwater mean TP for each DED versus each of the agricultural parameters. There are no clear trends for this catchment.

**Table 7.20 Summary statistics of Robe DEDs.**

| *Group* | *No. of Sites* | *Mean TP* | *Median TP* | *StdErr* | *Pasture (%)* | *Silage (%)* | *Farmed (%)* | *Cattle (No./ha)* | *Sheep (No./ha)* |
|---|---|---|---|---|---|---|---|---|---|
| Ballindine | 1 | 14 | 14 | na | 61 | 15 | 80 | 1.29 | 2.02 |
| Coonard | 1 | 20 | 20 | na | 51 | 10 | 65 | 1.25 | 1.38 |
| Hollymount | 7 | 121 | 21 | 89 | 58 | 12 | 73 | 1.17 | 3.25 |
| Kilcommon | 2 | 18 | 18 | 15 | 75 | 19 | 100 | 1.62 | 4.36 |
| Kilmaine | 6 | 73 | 35 | 46 | 57 | 14 | 81 | 1.24 | 4.55 |
| Neale | 2 | 74 | 74 | 42 | 35 | 7 | 56 | 0.60 | 3.12 |

**Figure 7.21 Scatterplots of between Robe mean groundwater TP and DED agricultural characteristics.**




## 7.4.6 Discussion

Examination of agricultural parameters using DED statistics suffered from scale and sample size inconsistencies. In Co. Limerick, a good spatial distribution of sites resulted in the analysis of over thirty DEDs. However, generally only one site was located in each DED, therefore, with n=1 sites, repeatability and representability may be questionable. In the Robe catchment there was much greater coverage within DEDs which should make the TP data more representative. However, fewer DEDs were examined making inter-DED comparisons difficult. The Fergus catchment had a more even spread amongst several DEDs, but as discussed in Section 7.3.6 regarding land cover, suffered from a disparity

between DED classes at the sampling location and the DEDs actually contributing water to a given site. This is particularly the case for some of the larger springs which have contributing areas of over 200 kilometres squared (Deakin, 2000). Ideally, the catchment areas of each spring and borehole would be delineated, and farm-to-farm surveys could more accurately estimate stocking densities and agricultural practices attributable to each site. Unfortunately the number of sites covered precluded such an approach. In addition, the DED data is almost 10 years old and may not be truly representative of current agricultural activities.

Despite these shortcomings, however, some trends did emerge. For the Limerick and Fergus catchments, there were positive relationships between pasture and groundwater TP. Silage and TP were also positively correlated in the Fergus catchment. Allott *et al.* (1998) reported strong positive relationships between Lake TP and cattle-based agriculture in the lake catchments. Pasture and silage production would fall into this category. The Robe catchment did not show such trends, indeed some negative correlations were identified between groundwater TP and pasture and cattle. This could reflect the dominance of sheep in the Robe catchment.

# CHAPTER 8. IMPLICATIONS OF GROUNDWATER PHOSPHORUS TO SURFACE WATER

## *8.1 Introduction*

The previous chapters examined the spatial and temporal circumstances when groundwater P levels exceed surface water thresholds. The objective of this chapter is to differentiate between groundwater and surface water loadings and, in doing so, quantify actual P loadings from groundwater to surface waters. In this way, groundwater systems that pose a threat to surface water may be identified. This objective was most easily achieved in the Fergus catchment, and to a lesser extent the Robe catchment, where the majority of the groundwater discharge is via karstic springs. In the Maigue and Deel catchments of Co. Limerick, groundwater discharge is largely as river baseflow and therefore P loadings are more difficult to calculate.

The karstic systems allowed the most immediate measure of the P load in groundwater discharges through the measurement of flows at springs and water analysis for P fractions. The P loading is then simply calculated by multiplying flow ($m^3s^{-1}$) by P concentration ($\mu g\ l^{-1}$) to get loading ($mg\ s^{-1}$). Many of the springs in the Fergus and Robe catchments provide substantial quantities of water to the surface water system. In this way the relative contribution of groundwater to the surface water load may be estimated.

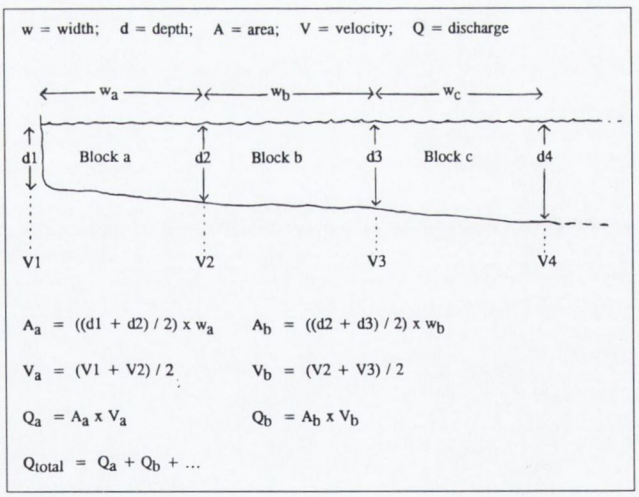
Less clear are estimations of baseflow P loadings. Baseflow may be estimated through separation of quickflow and baseflow from a catchment's hydrograph. This was carried out for the Deel and Maigue catchments. In this way catchments with a greater groundwater component may be identified. In catchments with small groundwater storage capacity the surface runoff pathway is expected to be the dominant mechanism of P movement from soil to water. In catchments with large groundwater storage capacity, subsurface movement of P should be more important. In the latter case, groundwater discharge may be an important diluter of surface water P levels, if groundwater P concentrations are relatively lower. However, if groundwater concentrations are comparable or higher than surface water P levels, then groundwater will be an important contributer to the surface water P load.

Each catchment area is examined below individually and followed by an overall discussion. The results sections for each catchment area comprise two parts; the first compares groundwater and surface water P concentrations, the second examines groundwater P loadings.

## *8.2 Methods for measuring flow at springs and rivers*

Flow measurements were taken at springs and river locations in the Fergus and Robe catchments. Flow was estimated by the velocity – area method (Shaw, 1988) using a ADS Sensa-RC2 Water Velocity Meter. In this method, the channel is divided withwise into a number of blocks (see Figure 8.1). The discharge for each block (i.e. velocity x cross-sectional area) is then added up to give the total river discharge. Transects were chosen where there was a minimum of eddying, and where the transect bed was of a most consistent depth. Generally flows measurements were taken at 0.5m or 1m interval along each transect, with smaller intervals being used for the smaller streams.

**Figure 8.1 Velocity area method for measuring flow in rivers and springs.**




Where the stream flow was over an uneven bed or strongly eddying, a salt dilution gauging method was adopted. Where the flow of the river Fergus was too great for direct flow velocity measurements, a floating object method was adopted.

## *8.3 Fergus catchment*

### 8.3.1 Introduction

As discussed in previous chapters the Fergus catchment represents a highly karstified aquifer. Coxon and Drew (2000) point out that "a significant proportion of the river flow does not follow the whole aboveground course, but takes a series of underground short-cuts from swallow holes in the river bed and lake shores to springs which feed the river further down-catchment". This strong interrelationship between surface water and groundwater emphasises the importance of identifying and quantifying P loadings from groundwater. The overall hydrology of the Fergus catchment and traced underground connections, which are discussed here, are presented in Section 3.2.5 and Figure 3.3.

The surface waters that were sampled in the Fergus catchment comprised river and lake samples. A total of six lakes and one turlough in the Fergus catchment were sampled (see Table 8.1). Lough Ballycullinan (FL04)was only sampled once. Lough George (FL05) and Lough Keogh (FLO6) were sampled at swallow holes where water from this lake discharged into groundwater. Lough Inchquin (FL03) was sampled at the outflow point. There were three sampling locations along the river Fergus. The complete Fergus River goes into a swallow hole at (FR01). Two bridges, Cross bridge (FR02) and Poplar Bridge (FR03) were also sampled. The location of these lakes and river sampling locations are presented in Figure 3.3 and Figure 3.4.

Flow measurements were made at on three occasions (Sept. 1998, July 1999 and Sept 1999) at the major springs and the three River locations feeding Lough Inchquin. Two springs feeding Lough Dromore (LD1 and LD2), which have underground connections from the swallow hole at Lough Keogh, were measured for flow in Sept 1998 and 1999. Further details on the techniques used to measure flow at these sites are presented in Section 4.2.7.

### 8.3.2 Results

Table 8.1 presents total P summary statistics for each of the surface water locations in the Fergus catchment. Full details of the result of each sampling occasion are presented in Appendix D. They all have noticeably lower standard errors than groundwater TP (see

Section 4.3.2). This is reflected in the fact that generally the mean and median values are almost equivalent. The three river locations have higher TP concentrations than the Lake sites (approximately double) with FL01 having the highest TP.

**Table 8.1 Summary statistics of TP at Fergus surface water sampling locations.**

| *Group* | *Code* | *Site Type* | *No. of samples* | *Mean* | *Median* | *StdErr* $\mu g\ l^{-1}$ | *StdDev* | *Max* | *Min* |
|---|---|---|---|---|---|---|---|---|---|
| L. Collaun | FL01 | Lake | 6 | 10 | 11 | 2 | 4 | 15 | 5 |
| L. Dromore | FL02 | Lake | 6 | 20 | 21 | 2 | 6 | 28 | 11 |
| L. Inchquin | FL03 | Lake | 7 | 24 | 26 | 4 | 11 | 38 | 10 |
| L. Ballycullinan | FL04 | Lake | 1 | 24 | 24 | na | Na | 24 | 24 |
| L. George | FL05 | Lake | 6 | 7 | 7 | 1 | 2 | 10 | 5 |
| L. Keogh | FL06 | Lake | 6 | 33 | 32 | 4 | 9 | 48 | 20 |
| Carron Turlough | FL07 | Turlough | 3 | 13 | 17 | 4 | 6 | 17 | 6 |
| An Clab | FR01 | River | 7 | 68 | 61 | 7 | 19 | 106 | 52 |
| Cross Bridge | FR02 | River | 5 | 39 | 31 | 8 | 19 | 68 | 22 |
| Poplar Bridge | FR03 | River | 5 | 47 | 38 | 8 | 18 | 70 | 30 |

Figure 8.2 presents boxplots of total P at each groundwater and surface water site type. Log transformed data is used in (A) to allow for better visual comparison. River P was significantly higher than Lake P ($p<0.0001$). Spring P was also significantly higher than Lake P ($p=0.0053$). Borehole P was not significantly different from any other site type. In (B) using untransformed data, the propensity of boreholes to yield extreme P values is clearly seen. Summary statistics of these P data are presented in Table 8.2.

**Figure 8.2 Overall site type boxplots of all major sampling runs in the Fergus. (A) Log TP (B) TP ($\mu g\ l^{-1}$).**

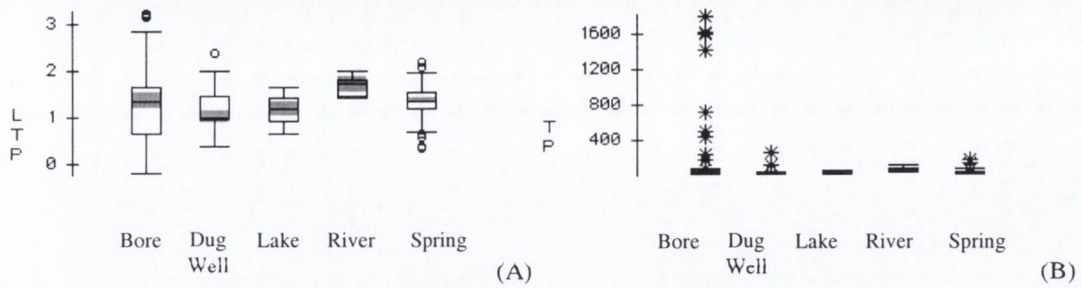


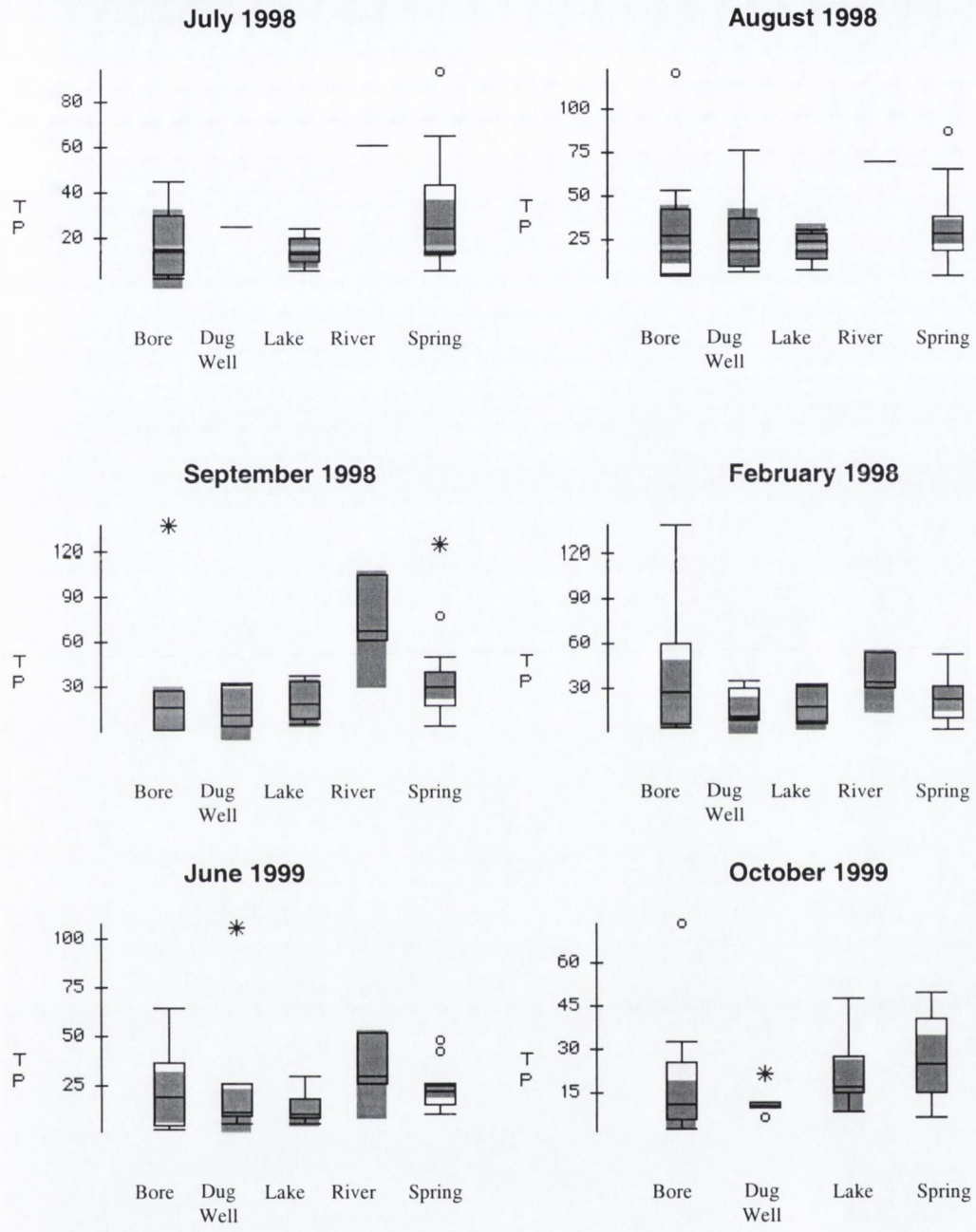

**Table 8.2 Summary statistics of total P for all combined major sampling runs in the Fergus catchment.**

| *Group* | *No. of Samples* | *Mean* | *Median* | *StdErr* | *StdDev* | *Maximum* |
|---|---|---|---|---|---|---|
| | | | | $\mu g\ l^{-1}$ | | |
| Borehole | 77 | 135 | 24 | 42 | 370 | 1814 |
| Dug Well | 34 | 28 | 11 | 8 | 46 | 259 |
| Lake | 33 | 19 | 17 | 2 | 11 | 48 |
| River | 11 | 54 | 55 | 7 | 24 | 106 |
| Spring | 94 | 30 | 24 | 3 | 25 | 163 |

These data were examined in more detail in Figure 8.3 where each of the six major sampling runs is presented individually. In all data from borehole FB03 were removed from the plot to allow better comparison. In the September 1998 run TP from FB06 was also removed. In October 1999 TP from FB06 and FB14 were also removed. These data were removed because they were extreme values which skewed the data and made comparisons between site types difficult. In the October 1999 run no river sites were sampled, since they had already been sampled in association with flow measurement in September 1999.

The plots in Figure 8.3 indicate that river TP is highest in all sampling runs. However, it should be noted that the river sites include FR01 and the two bridges (FR02 and FR03) all which are upstream of Lough Inchquin. In contrast, the lake and groundwater sites are distributed throughout the catchment. Therefore, it is not a true reflection of river TP levels throughout the catchment.

**Figure 8.3 Site type Boxplots of TP ($\mu g\ l^{-1}$) from the six major sampling runs in the Fergus catchment.**

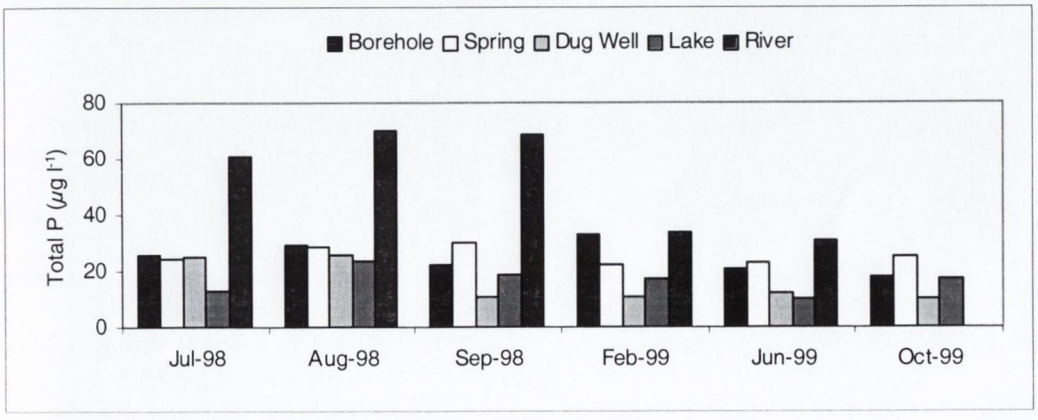



Summary statistics from these plots are presented in Table 8.3. Lowest lake TP occurred in July 1998 and June 1999. Lowest river TP occurred in February 1999 and June 1999. Figure 8.4 graphically presents the median TP data for each site type during the major sampling runs. It can be seen that the groundwater TP in springs and boreholes is consistently higher than lake TP.

**Table 8.3 Summary statistics of total P ($\mu g\ l^{-1}$) for each major sampling run in the Fergus catchment.**

| *Date* | *Site Type* | *Count* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|---|
| Jul-98 | Borehole | 7 | 247 | 26 | 228 | 603 | 1615 |
| | Spring | 14 | 33 | 24 | 6 | 24 | 94 |
| | Dug Well | 1 | 25 | 25 | NA | NA | 25 |
| | Lake | 6 | 14 | 13 | 3 | 7 | 24 |
| | River | 1 | 61 | 61 | NA | NA | 61 |
| Aug-98 | Borehole | 13 | 154 | 29 | 123 | 445 | 1632 |
| | Spring | 16 | 32 | 29 | 6 | 22 | 88 |
| | Dug Well | 7 | 28 | 26 | 9 | 24 | 76 |
| | Lake | 5 | 21 | 23 | 5 | 10 | 31 |
| | River | 1 | 70 | 70 | NA | NA | 70 |
| Sep-98 | Borehole | 10 | 227 | 23 | 178 | 563 | 1814 |
| | Spring | 16 | 35 | 30 | 8 | 30 | 125 |
| | Dug Well | 7 | 14 | 11 | 5 | 13 | 33 |
| | Lake | 6 | 21 | 19 | 6 | 14 | 39 |
| | River | 3 | 79 | 68 | 14 | 24 | 106 |
| Feb-99 | Borehole | 15 | 129 | 33 | 93 | 362 | 1430 |
| | Spring | 16 | 23 | 22 | 3 | 14 | 53 |
| | Dug Well | 7 | 19 | 11 | 4 | 12 | 36 |
| | Lake | 6 | 19 | 17 | 5 | 12 | 33 |
| | River | 3 | 40 | 34 | 7 | 13 | 55 |
| Jun-99 | Borehole | 16 | 66 | 21 | 45 | 180 | 738 |
| | Spring | 16 | 32 | 23 | 9 | 36 | 163 |
| | Dug Well | 7 | 61 | 12 | 36 | 94 | 259 |
| | Lake | 5 | 14 | 10 | 4 | 10 | 30 |
| | River | 3 | 36 | 30 | 8 | 14 | 52 |
| Oct-99 | Borehole | 16 | 86 | 18 | 40 | 160 | 515 |
| | Spring | 16 | 27 | 25 | 3 | 14 | 50 |
| | Dug Well | 5 | 12 | 10 | 3 | 6 | 22 |
| | Lake | 5 | 23 | 17 | 7 | 15 | 48 |
| | River | | | | | | |

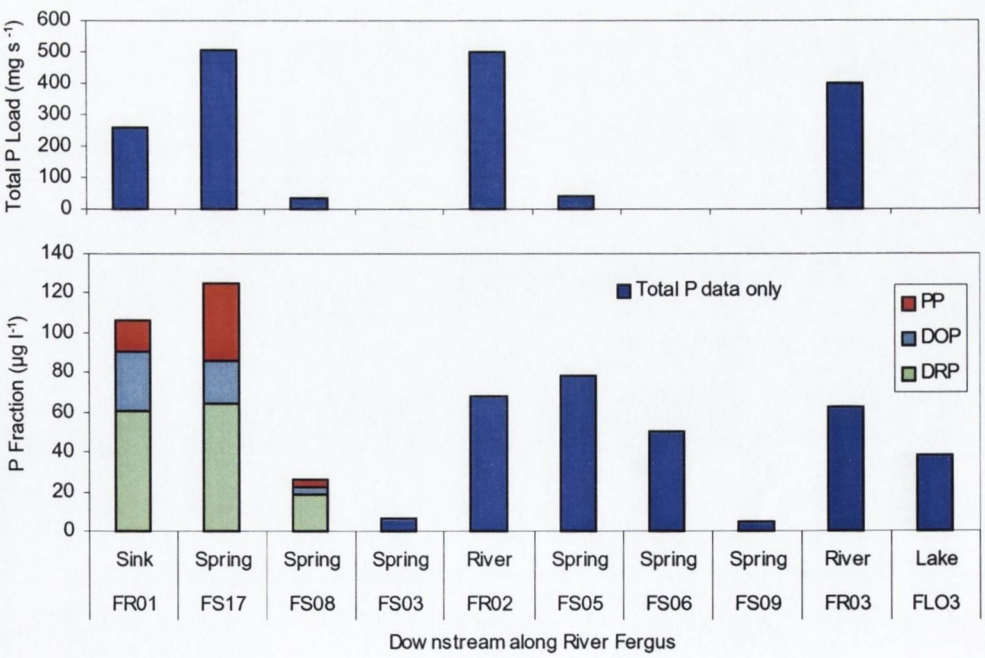
**Figure 8.4 Median TP levels at each site type during the major sampling runs.**



### 8.3.3 Groundwater phosphorus loadings

Flow measurements and P fraction analyses from sites located along the River Fergus before Lough Inchquin facilitate an assessment of the relative contribution of groundwater P to the lake P loading. Three flow measurement runs were carried out on these 'Inchquin Sites': September 1998 during high stage conditions; July 1999 during low stage conditions, and September 1999 during medium stage conditions. Note that initially in September 1998 two springs at the Elmvale group of springs, FS05 and FS06 were sampled. Thereafter an additional site, FS07, was sampled before the confluence with the Fergus river to ensure that all water from these springs was accounted for (see Figure 4.10). The results of the flow measurements and P fraction analysis is presented in Appendix C. Figure 8.5, below, presents data from the September 1998 flow measurement run. The bottom half of the graph presents total P data (and P fractions where available) for each of the sites and the top section presents TP loadings where flow data have been obtained.

**Figure 8.5 September 1998 high stage conditions: Total P Loadings and P concentrations along the River Fergus.**

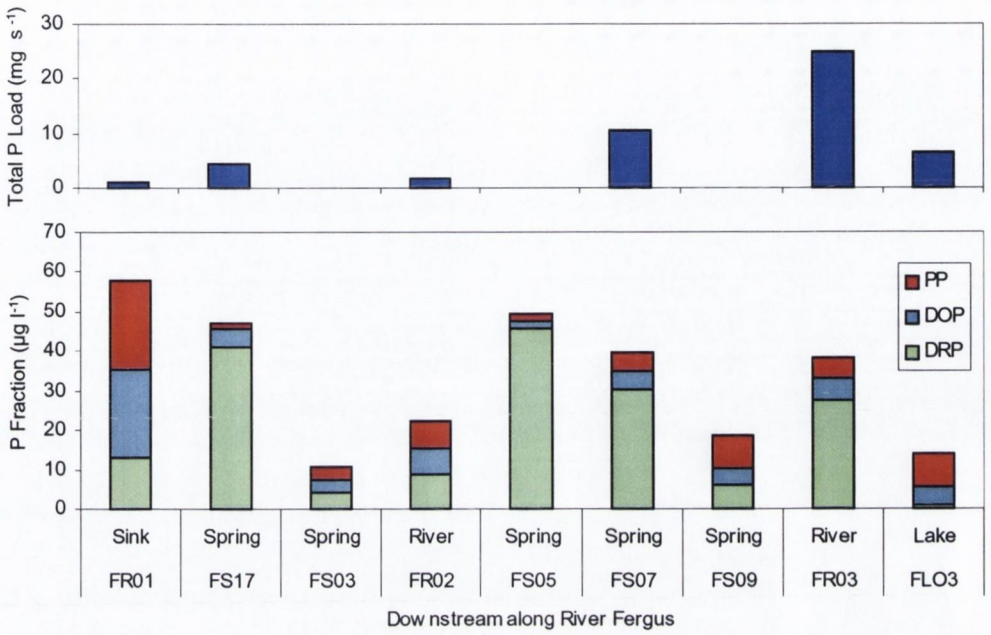


TP loading from Poulnaboe is almost double that of FR01. Therefore at this stage some 50% of the P loading in the river is derived from groundwater. However, it should be noted that this 50% of "groundwater" could itself have derived from both diffuse groundwater recharge and via point recharge at sinking streams (see Section 3.2.5 for more information on traced underground connections in the Fergus catchment).

The P fractions at FR01 and FS17 are similar in terms of DRP and DOP but the PP concentrations at FS17 is almost double that of FR01. Consequently the PP load has almost doubled at FS17. The P loadings at Cross Bridge (FR02) and Poplar Bridge (FR03) along the Fergus indicate that the initial P loading from FS17 is maintained until the Fergus River reaches Lough Inchquin. Downstream of FS17 there are minor groundwater P loading contributions from FS08 and FS05. There is a slight dip in P loading at Poplar Bridge (FR03).

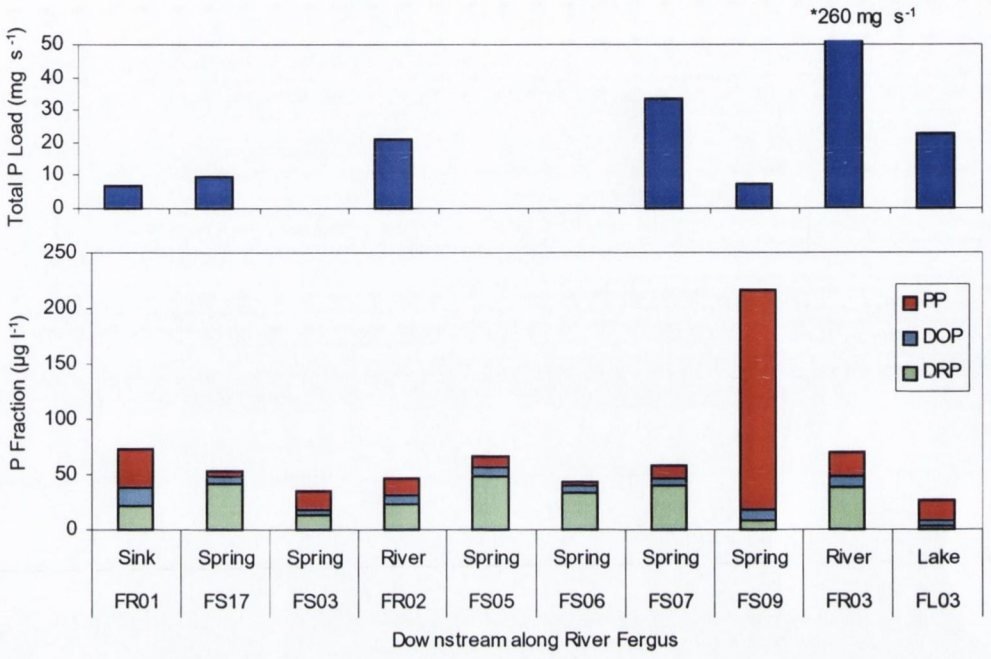
Figure 8.6, below, presents data from the July 1999 flow measurement run. Full P fractionation was carried out at each sampling site. Low stage conditions were apparent during this run and the outflow of Lough Inchquin (FL03) was also gauged. The proportions of the P fractions at FR01 and FS17 contrast starkly. The majority of the P at FR01 is DOP and PP with minor amounts of DRP. In contrast, the water at FS17 is mainly DRP with minor amounts of DOP and PP. Once again, at FR01 and FS17 are similar but there is a large differential in loading. The TP load at Poulnaboe is almost four times that of FR01. Therefore at this stage approximately 75% of the P load to the Fergus is derived from water travelling underground to FS17 (excluding the contribution from the Fergus River at FR01).

**Figure 8.6 July 1999 Low stage conditions. Total P Loadings and P concentrations along the River Fergus.**




There is a slight decrease in flow and load at Cross bridge which may be due to gauging error or perhaps loss of water to groundwater through the river bed. The single largest contribution to the river P load is from the Elmvale springs and most of this is as DRP. The TP load from the Elmvale springs is almost 2.5 times that of the load at Poulnaboe. The P load measured at Poplar Bridge, which should incorporate this input from Elmvale, does indeed increase (25 mg $s^{-1}$ TP) but to a level that cannot be accounted for solely by the contributions from Poulnaboe and Elmvale (15 mg $s^{-1}$ TP combined). This discrepancy could be explained by flow gauging error, either an overestimate at Poplar Bridge or an underestimate at Elmvale. It may also represent an underestimating of the load from the Kilnaboy spring. The Kilnaboy spring was gauged at the spring source and not near the confluence to the River Fergus. At any rate, up to the Poplar Bridge approximately 90% of the P load to the River Fergus was direct contributions from springs. At Poplar bridge, before the river discharges to Lough Inchquin most of the river P load is as DRP. At the outflow of Lough Inchquin DRP levels are almost below detection limits with the majority of TP comprising DOP and PP. The DRP load from the Fergus is probably being used up through algal production or precipitating out (e.g. as hydroxyapatite, see Section 4.6.6). Figure 8.7 presents flow measurement data from the September 1999 run which occurred during medium stage conditions.

**Figure 8.7 September 1999 Medium stage conditions. Total P Loadings and P concentrations along the River Fergus. (*) Poplar Br. Loading (FR03).**




This time the P load at FS17 was closer to that of FR01 (10 and 7 mg $s^{-1}$ TP respectively), with some 30% of the TP load groundwater derived. The load doubles at Cross Bridge (FR02), which is unusual because FS08 was dry and so, other than gauging error, the river must have gained flow from the riverbed. There is a further consistent input as in the two previous runs from the Elmvale springs (FS05/FS06/FS07). However, there is a huge increase in flow (3.7 cumecs) at Poplar Bridge (FR03) which cannot be explained solely by the Elmvale springs. Approximately 2.7 cumecs is subsequently unaccounted for. This additional flow must either come from point inputs downstream of FS09 or via the riverbed. FS09 was experiencing some sort of organic pollution as reflected in the abnormally high PP levels.

Less information was collected for FS13 and FS14, both which feed L. Dromore and both which have been traced from L. Keogh (see Figure 3.4). Table 8.4 presents flow data and TP loadings from these springs to L. Dromore for Sept. 1998 and 1999.

**Table 8.4 Summary flow data from Lough Dromore springs FS13 and FS14.**

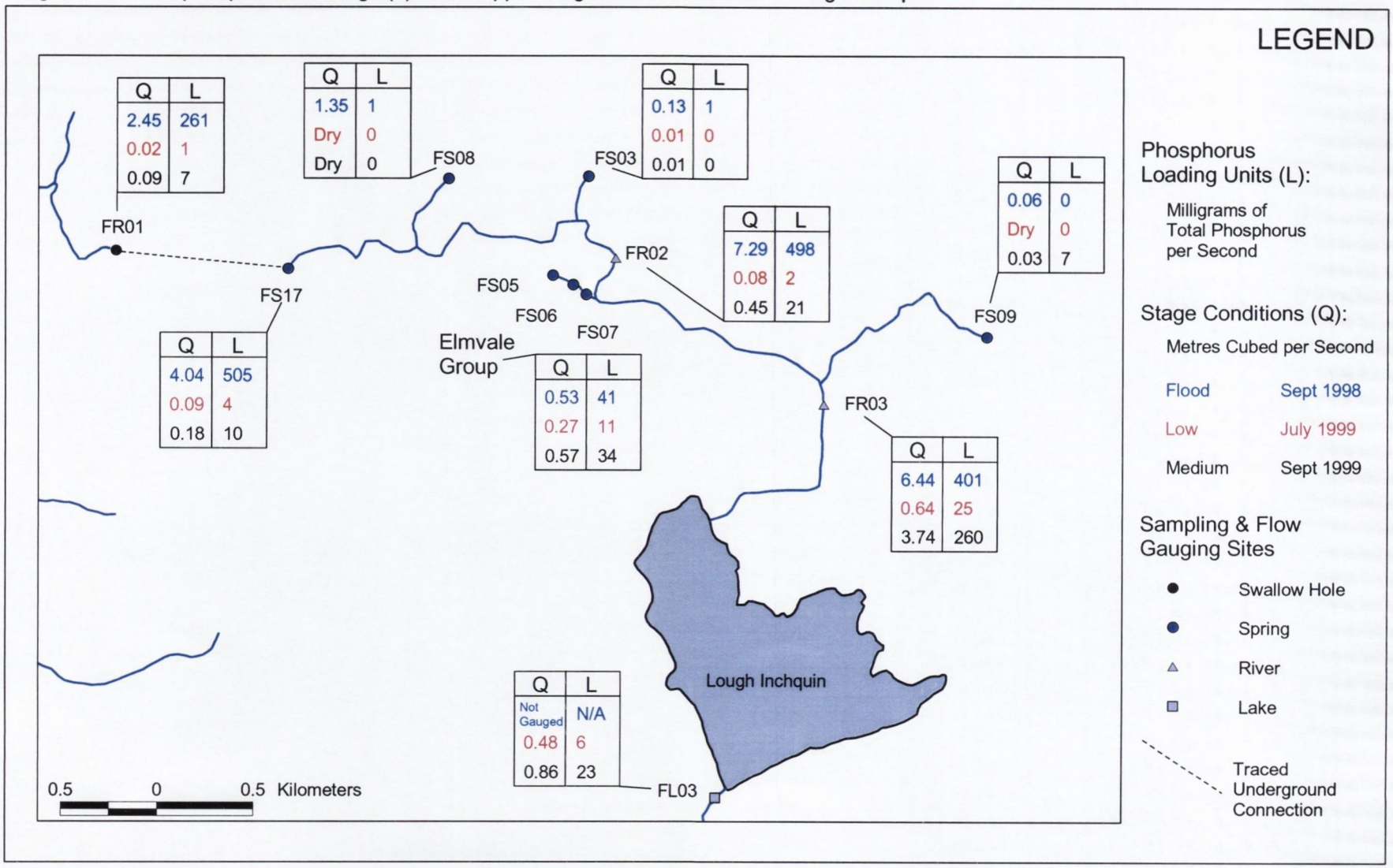
| *Site* | *Sept 1998 flow gauging* | | | *Sept 1999 flow gauging* | | | | |
|---|---|---|---|---|---|---|---|---|
| | Q ($m^3s^{-1}$) | TP ($\mu g\ l^{-1}$) | TP Load ($mg\ s^{-1}$) | Q ($m^3s^{-1}$) | DRP ($\mu g\ l^{-1}$) | DOP ($\mu g\ l^{-1}$) | PP ($\mu g\ l^{-1}$) | TP Load ($mg\ s^{-1}$) |
| FS13 | 0.062 | 30 | 1.9 | 0.087 | 30 | 15 | 14 | 5.1 |
| FS14 | 0.281 | 40 | 11.2 | 0.342 | 30 | 13 | 19 | 21.2 |

### 8.3.4 Discussion

Phosphorus concentrations varied greatly between surface water and groundwater sites type. There were several boreholes that had extreme TP levels far higher than river and Lake. Groundwater from these sites is probably contaminated by nearby localised point sources and therefore should be relatively easy to control and manage. Whilst the TP levels in the river locations upstream of Lough Inchquin were quite high relative to groundwater TP, it should be noted that large proportions of the water is derived from springs feeding the Fergus. Groundwater TP from springs and boreholes, which was mainly as DRP, was consistently higher than that of lakes in the catchment. This concentration gradient would tend to indicate that groundwater is a significant source of P to these lakes. The sharp reduction in TP and especially DRP at Lough Inchquin is probably caused by algal uptake and by co-precipitation with carbonates (Otsuki and Wetzel, 1972). This pattern was reflected in the increase in saturation index of hydroxyapatite in Section 4.6.6.

Actual P loads were examined in the case of L. Inchquin. Figure 8.8 presents the TP loadings for each spring sampled before L. Inchquin. During low stage conditions up to 90% of the load may be derived from springs feeding the Fergus River. During high stage conditions this figure is reduced to about 50%. Drew (1988) suggests that all these springs except FS17 are fed predominantly by diffuse input recharge rather than by concentrated recharge via swallowholes. He estimates that irrespective of stage diffuse recharge account for about 95% of outflow from the springs.

Figure 8.8 Total phosphorus loadings (L) in the Upper Fergus Catchment before Lough Inchquin.




| Q | L |
|---|---|
| 2.45 | 261 |
| 0.02 | 1 |
| 0.09 | 7 |

| Q | L |
|---|---|
| 1.35 | 1 |
| Dry | 0 |
| Dry | 0 |

| Q | L |
|---|---|
| 0.13 | 1 |
| 0.01 | 0 |
| 0.01 | 0 |

| Q | L |
|---|---|
| 0.06 | 0 |
| Dry | 0 |
| 0.03 | 7 |

| Q | L |
|---|---|
| 7.29 | 498 |
| 0.08 | 2 |
| 0.45 | 21 |

| Q | L |
|---|---|
| 4.04 | 505 |
| 0.09 | 4 |
| 0.18 | 10 |

| Q | L |
|---|---|
| 0.53 | 41 |
| 0.27 | 11 |
| 0.57 | 34 |

| Q | L |
|---|---|
| 6.44 | 401 |
| 0.64 | 25 |
| 3.74 | 260 |

| Q | L |
|---|---|
| Not Gauged | N/A |
| 0.48 | 6 |
| 0.86 | 23 |

Discrepancies were apparent at Poplar Bridge (FR03) just after the confluence from FS09. Drew (1988) notes that successively higher level springs become active at FS09 under wetter conditions. Measurement of flow at FS09 closer to the confluence with the Fergus River could have better ascertained if this was the case. However, this discrepancy was not evident in September 1998 during high stage conditions, when perhaps flow to FS09 is bypassed. Therefore, flow paths to FS09 may be preferentially used depending on stage conditions. These discrepancies highlighted the potential margins for error in this approach if the flow gauging stations are not accurately positioned or if the stage conditions are not taken into account.

Overall, the substantial majority of the TP load to Lough Inchquin is groundwater. The Elmvale springs provide the greatest single P load during low and medium stage conditions. During high stage conditions FS17 provided the greatest groundwater P load. In all cases DRP was the dominant fraction in all groundwater P loads. The TP loadings to Lough Dromore are probably strongly influenced by point recharge at sinks like FL06. Given the rapid travel times from this sink to these springs, surface water upstream of Lough Keogh will largely dictate the P load to the L. Dromore at these springs.

## *8.4 Robe catchment*

### 8.4.1 Introduction

The River Robe flows into Lough Mask, a large (80 $km^2$) mesotrophic lake (Lucey *et al.* 1999). Several of the springs sampled in this study flow directly into the Robe or into one of its tributaries (see Figure 3.6). The latest assessment of the River Robe indicate median unfiltered MRP values ranging from 30 to 64 $\mu g\ l^{-1}$ over the 1995-97 monitoring period (Doris *et al.*, 1999). Biological Quality Rating values ranged from 4-5 (unpolluted) to 3 (moderately polluted). During the same monitoring period there was a noticeable decrease in river quality around Crossboyne Bridge (RR01), which was followed by an increase in quality at Foxhill Bridge (RR02) and a subsequent decrease in quality after Ballinrobe before the river discharges into Lough Mask. Both Crossboyne Bridge and Foxhill Bridge were sampled during the groundwater sampling programmes in the Robe catchment. Groundwater P concentrations described in Section 4.3, are here compared with surface water P data in the River Robe. Several underground connections have been traced

between sinks/boreholes and springs, as discussed in Section 3.3.5. The hydrogeology of the Robe catchment has been described as intermediate in type between a non-karstic diffuse flow aquifer, and the conduit dominated groundwater flow system characteristic of most karstic terrains (Coxon and Drew, 1986). Two surface water sampling sites were located on the Robe River. Both were taken at bridges. Foxhill Bridge (RR02) is located along the R331 regional road, 6km northeast of Ballinrobe and near the village of Hollymount. Crossboyne Bridge (RR01) is located further upstream, some 16 km northeast of Ballinrobe and near the village of Ballindine (see Figure 3.6).

Flow measurements were taken at five springs, but RS05 was only gauged once. The others were gauged on three occasions, Sept. 1998. July 1999 and Sept. 1999, except RS01 which was dry during July 1999. RS06 and RS01 springs flow directly into the Robe. The RS04 spring flows into the Balkan River which is a tributary of the Robe. RS03 spring is the source of the Bunnadober River and flows directly into Lough Mask. RS05 spring feeds a stream which eventually drains to Lough Corrib in the south. This spring is outside the topographic Robe catchment boundary but is included because water has been traced from a turlough in the catchment to Fountainhill spring (see Figure 3.6).

### 8.4.2 Results

Table 8.5 presents total P summary statistics for each of the river sites. Foxhill Bridge (RR02) generally had slightly lower TP than the Crossboyne Bridge (RR01). Figure 8.9 illustrates how this trend was maintained during the major groundwater sampling events.

**Table 8.5 Summary statistics of total P ($\mu g\ l^{-1}$) River Robe sampling locations.**

| *Group* | *Count* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* | *Min* |
|---|---|---|---|---|---|---|---|
| Foxhill Bridge(RR02) | 6 | 44 | 39 | 8 | 19 | 68 | 23 |
| Crossboyne Bridge (RR01) | 6 | 49 | 50 | 7 | 18 | 71 | 27 |

**Figure 8.9 Temporal variations in TP at Robe River sites.**

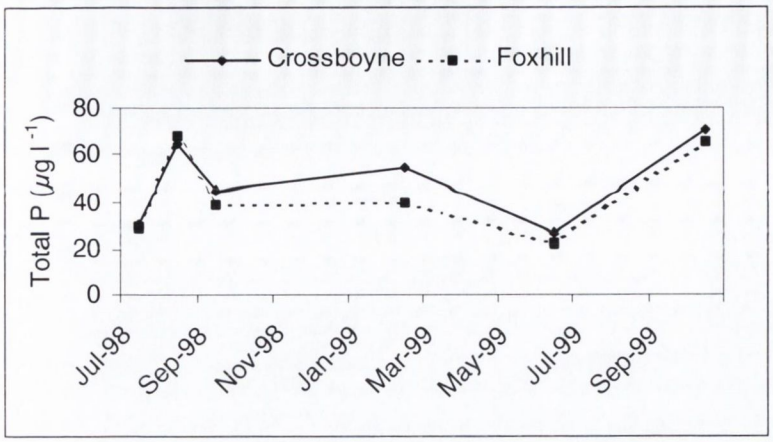



Figure 8.10 presents total P boxplots of each site type including the river sites. The large number of outliers in the borehole group (A) is solely due to the RB02 and RB07 boreholes. Section 6.3.5 describes in more detail the elevated levels reported at these sites. Once removed (B) a clearer comparison between site types can be made. Table 8.6 presents summary statistics for all major sampling runs. The river sites had highest median TP levels and were significantly higher than springs ($p<0.0001$) but not boreholes (excluding RB02 and RB07).

**Figure 8.10 Overall site type boxplots of all major sampling runs.**

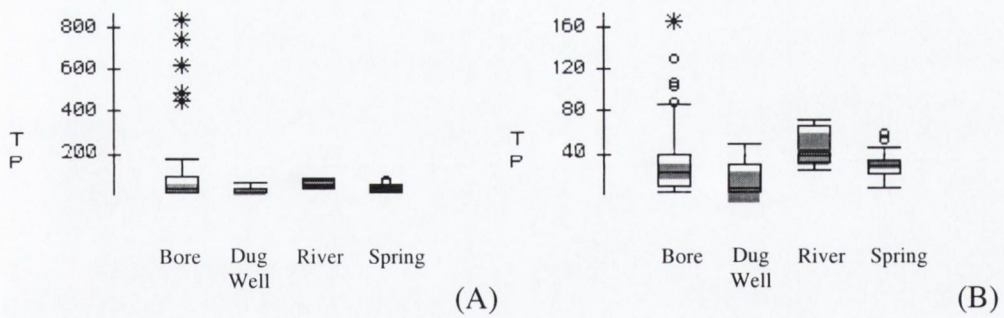



**Table 8.6 Summary statistics of major sampling runs in Robe (Figure 8.10).**

| *Group* | *No. of samples* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|
| Borehole | 45 | 99 | 21 | 30 | 200 | 843 |
| Dug Well | 8 | 14 | 5 | 6 | 17 | 48 |
| River | 12 | 46 | 42 | 5 | 18 | 71 |
| Spring | 33 | 26 | 26 | 2 | 12 | 57 |

Figure 8.12 presents of each of the six major sampling runs in the Robe catchment. A more clearer temporal comparison of median TP is presented in Figure 8.11 below.

**Figure 8.11 Median TP comparison between River Robe and groundwater sites.**

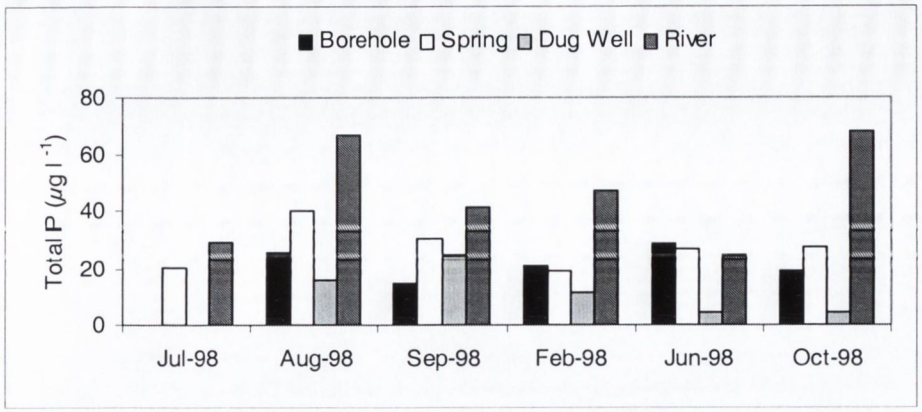
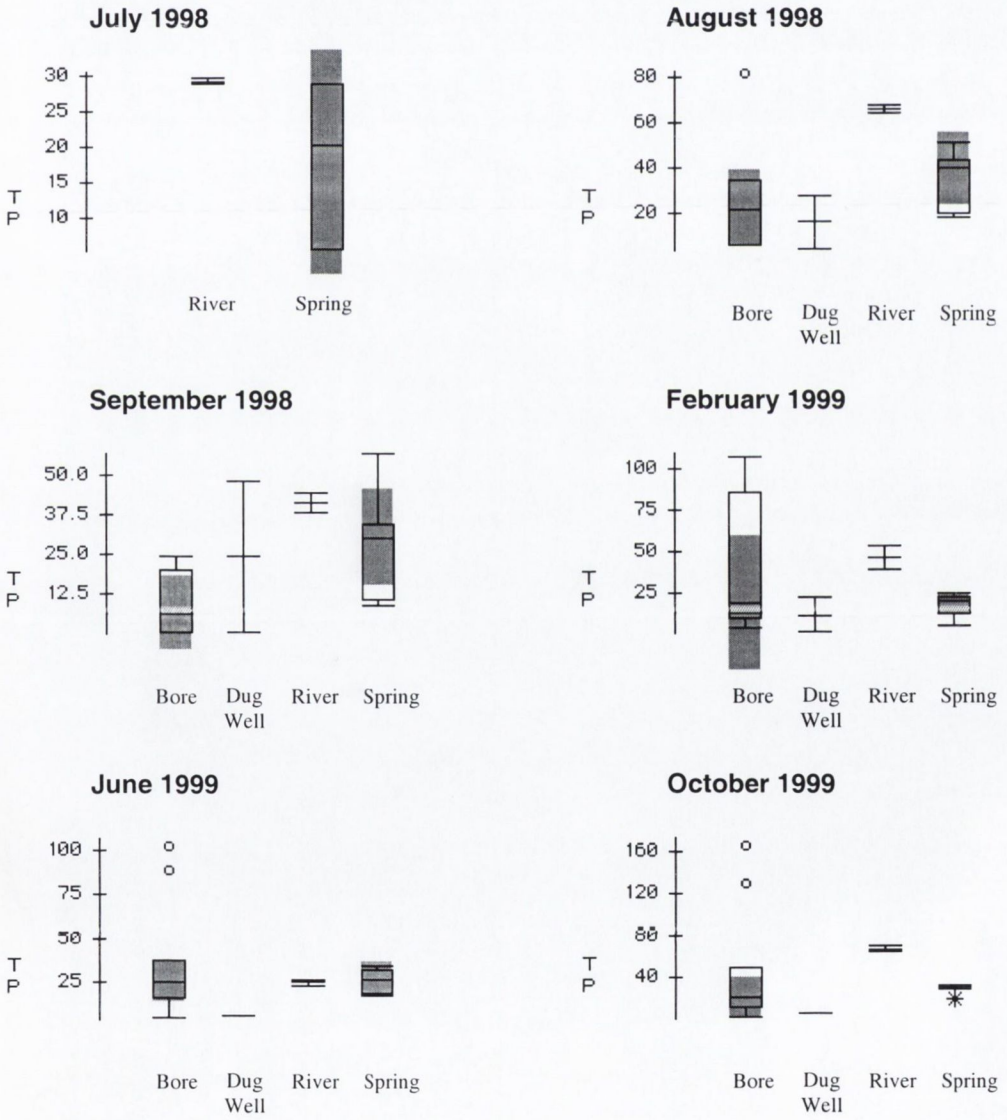



**Figure 8.12 Site type boxplots of TP ($\mu g\ l^{-1}$) from the six major sampling runs in the Robe catchment.**



Summary statistics of each of these sampling runs are presented in Table 8.7. As can be seen from this table and Figure 8.11, median river TP is lowest during the July 1998 and June 1999 sampling runs. Median river TP is greater than the groundwater on all occasions except on June 1999 when both spring and boreholes had slightly higher median TP than the river.

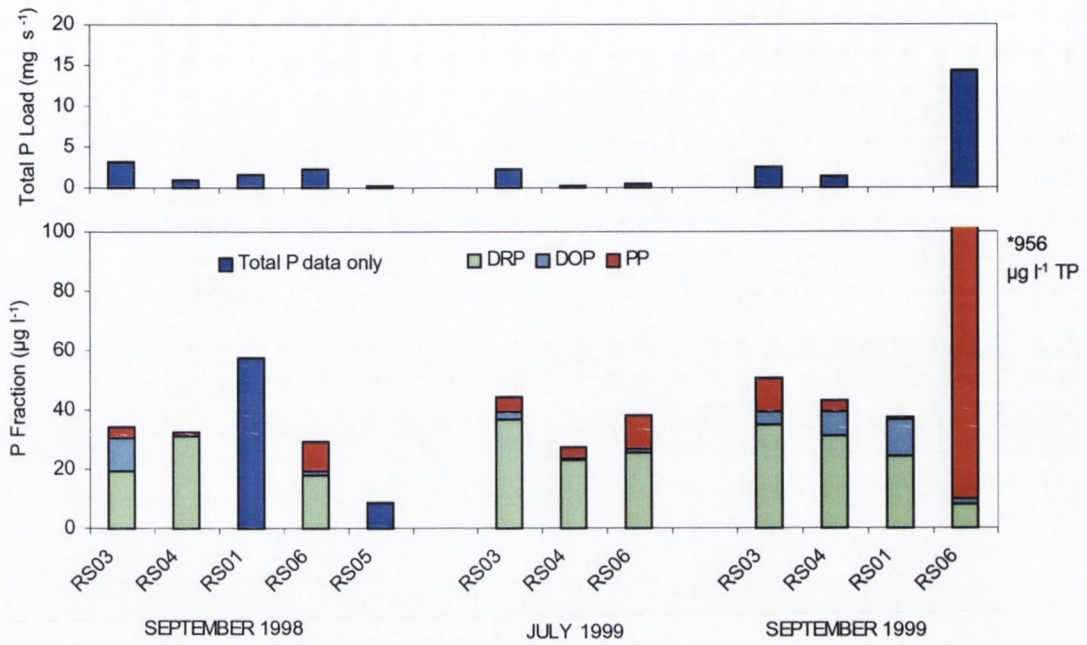
**Table 8.7 Summary statistics for TP ($\mu g\ l^{-1}$) for each major sampling run in the Robe catchment.**

| *Date* | *Site Type* | *Count* | *Mean* | *Median* | *StdErr* | *StdDev* | *Max* |
|---|---|---|---|---|---|---|---|
| Jul-98 | River | 2 | 29 | 29 | 0 | 1 | 30 |
| | Spring | 4 | 19 | 20 | 5 | 10 | 29 |
| Aug-98 | Borehole | 8 | 80 | 25 | 54 | 152 | 449 |
| | Dug Well | 2 | 16 | 16 | 12 | 17 | 28 |
| | River | 2 | 66 | 66 | 2 | 3 | 68 |
| | Spring | 6 | 36 | 40 | 6 | 14 | 52 |
| Sep-98 | Borehole | 9 | 145 | 15 | 92 | 276 | 748 |
| | Dug Well | 2 | 25 | 25 | 24 | 34 | 48 |
| | River | 2 | 41 | 41 | 3 | 4 | 44 |
| | Spring | 6 | 29 | 31 | 7 | 18 | 57 |
| Feb-99 | Borehole | 9 | 127 | 21 | 90 | 271 | 843 |
| | Dug Well | 2 | 12 | 12 | 10 | 14 | 22 |
| | River | 2 | 47 | 47 | 8 | 11 | 55 |
| | Spring | 6 | 17 | 19 | 3 | 7 | 24 |
| Jun-99 | Borehole | 10 | 96 | 29 | 60 | 188 | 624 |
| | Dug Well | 1 | 5 | 5 | NA | NA | 5 |
| | River | 2 | 25 | 25 | 2 | 3 | 27 |
| | Spring | 6 | 26 | 27 | 3 | 8 | 35 |
| Oct-99 | Borehole | 9 | 46 | 19 | 20 | 60 | 167 |
| | Dug Well | 1 | 4 | 4 | NA | NA | 4 |
| | River | 2 | 68 | 68 | 3 | 4 | 71 |
| | Spring | 5 | 26 | 28 | 2 | 5 | 31 |

### 8.4.3 Groundwater Phosphorus Loadings

Major springs were also flow gauged three times: September 1998; July 1999, and; September 1999. Like the Fergus catchment lowest flows were obtained during the July 1999 run. However, the Robe springs were far less flashy, and did not change by large orders of magnitude as many of the Fergus springs did. The contamination event at Kilrush discussed in previous chapters was also picked up during the September 1999 flow gauging run. Figure 8.13 presents the P loadings

**Figure 8.13 Phosphorus fractions and loadings from the major springs of the Robe catchment.**




RS03 consistently provided a TP load of 2.2-3.3 mg $s^{-1}$. This represented the largest load of all the springs. However, only a particular spring at RS04 was flow gauged and so the load from this set of springs could be here. Generally the P load from all springs is dominated by DRP. The exception being RS06 in September 1999. As discussed earlier (Section 6.5.2) this spring was subject to severe organic contamination between July and September 1999. This is reflected in the high TP and especially particulate P load during the September 1999 flow gauging run. The load from this flow at RS06 (14.3 mg $s^{-1}$) is four times higher than the highest RS03 load.

The P loads in the river during the times sampled are estimated in Table 8.8 using flow data from the EPA. During the low flow period of 11 Jun 1999 , the RS06 P load estimate through the contamination event (14.3 mg $s^{-1}$) is relatively high, comprising about 50% of the TP load in the river Robe. In contrast, the highest load (3.3 mg $s^{-1}$) from the RS03 spring only represents about 13% of the averaged P load in the Robe River during this low flow period. However, in comparison to the 7 October 1999 high flow period, the RS06 pollution event only represents about 8% of the TP load in the river and the highest RS03 TP load represents about 2%.

**Table 8.8 Estimated total P loading at each of the Robe surface water sites.**

| | *TP 11 Jun 99* | *TP 3 Oct 99* | *TP load 11 Jun 99* | *TP load 3 Oct 99* |
|---|---|---|---|---|
| | $\mu g\ s^{-1}$ | | $mg\ s^{-1}$ | |
| Foxhall Bridge | 22.7 | 65.3 | 22.9 | 161.2 |
| Crossboyne | 27.1 | 70.7 | 27.3 | 192.1 |
| Flow in Robe ($m^3s^{-1}$) *(nearest date)* *Flow data source: EPA* | 1.01 (11 Jun 1999) | 7.04 (7 Oct 1999) | | |

### 8.4.4 Discussion

The TP levels at Crossboyne Bridge were consistently higher than levels further downstream at Foxhill Bridge. This is consistent with the Biological Quality Rating values mentioned in the introduction (Section 3.3.6) for the 1995-1997 monitoring period. Drew and Daly (1993) note that there is considerable interchange between river flow in the Robe and groundwater. For example, they state that from mid-winter to late spring, flows downstream of RS06 are disproportionately high, up to 3 $m^3s^{-1}$ higher than upstream. Therefore, there are large inflows from groundwater to the river during high water table conditions. In the summer and late autumn the reverse happens and water is lost via the stream bed to groundwater as water table levels are below the level of the river. This phenomenon may result in dilution of River P levels by less concentrated groundwater and could explain the concentration difference between Crossboyne and Foxhill at least in the winter and late spring. TP levels in the River Robe were lowest during the July 1998 and June 1999 sampling runs when surface waters are at most risk to algal growth. During the June 1999 sampling run median groundwater TP levels at boreholes and springs were higher than median river TP. Therefore groundwater discharges at springs, as river baseflow and directly to Lough Mask shores may be important nutrient sources.

RS03 provided the largest consistent single load to surface waters. At its highest, this load from RS03 represents about 13% of the P load in the Robe River discharging to Lough Mask during low flow conditions. RS06 generally provide low P loads, however once the source became contaminated the spring acted as a direct link between the P source and the Robe River. During low flow conditions in the Robe River, this represents approximately 50% of the total P load discharging into Lough Mask. This illustrates how these springs

can act as a conduit, linking point sources on land to surface water, and discharging significant P loadings. Once identified these point sources should be relatively easy to control and manage.

## *8.5 Limerick Catchments (Deel and Maigue)*

### 8.5.1 Introduction

Some eight major river catchments are located in Co. Limerick (see Figure 3.8). Of these the Deel and the Maigue catchments are the largest. This is reflected in the distribution of the groundwater sampling locations. Out of a total of forty-one sites, fourteen are located in the Deel catchment and eighteen in the Maigue catchment. Therefore, for the purposes of examining surface water P levels in this chapter, these two catchments were focused on. The Deel catchment covers approximately 540km$^2$ of Co. Limerick, and the Maigue catchment covers approximately 1080km$^2$ of Co. Limerick. The Deel and Maigue catchments are exceptionally poor in water quality terms compared with other Irish catchments. These catchments were unique during the 1995-1997 EPA sampling period in that all of the 38 stations sampled in these catchment had median MRP levels greater than the eutrophication threshold of 30 $\mu$g l$^{-1}$ (Stapleton *et al.*, 2000). These high P levels are in line with the biological assessment of this period, which shows widespread eutrophication in both catchments.

### 8.5.2 Material and Methods

No surface water samples were taken during the groundwater sampling program in Co. Limerick. It was hoped that surface water data from the 1998-2000 EPA River Monitoring Programme would have been available for this study to allow comparison of contemporaneous groundwater and surface water P concentrations. Unfortunately, these data were not available in time for this study and reliance was made on data from the 1995-1997 monitoring programme (Doris *et al.*, 1999). This time lag is not considered to be significant given that since the 1980's both catchments have consistently reported Biological Quality Ratings or Q Values of either 3 or 3-4 which designate moderate or slightly polluted river water respectively.

Flow data for the 1991-1994 period were obtained from the EPA for flow monitoring stations at Rathkeale and Croom, for the Deel and Maigue catchments respectively (see Figure 3.8). Long term mean flow data for these stations were obtained from the Office of Public Works (OPW). These data were used to estimate the baseflow component of these catchments and to evaluate their groundwater storage component. The boundary between surface runoff and baseflow is difficult to define and depends very much on the geological structure and composition of the catchment (Shaw, 1988). In this study the groundwater flow component of each catchment was calculated by visually separating quickflow from baseflow on each hydrograph. This method is quite subjective, but will at least provide indicative proportions of baseflow for comparison between the two catchments. These hydrograph-separations are presented in Appendix C. The area under the each baseflow curve was calculated and presented here as a proportion of the total flow in each river.

The long term mean flow data were used to construct flow duration curves for each of these catchments. A flow duration curve shows the percentage of the time that a given flow is equalled or exceeded during a given year or periods of years. To make comparisons between the Maigue and Deel Rivers which have different average flows, the flows may be expressed as a percentage or proportion of the long term mean flow. The slope of a flow duration curve is a measure of streamflow variability. A steep slope will indicate that the river has a high proportion of quickflow, whereas a more gentle slope indicates a more even regime. The shape of the curve at its lower end characterises the perennial storage in the catchment so that a flat lower end indicates a large amount of storage (Ward and Robinson, 1989).

### 8.5.3 Baseflow estimates

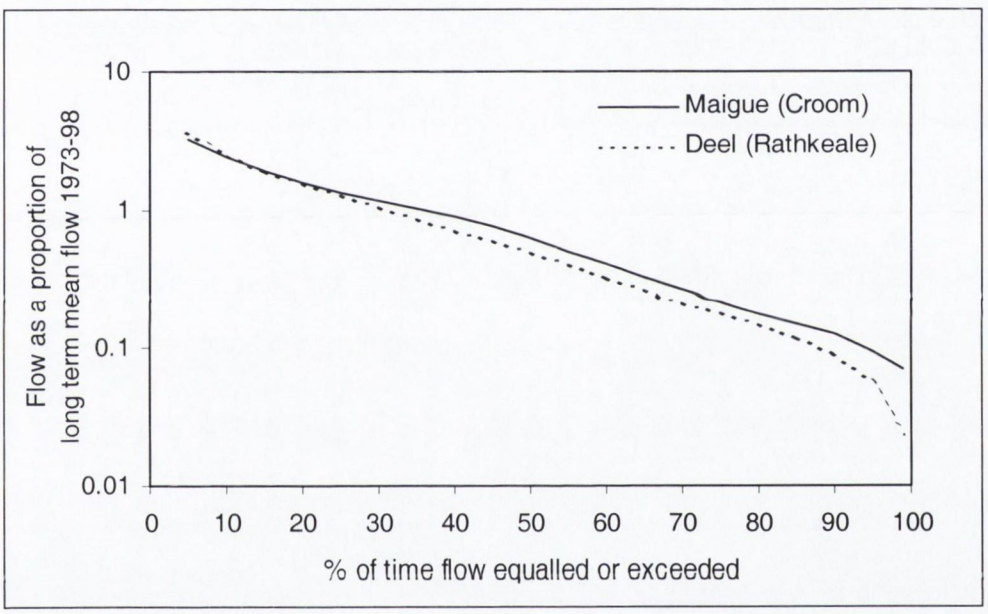
Hydrographs showing baseflow-separation curves for the Deel and Maigue catchments and baseflow calculations are presented in Appendix C. Table 8.9 presents summary data for the estimations of baseflow as a percentage of total flow in the Maigue and Deel rivers. The Maigue River has almost twice as much baseflow as the Deel River.

**Table 8.9 Baseflow estimate for the Maigue and Deel Rivers.**

| | *Total Q over 4 years 1991-1994 ($m^3$)* | *Estimated baseflow 1991-1994 ($m^3$)* | *Baseflow as a percentage of total Q* |
|---|---|---|---|
| Maigue (Croom) | $1.66 \times 10^9$ | $6.79 \times 10^8$ | 41% |
| Deel (Rathkeale) | $1.04 \times 10^9$ | $2.42 \times 10^8$ | 23% |

Flow duration curves were constructed using mean flow data from the OPW for the period 1973-1998. The mean flows for each river are expressed as a proportion of long term mean flow over the period '73 - '98 to allow comparisons between rivers (see Figure 8.14). Both rivers have similar slopes indicating comparable streamflow variability. However, they differ in the lower end of each curve. The Deel curve steeply drops off, whereas the a more gentle decline is present in the Maigue curve. This corroborates the difference in baseflow as a proportion of total flow listed in Table 8.9 and indicates that the Maigue catchment has a more constant baseflow input due to greater groundwater storage capacity.

**Figure 8.14 Flow duration curves for the Maigue and Deel catchments.**




## 8.5.4 Phosphorus results

*Deel Catchment*

Unfiltered MRP data (see Section 1.4 for a description of this form of P) were obtained from Doris *et al.* (1999) for seven stations along the River Deel in the 1995-1997 monitoring programme. These data were collected in 1996. Table 8.10 presents minimum, median and maximum unfiltered MRP data for several stations along the River Deel in this year. The stations are arranged in descending order downstream (see Figure 3.8). As mentioned in the introduction, none of the stations have median levels below 30 $\mu g\ l^{-1}$. Indeed, not even the minimum levels reported at these stations are below this threshold.

**Table 8.10 Summary phosphorus data (Doris *et al.*, 1999) along the River Deel in 1996.**

| *Station No.* | *Location* | *Unfiltered MRP ($\mu g\ l^{-1}$)* | | |
|---|---|---|---|---|
| | | Minimum | Median | Maximum |
| D0300 | Broken Bridge | 30 | 121 | 506 |
| D0500 | 800m u/s of Castlemahon | 121 | 163 | 512 |
| D0700 | Bridge near Killaready | 33 | 119 | 325 |
| D0800 | Grange Bridge | 112 | 154 | 283 |
| D1100 | Rathkeale Bridge | 55 | 141 | 230 |
| D1300 | Kilcool Bridge | 73 | 100 | 234 |
| D1400 | Askeaton Bridge | 45 | 200 | 248 |

Table 8.11 presents mean total P data for the groundwater sites in the Deel catchment. The sites are presented in descending order by median TP value. The overall median value was very low (13 $\mu g\ l^{-1}$) in comparison to the above Deel River MRP values. A possible region of concern is in the mid-west of the catchment around LD01, LB14 and LB12 (see Figure 3.8). At these sites median TP levels (mean for LB12) are higher than median in-river MRP levels.

**Table 8.11 Summary total P statistics for groundwater sites in the Deel catchment.**

| *Site Name* | *Site Type* | *Median* | *Mean* | *Maximum* | *Minimum* | *Count* |
|---|---|---|---|---|---|---|
| | | | ($\mu g\ l^{-1}$) | | | (n) |
| LD01 | Dug Well | 180 | 161 | 220 | 84 | 3 |
| LB14 | Borehole | 120 | 120 | 213 | 27 | 2 |
| LB07 | Borehole | 33 | 38 | 64 | 23 | 4 |
| LB30 | Borehole | 29 | 29 | 41 | 17 | 2 |
| LB13 | Borehole | 20 | na | na | na | 1 |
| LB12 | Borehole | 17 | 289 | 839 | 13 | 3 |
| LB03 | Borehole | 14 | na | na | na | 1 |
| LB02 | Borehole | 13 | na | na | na | 1 |
| LS07 | Spring | 13 | 11 | 13 | 7 | 3 |
| LB18 | Borehole | 9 | 9 | 13 | 5 | 2 |
| LS01 | Spring | 6 | na | na | na | 1 |
| LS04 | Spring | 5 | 4 | 5 | 4 | 3 |
| LS08 | Spring | 5 | 5 | 9 | 3 | 4 |
| LB11 | Borehole | 3 | 3 | 3 | 3 | 2 |
| Total | | 61 | 13 | 839 | 3 | 32 |

*Maigue Catchment*

Unfiltered MRP data were obtained from Doris *et al.* (1999) for seven stations along the River Maigue included in the 1995-1997 EPA monitoring programme. These data were also collected in 1996. Table 8.12 presents minimum, median and maximum unfiltered

MRP data for several stations along the River Maigue in this year. The stations are arranged in descending order downstream and their location is presented in Figure 3.8. As mentioned in the introduction, none of the stations have median levels below 30 $\mu g\ l^{-1}$. However, unlike the Deel, several of the stations have minimum MRP levels below this threshold.

**Table 8.12 Summary phosphorus data (Doris *et al.*, 1999) in the River Maigue 1996.**

| *Station No.* | *Location* | *Unfiltered MRP ($\mu g\ l^{-1}$)* | | |
|---|---|---|---|---|
| | | Minimum | Median | Maximum |
| M0200 | Creggane Bridge | 30 | 165 | 470 |
| M0300 | Bruree Bridge | 20 | 130 | 470 |
| M0400 | Howardstown Bridge | 20 | 200 | 510 |
| M0500 | Br. Near Rosstemple | 10 | 165 | 460 |
| M0600 | Cherrygrove Bridge | 30 | 150 | 450 |
| M0700 | Bridge in Croom | 20 | 130 | 450 |
| M0900 | Castleroberts Bridge | 10 | 120 | 400 |

Table 8.13 presents summary total P statistics for groundwater sites in the Maigue catchment. The sites are listed in descending order of median TP. The combined Maigue catchment groundwater sites had higher median TP levels (25 $\mu g\ l^{-1}$) than the Deel. This level, whilst far lower than the median MRP concentrations in the Maigue River, exceeded average minimum levels in the Maigue River (20 $\mu g\ l^{-1}$). Furthermore, eight of the eighteen groundwater sites had median TP levels greater than the 30 $\mu g\ l^{-1}$ threshold for eutrophication in Irish rivers. These sites are evenly distributed south of Croom. LB25 and LB04 had highest TP levels which often exceeded the median MRP values of the River Maigue. TP levels in LB26 were also consistently high.

**Table 8.13 Summary total P ($\mu g\ l^{-1}$) statistics for groundwater sites in the Maigue catchment.**

| *Site Name* | *Site Type* | *Median* | *Mean* | *Maximum* | *Minimum* | *No. of Samples* |
|---|---|---|---|---|---|---|
| LB25 | Borehole | 539 | 651 | 1196 | 219 | 3 |
| LB04 | Borehole | 136 | 176 | 403 | 27 | 4 |
| LB26 | Borehole | 82 | 83 | 86 | 81 | 3 |
| LB24 | Borehole | 79 | 79 | 82 | 77 | 4 |
| LB20 | Borehole | 69 | 69 | 72 | 67 | 4 |
| LB09 | Borehole | 43 | 37 | 47 | 21 | 3 |
| LB21 | Borehole | 40 | 49 | 79 | 38 | 4 |
| LB22 | Borehole | 38 | 40 | 50 | 34 | 4 |
| LB23 | Borehole | 22 | 22 | 23 | 21 | 2 |
| LB16 | Borehole | 21 | 80 | 208 | 11 | 3 |
| LB08 | Borehole | 11 | 10 | 13 | 5 | 4 |
| LB27 | Borehole | 11 | 10 | 12 | 7 | 3 |
| LD02 | Dug Well | 10 | 9 | 12 | 5 | 3 |
| LB19 | Borehole | 9 | 10 | 11 | 9 | 3 |
| LB15 | Borehole | 5 | 6 | 11 | 2 | 2 |
| LB01 | Borehole | 3 | 4 | 8 | 1 | 3 |
| LB06 | Borehole | 2 | 2 | 3 | 2 | 2 |
| LB10 | Borehole | 2 | 2 | 3 | 2 | 2 |
| Total | | 25 | 76 | 1196 | 1 | 56 |

### 8.5.5 Discussion

The Deel and Maigue have had consistently high MRP values and unsatisfactory Biological Quality Rating values (Stapleton *et al.*, 2000; Lucey *et al.*, 1999; Doris *et al.*, 1999). Clinton's (1987) study of water quality in the River Deel concludes that the bulk of P in the river arises from diffuse sources rather than municipal waster discharges. Overall median groundwater TP levels in the Deel catchment were far lower than even the minimum in-river Deel MRP levels. There are some groundwater locations with localised elevated TP which may act as point source to the Deel waterways. However, the overall low P levels in groundwater would tend to indicate that even during low flow conditions groundwater does probably not negatively impact on the River Deel. Indeed, it may be a positive factor by diluting river water with low P groundwater. As discussed in the Chapter Seven, the widespread occurrence of gley soils and low permeability subsoils in the Deel catchment will encourage more overland flow and less interaction with groundwater. This agrees with the baseflow separation and flow duration curves for the Deel River, which indicated low groundwater storage capacity in this catchment compared to the Maigue River. This could reflect the disparity between river and groundwater P levels.

In contrast, the Maigue groundwater sites had higher overall median TP levels than the minimum MRP in-river Maigue levels. A large proportion of the groundwater sites also had TP levels approaching median MRP levels in the Maigue River. Therefore, during low flow conditions groundwater discharges may be an important contributor to the Maigue River. More free draining soils dominate the Maigue catchment, which would result in greater interaction between surface water and groundwater. This concurs with the baseflow separation estimates and the flow duration curve for the Maigue River, which indicated a larger groundwater storage capacity and input than the Deel River. A limnological study of one of Co. Limerick's few lakes, Lough Gur, reported in-lake TP concentrations ranging between 45 and 97 $\mu g\ l^{-1}$ and MRP levels ranging between 1 and 35$\mu g\ l^{-1}$ (King and O'Grady, 1994). The nearby LB26 borehole reported median TP levels between 82 $\mu g\ l^{-1}$ and during the July 1999 sampling run 100% of TP (81 $\mu g\ l^{-1}$) was measured as DRP. These points tend to indicate that groundwater P is a far more important component of nutrient transfer within the Maigue catchment than for the Deel catchment.

### *8.6 Overall conclusions*

The three catchment areas presented a range of groundwater-surface water interaction scenarios. The Fergus catchment exhibited strong interaction between groundwater and surface waters due to the high degree of karstification. The Elmvale spring group are providing the most sustained groundwater P input to the upper Fergus catchment and the vast majority of this is as dissolved reactive P. These springs become the headwaters of the Fergus during low flow conditions and as such their P load will be a significant contribution to L. Inchquin. In these type of situations groundwater P cannot be ignored.

Point source P loads via groundwater will always be a potential occurrence in karstic aquifers such as the Fergus catchment. However, this was most clearly demonstrated in the Robe catchment. During these events such spring inputs to rivers can constitute up to half the P load in a river, as was the case for the Robe during the contamination of RS06 spring. Under low flow conditions this potential threat is highest. Otherwise, the overall P load from the measured springs was modest compared to the P load of the receiving river. The baseflow inputs are less clear in the Robe due to the alternating gaining and loss of water along the streambed seasonally. In summer and early autumn surface water may transport P to groundwater via the streambed, which is later discharged to the Robe and Lough Mask

as baseflow and springs. However, between winter and spring groundwater baseflow discharges greatly augment the flow in the river and may dilute P concentrations in the receiving waters.

The Maigue and Deel catchments provide examples of more coventional hydrogeological situation than the extremes of karstic aquifers described above. In discharge terms, groundwater does not appear to be a large component of flow in the Deel catchment. Generally P concentrations in the Deel groundwaters were far lower than levels reported in the river. The widespread occurrence of gley soils in the Deel catchment will contribute to this hydrological regime. In these situations, surface runoff is likely to be the main mode of P transport. Groundwater P inputs will be minimal. Discharge in the Maigue catchment is significantly augmented by groundwater storage. Therefore, the P load in groundwater will be important either in a contributory manner or as a diluting component. Groundwater P concentrations were higher overall in the Maigue catchment than the Deel catchment. However, the Maigue P concentrations are still lower than those in the river. The only scenario where groundwater P would significantly contribute to the Maigue river P loading would be where median groundwater baseflow concentrations coincide with minimum reported river P levels. The data presented here cannot ascertain this; detailed temporal monitoring of river and groundwater P levels in the Maigue catchments would be required to resolve this issue.

Overall, the evidence presented here indicates that groundwater P in the karstic aquifers of Ireland constitutes a significant and sometimes dominant contribution to P loading in surface waters. Surface water catchments located on non-karstic aquifers are less vulnerable to P loading from groundwater.

# CHAPTER 9. CONCLUSIONS

## *9.1 Review of thesis objectives*

This project aimed to examine phosphorus levels in a range of Irish hydrogeological situations, both to fill this gap in basic scientific knowledge, and to determine the circumstances in which concentrations likely to trigger eutrophication in surface waters are prone to occur. The possibility of naturally elevated levels of groundwater P due to geological sources was investigated, but the main focus was on determining the hydrogeological factors which allow P from anthropogenic sources to enter the saturated zone and pass through the aquifer, discharging at springs and as river baseflow.

Two tiers of assessment were adopted. The first involved the assessment of national groundwater P levels across the Republic of Ireland using data from the Environmental Protection Agency (EPA) national groundwater quality monitoring programme (NGQMP). The objectives of this assessment were to gauge the range and distribution of groundwater P nationally and to interrogate the data spatially using a geographical information system (GIS) with several land cover datasets. In this way, it was hoped that some important indicators of groundwater P levels would emerge and provide a platform for the detailed field research of suitable catchment areas.

This second tier of assessment saw the detailed study of three catchment areas, the Robe catchment in Co. Mayo, the Fergus catchment in Co. Clare and Co. Limerick (Deel and Maigue catchments). Research in these catchment areas asked four primary questions. Firstly, what are the groundwater P levels in each catchment area and do they vary temporally and hydrochemically? Secondly, do the hydrogeological characteristics of the aquifers in these catchment areas influence groundwater P levels? Thirdly, what are the land use cover and activities above these aquifers and does a particular cover or activity yield higher P concentrations in groundwater? Finally, to what extent are the groundwater P levels in these aquifers impacting on surface water?

## 9.2 Overall Conclusions

The groundwater phosphorus data, unfiltered molybdate reactive P (MRP unf.), from the EPA NGQMP 1995-1997 provided a valuable snapshot of the P status of Irish aquifers. Overall, the P levels are low (17 $\mu g\ l^{-1}$ MRP unf.) and distributed with a characteristic positive skew. Approximately one quarter of the P data was at levels that result in adverse conditions in Irish rivers. Higher P levels were reported for boreholes than for springs and dug wells. Ownership of the groundwater source was not a contributory factor. This was an interesting factor because typically the small private and group water schemes are reported as more vulnerable to pollution and quality variation than the public schemes (e.g. EPA, 1997). This is mainly cited for bacteriological pollution where many of the rural schemes will not have any form of disinfectant. However, groundwater phosphorus levels were not significantly different between public, group and private groundwater schemes. There were no clear spatial distribution patterns nationally for the majority of the EPA groundwater sites; however, sites with elevated groundwater P concentrations were generally located in the eastern half of the country. Greater population densities in this portion of the country and more intensive agricultural practices may be contributary factors. There were few useful relationships derived from interrogating this dataset with various land cover maps. Issues of scale and accuracy of the various land cover datasets were highlighted. The primary problem with obtaining useful results from this approach was trying to resolve comparing small point data (e.g. a borehole) with large polygons several kilometres squared in size. The fact that much of the processes controlling P movement from soil to groundwater are at local scale probably resulted in the lack of relationships in this analysis. Nonetheless, one strong relationship did emerge when the surface water quality status of each hydrometric region was examined with the national groundwater P dataset. Aquifers located in poor water quality hydrometric regions had the highest groundwater P concentrations. The corollary was also evident; groundwater sites with lowest P levels were located in hydrometric regions with the highest percentage of unpolluted river length. This highlights the inextricable link between surface water and groundwater and the importance of a combined approach in management terms for all contaminants including phosphorus. Overall, the national groundwater P dataset provided useful information on concentrations and broad distribution patterns but fell short of providing potential causative factors determining P levels in groundwater. The catchment areas studied provided greater scope for more detailed investigations.

The three catchment areas were chosen on the base of available hydrogeological information and the presence of existing surface water quality issues. Highest median total phosphorus (TP) levels were reported in the Fergus and Robe catchment, where the aquifers were influenced to varying degrees by karstification. The Limerick sites had lowest median TP levels. Approximately one third of the sites had TP levels higher than concentrations which result in adverse conditions in Irish lakes. The national dataset and the studied catchments highlighted the problems associated with comparing different P fractions. The threshold for eutrophication in Irish rivers, 30 $\mu g\ l^{-1}$ MRP (unf.), cannot be directly compared to the TP concentrations in the studied catchments. Nonetheless, it is expected that at least one third of the sites in the studied catchments also exceed this threshold. Similar to the national dataset extreme P levels were rare and generally occurred at boreholes. Springs and dug wells appear less vulnerable to such extremes in P concentrations. This could reflect the vulnerability of boreholes to contamination due to poorly constructed or protected wellheads. Of the measured P fractions total dissolved P (TDP) and dissolved reactive P (DRP) comprised the majority of TP (greater than 80%) in groundwater. Particulate P levels were low, but greatest in the Fergus and Robe catchments, and especially at springs. Karstification in these catchments would facilitate rapid, turbulent flow along conduits which would best provide the required energy to transport particulates.

The main hydrochemical facies in each catchment was calcium bicarbonate reflecting the dominance of limestone rocks in these aquifers. Analysis of the field parameters pH, electrical conductivity (EC) and dissolved oxygen (DO) provided no clear trends. There were tentative positive relationships between TP and EC and negative relationships with pH and DO. Positive relationships with DO could reflect greater influence of surface water recharge in the aquifer. This could be particularly true in the Fergus catchment where point recharge via swallow holes is common. More clear were the relationships between variation of EC and TP levels in the Fergus and Robe catchments. Total P at springs in both catchments were significantly positively correlated with the coefficient of variation of EC. Boreholes in the Robe, but not the Fergus, also indicated this trend. Therefore, high EC variability appears to be a good indicator of groundwater P levels especially for karstic springs. Saturation indices of calcite and hydroxyapatite were examined in the Fergus and Robe catchments to ascertain whether these minerals influenced groundwater P levels.

Degree of saturation with both minerals were positively correlated probably reflecting the calcium component in each, and both increased along a flow path to Lough Inchquin. It is likely that this reflects the increasing dominance of calcium rich waters. Waters at Lough Inchquin were closest to saturation with respect to hydroxyapatite, therefore precipitation of the mineral is probably among the factors limiting P levels in this lake. Hydroxyapatite saturation was positively correlated with pH and DRP.

Several key hydrogeological factors emerged as potentially important controls on groundwater P levels. Sites with greater abstraction rates had lower TP levels. This trend was also reflected in the EPA NGQMP data. This probably represents a dilution effect. Extreme TP levels were found where the standing water level was less than 10m below ground level. Where the water table was less than 10m below ground level, there was no clear relationship with water table depth. It is likely that other non-hydrogeological factors become important in shallower water tables. In the Limerick area, sites located in till with gravel, a high permeability subsoil, had highest TP levels. In contrast, sites in Namurian till, a low permeability subsoil, of the Fergus catchment had lowest TP levels. In the Fergus catchment, sites located in the regionally important aquifer which is conduit flow dominated had higher TP levels than sites located in the locally important aquifers. Sites in Namurian bedrock had lower TP levels than other bedrocks the Fergus and Limerick catchments. Despite the presence of phosphatic shales in the Fergus catchment, geological P did not appear to be a potential source of groundwater P based on the sites sampled. Total P levels generally increased with groundwater vulnerability as defined by the Geological Survey of Ireland, but lack of relationships between TP and depth to bedrock probably decreased the strength of this trend. Overall, Quaternary deposits and karstification appears to be the key hydrogeological factors influencing groundwater P levels.

Groundwater quality is often considered more stable than that of surface waters mainly due to longer residence times and less response to recharge events. Obvious exceptions to this rule are karst aquifers. However, during the course of this study groundwater P exhibited general stability across the catchments. The more intensive sampling programme in the Fergus and Robe catchments indicated greater variability and hydrological response. Particulate P (PP) and dissolved organic P (DOP) exhibited greatest hydrological response, with DRP displaying a more dulled reaction. All fortnightly sampled springs in the Fergus

and Robe catchments increased in P concentrations after the first major autumnal rains in September 1999. Subsequent rainfall peaks appeared to have a lesser impact on P levels. This response to the first autumnal rains probably reflects a hydrological switch where the catchments change from a soil moisture deficit to a soil moisture surplus situation. This is therefore the first time after the summer where large effective rainfall occurs across the catchments generally. Thus, there appears to be an initial dislodging of loosely bound PP and DOP during these first rains, which are transported to groundwater, followed by a diminishing returns effect thereafter. The daily autosampling results at the Robe spring (RS06) highlighted the need to adopt storm event driven sampling rather than discrete sampling in karstic springs. Such short term pollution events will be of particular concern during the summer months, during low stage conditions when in-river P concentrations are typically low due to plant uptake and when overland flow will be low due to soil moisture deficit build up. Even small volumes of P rich contamination being transmitted via springs could have a dramatic effect on surface water productivity and ecology. Identification and management of sinks and springs in karstic areas presents an urgent and demanding challenge.

Soil hydrology was identified as an important factor on groundwater P concentrations. The primary free-draining soils in each catchment are the Grey Brown Podzolics and Brown Earths in all three areas, with the Rendzinas specifically in the Fergus catchment. In these soils saturated/piston flow may be the dominant pathway of P to groundwater. The primary poorly drained soils in each catchment are the Gleys. In these soils, preferential flow may provide a pathway to groundwater. In either case, groundwater under Gley soils had lower P levels than Grey Brown Podzolics and Brown Earths. These trends tie in with permeabilities of the Quaternary deposits underlying these soils, emphasising the importance of the unsaturated zone on limiting P movement to groundwater.

The CORINE land cover class (O'Sullivan, 1994) did not reveal any clear relationships with groundwater P. Groundwater under high productivity grassland often had among the highest P levels, but these differences were not significant. This lack of trends is similar to that reported for the EPA NGQMP data. The problem of resolving point data with large polygons is the likely cause. Given that critical source areas have been seen to produce the majority of P loss from soil to water, generic land cover classes may not be refined enough to show clear relationships with groundwater P. The units used for assessing agricultural

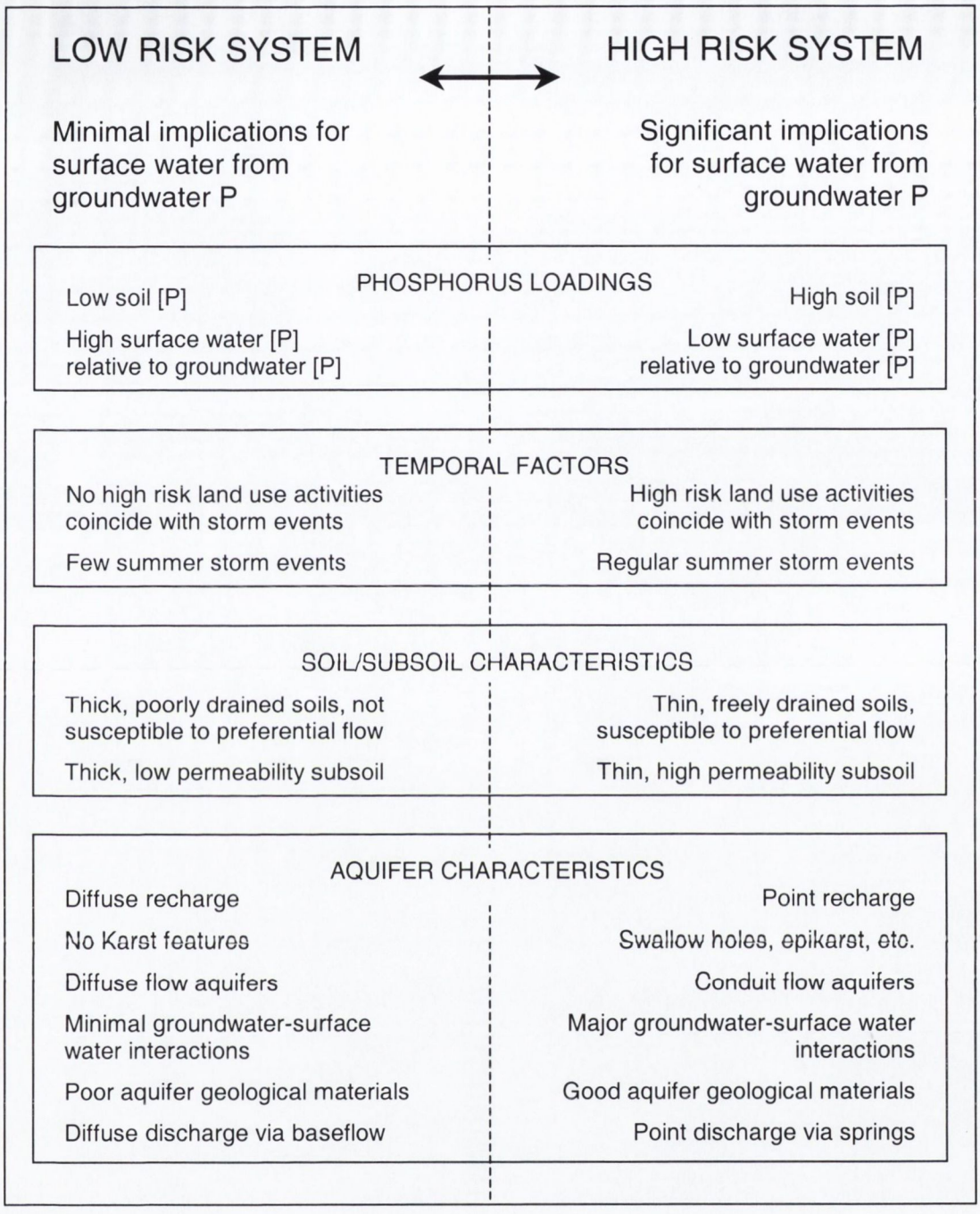
census data (district electoral divisions; DED)) also suffered from problems of scale and incompatibility with point data. However, TP was correlated with percentage pasture cover in the Limerick and Robe catchments. For both these land coverage datasets a problem became evident when applied to karstic systems, particularly the Fergus catchment. The point-in-polygon assessment employed, failed to recognise that the majority of water at a particular spring may be derived from a land cover class or DED remote from the where the spring emerges. Therefore these types of coverage need to be used with caution in karstic environments. A more accurate approach would be to delineate the catchment boundary of individual springs and carry out farm-to-farm surveys within these spring catchments.

Groundwater P loading appears less important than other P transfer mechanisms in the catchments studied in Co. Limerick. The P levels in the Deel and Maigue catchments were extremely high compared to other Irish river catchments. The overall low P concentrations in the groundwaters of these catchments may therefore provide a dilution effect on river P levels. Groundwater P contributions may be more important in low P systems, where groundwater provides a large component of river discharge.

The contribution of groundwater P to surface waters was greatest in the karstic systems. Both the Fergus and Robe catchments experienced significant groundwater P contributions to their surface waters. In the upper Fergus catchment, during low flow conditions, groundwater P provided the majority of the P load to surface water. Point source P loads in the karstic aquifers, as experienced in the Robe catchment, can provide rapid linkages to river and lakes from on land P sources which may be remote from surface water.

Figure 9.1 presents a conceptual diagram based on the findings of this research and in the conext of international research on phosphorus transfer from land to surface waters. This figure aims to identify systems where there the risk posed by groundwater phosphorus to surface water is significant.

**Figure 9.1 Conceptual diagram to identify the risk posed by groundwater phosphorus to surface water.**




The characteristics identified in low risk and high risk systems are not mutually exclusive. A mixture will exist in any given environment. However, as elements of either risk category begin to dominate, so will the degree of impact that groundwater P has on surface water.

### 9.3 Recommendations and scope for further research

Phosphorus analysis in any form is rarely included in groundwater quality analyses, nor is phosphorus normally considered a contaminant during hydrogeological investigations. This research has highlighted situations where P can be transmitted from soil through groundwater to surface waters at environmentally significant levels. Aquifers with any degree of karstification are particularly vulnerable. Therefore, it is recommended that regulatory bodies carry out groundwater P analysis in such situations. Contaminated land investigations involving septic systems, sewage sludge and intensively farmed land should also incorporate groundwater P analysis. Any form of P analysis is desirable, however, the preference should be for total P where possible to ensure that contributions from all P forms are taken into account. Better delineation of karstic spring catchment boundaries is urgently required at vulnerable locations, so that the areas that may be impacted by a point source P event can be identified.

The EPA NGQMP will soon be publishing data for the 1998-2001 monitoring period. This will include more sampling points, improving the national coverage for spatial analysis. When combined with the previous monitoring period, a six year set of data should allow for some national temporal analysis.

The studied catchments areas offer scope for further research in several ways. Flow triggered sampling at the springs in the Fergus and Robe catchments will better characterise the P load fluctuations temporally. Hydrograph separation in the Robe catchment may resolve baseflow contributions during different periods of the year.

More detailed land cover and land use information is required to better link groundwater levels to specific agricultural practices and land cover types. This is probably best achieved through farm to farm surveys. Active involvement of the landowners would be required early on in any such study. Boreholes and springs identified with high groundwater P levels in this study would provide the basis for more detailed site investigations.

Catchments with significant groundwater storage and with less extreme river P levels (unlike the Deel and Maigue catchments) should be chosen for further analysis of baseflow contributions to surface water. Daily flow data combined with regular surface water and groundwater P data would form the basis of such a study. As more groundwater protection schemes are completed greater integration between hydrogeological and hydrological factors can be applied to such studies. The integration of surface water and groundwater management in River Basin Districts under the Water Framework Directive will provide the legislative basis for such further studies.

# REFERENCES


Abrams, M. M. and Jarrell, W. M. (1995) Soil phosphorus as a potential nonpoint source for elevated stream phosphorus levels. *Journal of Environmental Quality*, **24**: 132-138.

Ahmad, A. R., Zulkefli, M., Ahmed, M., Aminuddin, B. Y., Sharma, M. L. and Mohd Zain, M. (1994) Environmental impacts of agricultural inorganic pollution on groundwater resources of the Kelantan Plain, Malyasia. *Proceedings of an international conferfence: Agricultural impacts on groundwater quality*, Kelantan, Malayasia, 8-21.

Allott, N. (1990) *Limnology of six Irish western lakes.* Unpublished PhD thesis, Trinity College Dublin.

Allott, N., Free, G., Irvine, K., Mills, P., Mullins, T. E., Bowman, J. J., Champ, W. S. T., Clabby, K. J. and McGarrigle, M. L. (1998). In: Giller, P. (ed.) *Land use and aquatic systems in the Republic of Ireland.* Studies in Irish Limnology, The Marine Institute, Dublin, 1-18.

Andrews, J. E., Brimblecombe, P., Jickells, T. D. and Liss, P. S. (1996) *An Introduction to Environmental Chemistry*, Blackwell Science, Norwich.

APHA (1989) *Standard methods of analysis of water and waste water*, Washington DC.

Bastiman, B. (1976) Factors affectings silage effluent production. *Experimental Husbandry*, **31**: 40-46.

Boyer, D. G. and Pasquarell, G. C. (1999) Agricultural land use impacts on bacterial water quality in a karst groundwater aquifer. *Journal of the American Water Resources Association*, **35(2)**: 291-300.

Breeuwsma, A. and Reijerink, J. G. A. (1992) Phosphate-saturated soils: a"new" environmental issue. *Proceedings of the European state-of-the-art conference on delayed effects of chemicals in soils and sediments*, Veldhoven, The Netherlands, 79-85.

Breeuwsma, A., Reijerink, J. G. A. and Schoumans, O. F. (1995). Impact of manure on accumulation and leaching of phosphate in areas of intensive livestock farming. In: K. Steel, (ed.) *Animal waste and land-water interface*, Lewis Publishers, 239-249.

Brookes, P. C., Heckrath, G., Smet, D., J., Hofman, G. and Vanderdeelen, J. (1997). Losses of phosphorus in drainage water. In: H. Tunney, O. T. Carton, P. C. Brookes, and A. E. Johnston, (eds.) *Phosphorus Loss from Soil to Water.* CAB International, Walingford, 253-271.

Burrough, P. A. (1994) *Principles of GIS for land resources assessment.* Clarendon Press, Oxford.

Burrough, P. A. and McDonnell, R. A. (1998) *Principles of GIS*, Oxford University Press, Oxford.

Carlyle, G. C. and Hill, A. R. (2001) Groundwater phosphate dynamics in a river riparian zone: effects of hydrologic flowpaths, lithology, and redox chemistry. *Journal of Hydrology*, **247**: 151-168.

Caulcutt, R. and Boddy, R. (1983) *Statistics for analyical chemists*, Chapman and Hall, London.

CEC (Council of the European Communities) (1976) Council Directive of 4 May 1976 on pollution caused by certain substances discharged into the aquatic environment of the Community.

CEC (Council of the European Communities) (1980) Council Directive of 15 July 1980 relating to the quality of water intended for human consumption. *Official Journal of the European Communities*, L 229/11.

CEC (Council of the European Communities) (1991) Council Directive of 21 May 1991 concerning urban waste water treatment (91/271/EEC). *Official Journal of the European Communities,* L 135/40.

CEC (Council of the European Communities) (1998) Council Directive of 3 November 1998 on the quality of water intended for human consumption (98/83/EC). *Official Journal of the European Communities*, No. L 330/32.

Champ, W. S. T. (1998). Phosphorus/chlorophyll relationships in selected Irish lakes: ecological consequences and suggested criteria for ecosystem management. In: Wilson, J.G. (ed.) *Eutrophication in Irish Waters*, Royal Irish Academy, Dublin, 91-105.

Chapman, D. (1996) *Water quality assessments: a guide to the use of biota, sediments and water in environmental monitoring*, E & FN Spon, London.

Chen, J. S., Mansell, R.S., Nkedi-Kizza, P. and Burgoa, B.A. (1996) Phosphorus transport during transient, unsaturated water flow in an acid sandy soil. *Soil Science of America Journal*, **60**: 42-48.

Clinton, S. E. (1987) *Water quality in the River Deel County Limerick - its future management*, Masters Thesis, University of Dublin, Trinity College, Dublin.

Close, M. E. and Davies-Colley, R. J. (1990) Baseflow water chemistry in New Zealand rivers 2. Influence of environmental factors. *New Zealand Journal of Marine and Freshwater Research*, **24**: 343-356.

Cook, P. J. and Shergold, J. H. (1983) Phosphates study progresses. *Geotimes*, 14-15.

Coulter, B. S., McDonald, E., Murphy, W. E. and Lee, J. (1999) Visual environmental data on soils and landuse. *ARMIS 4496*, TEAGASC Johnstown Castle Research Centre, Wexford.

Coxon, C. (1986) *A study of the hydrology and geomorphology of turloughs*. Unpublished PhD thesis, Trinity College Dublin, 428pp.

Coxon, C. (1995). Groundwater vulnerability and protection issues in the lower Fergus catchment, Co. Clare. Hydrogeological Aspects of Groundwater protection in Karstic Areas (COST Action 65 Final Report), European Commission D-G XII, Luxembourg, pp162-169.

Coxon, C. and Drew, D. (1986). Groundwater flow in the lowland limestone aquifer of eastern Co. Galway and eastern Co. Mayo, western Ireland. In: Paterson, K. and Sweeting, M.M. (eds.) *New Directions in Karst*, Geo Books, Norwich, 259-279.

Coxon, C. and Drew, D. (1998). Interaction of surface water and groundwater in Irish karst areas: implications for water-resource management. In: J. V. Brahana, (ed.) *Gambling with groundwater - physical, chemical and biological aspects of aquifer-stream relations*, American Institute of Hydrology, St. Paul, Minnesota, pp161-168.

Coxon, C. and Drew, D. (2000). Interdependence of groundwater and surface water in lowland karst areas of western Ireland: management issues arising from water and contaminant transfers. In: N. S. Robins and B. D. R. Misstear, (eds.) *Groundwater in Celtic Regions: Studies in Hard Rock and Quaternary hydrogeology*, The Geological Society of London.

Coxon, C. and Thorn, R. H. (1989) Temporal variability of water quality and the implications for monitoring programmes in Irish limestone aquifers. *Groundwater Management: Quantity and Quality*, Proceedings of the Benidorm Symposium, 111-120.

CSO (Central Statistics Office) (1991) *Census of agriculture*, Central Statistics Office.

Daly, D. (1985) Groundwater quality and pollution in Ireland with particular reference to the effects of agricultural activities. *Impact of Agriculture on Groundwater in Ireland (proceedings of a joint agricutural and hydrogeologists meeting, 12-15 June 1984)*, Dublin, 65-85.

Daly, D. (2000) Practical approaches to preventing pollution of wells. *The Sherkin Island Marine Station Environmental Conference: Water, is its quality deteriorating? 4-5 May 2000*, Carrigaline, Co. Cork.

Daly, D. and Warren, W. P. (1998). Mapping groundwater vulnerability: the Irish perspective. In: N. S. Robins, (ed.) *Groundwater Pollution, Aquifer Recharge and Vulnerability*, Geological Society, Special Publications, London, 179-190.

Daly, D., Thorn, R. and Henry, H. (1993) Septic Tank Systems and Groundwater in Ireland. *RS 93/1*, Geological Survey of Ireland, Dublin.

Daly, F., Hand, D.J., Jones, M.C., Lunn, A.D. and McConway, K.J. (1995) *Elements of statistics*. The Open University, Addison-Wesley, Harlow, England.

Daly, K., Coulter, B. and Mills, P. (2000). National phosphorus model. In: H. Tunney, (ed.) *Quantification of phosphorus loss from soil to water*, Environmental Protection Agency.

Daly, K., Mills, P., Coulter, B. and McGarrigle (2002) Modeling phosphorus concentrations in Irish rivers using land use, soil type and soil phosphorus data. *Journal of Environmental Quality*, **31(2)**: 590-598.

Deakin, J. (1994) *Groundwater protection in County Limerick*, University of Dublin, Trinity College, Dublin.

Deakin, J. (2000). Groundwater protection zone delineation at a large karst spring in western Ireland. In: N. S. Robins and B. D. R. Misstear, (eds.) *Groundwater in Celtic Regions: Studies in Hard Rock and Quaternary hydrogeology*, The Geological Society of Ireland, 89-98.

Deakin, J. and Daly, D. (2001) Draft Co. Clare Groundwater Protection Scheme. , Geological Survey of Ireland, Dublin.

Deakin, J., Daly, D. and Coxon, C. (1998) *County Limerick Groundwater Protection* Scheme. Geological Survey of Ireland, Dublin.

DELG (Department of the Environment and Local Government) (1999) Dempsey and Wallace announce industry agreement to phase out phosphorus in domestic laundry detergents. Department of the Environment and Local Government, Dublin.

DELG (Department of the Environment and Local Government), Environmental Protection Agency and Geological Survey of Ireland (1999) *Groundwater Protection Schemes.* Department of the Environment and Local Government, Dublin.

DELG. (Department of the Environment and Local Government) (1998) Local Government (Water Pollution) Act 1977 (Water Quality Standards for Phosphorus) Regulations, 1998. Statutory Instrument No. 258 of 1998, Government Supplies Agency, Dublin.

DELG. (Department of the Environment and Local Government) (1999) Dempsey and Wallace announce industry agreement to phase out phosphorus in domestic laundry detergents. Department of the Environment and Local Government, Dublin.

Dils, R. M. (1997) *Phosphorus fractionation in hillslope hydrological pathways contributing to agricultural runoff*, PhD Thesis, University of Sheffield.

Dils, R. M. and Heathwaite, A. L. (1999) The controversial role of tile drainage in phosphorus export from agricultural land. *Water Science and Technology*, **39(12)**: 55-61.

Dils, R. M., and Heathwaite, A. L. (1996) Phosphorus fractionation in hillslope hydrogeological pathways contributing to agricultural runoff. *Advances in Hillslope Hydrology*, Anderson, S., (ed.), John Wiley and Sons, Chichester, pp. 229-252.

Doak, M. (1995) The vulnerability to pollution and hydrochemical variation of eleven springs (catchments) in the karst lowlands of the west of Ireland. Hydrogeological Aspects of Groundwater protection in Karstic Areas (COST Action 65 Final Report), European Commission D-G XII, Luxembourg, pp. 151-156.

DoE (Department of Environment) (1997) Managing Ireland's rivers and lakes. A catchment-based strategy against eutrophication. , Department of the Environment, Dublin.

Doris, Y., McGarrigle, M. L., Clabby, K. J., Lucey, J., Neill, M., Flanagan, M., Quinn, M. B. and Lehane, M. (1999) *Water Quality in Ireland 1995-1997 Statistical Compendium of River Quality Data.* Environmental Protection Agency, Wexford.

Drew, D. (1988) The hydrology of the upper Fergus River catchment, Co. Clare. *Proceedings of the University of Bristol Spelaeological Society*, **18(2)**: 265-277.

Drew, D. (1990) The hydrology of the Burren, County Clare. *Irish Geography*, **23(2)**: 69-89.

Drew, D. (1995). Assessing the risk of groundwater contamination due to recent agricultural practices in the Burren karst, western Ireland. Hydrogeological aspects of groundwater protection in karstic areas (COST Action 65 Final Report), Eurpoean Commission D-G XII, pp 157-162, Luxembourg, 157-162.

Drew, D. (1996a) Lisdoonvarna springs and spa wells, County Clare, Ireland. *Environmental Geology*, **27**: 97-98.

Drew, D. (1996b) Agriculturally induced environmental changes in the Burren Karst, Western Ireland. *Environmental Geology*, **28(3)**: 137-144.

Drew, D. and Daly, D. (1993) *Groundwater and karstification in mid-Galway, south Mayo and north Clare.* Geological Survey of Ireland, Dublin.

Driescher, E. and Gelbrecht, J. (1993) Assessing the diffuse phosphorus input from subsurface to surface waters in the catchment of the Lower River Spree (Germany). *Water Science and Technology*, **28(3-5)**: 337-347.

Ecock, K. (1981) *Cave patterns and hydrology in the Burren Co. Clare.* Unpublished dissertation for B.A. Geography Department, Trinity College Dublin.

EEA (European Environment Agency) (1999) Groundwater quality and quantity in Europe: Data and basic information. *No. 22*, European Environment Agency, Copenhagen.

EEA (European Environment Agency) (2000) Inland waters - Annual topic update 1999. *1/2000*, European Environment Agency, Copenhagen.

Eghball, B., Binford, G.D. and Baltensperger, D.D. (1996) Phosphorus movement and adsorption in a soil receiving long-term manure and fertilizer application. *Journal of Environmental*, **25**: 1339-1343.

Eisenreich, S. J., Bannerman, R. T. and Armstrong, D. E. (1975) A simplified phosphorus analysis technique. *Environmental Letters*, **9(1)**: 43-53.

EPA (Environmental Protection Agency) (1994) *Groundwater monitoring programme and index of representative groundwater monitoring points*. Environmental Protection Agency, Dublin.

EPA (Environmental Protection Agency) (1997) *Environmental Quality Objectives and Environmental Quality Standards, the Aquatic Environment: A Discussion Document.* Environmental Protection Agency, Wexford.

EPA (Environmental Protection Agency) (2001) Parameters of Water Quality: Interpretations and Standards. , Environmental Protection Agency, Wexford.

EU Water Framework Directive (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000, establishing a framework for Community action in the field of water. OJ L 327, 22-12-2000, pp1-72.

Evans, W. R. and Bauld, J. (1993) Towards and Australian groundwater quality assessment program. *Journal of Australian Geology and Geophysics*, **14**: 307-311.

Fetter, C. W. (1999) *Contaminant Hydrogeology*, Prentice Hall, London.

Fetter, C. W. (2001) *Applied hydrogeology*, Prentice Hall, New Jersey.

Filippelli, G. M. and Souch, C. (1999) Effects of climate and landscape development on the terrestrial phosphorus cycle. *Geology*, **27(2)**: 171-174.

Finch, T. (1971) *Soils of County Clare*, An Foras Talúntais, Dublin.

Finch, T. and Ryan, P. (1966) *Soils of County Limerick*, An Foras Talúntais, Dublin.

Flanagan, P. (1992) *Parameters of water quality*, Environmental Research Unit, Dublin.

Ford and Williams (1989) *Karst geomorphology and hydrology*. Chapman and Hall, London.

Foy, R. H. a. D., R. (1998) *Practical and innovative measures for the control of agricultural phosphorus losses to water. Proceedings of the Phosphorus Workshop 1998*, OECD, Antrim.

Freeze, R., and Cherry, J.A. (1979) *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, N.J. 07632.

Fritz, S. J. (1994) A survey of charge-balance errors on published analyses of potable ground and surface waters. *Ground Water*, **32(4)**: 539-546.

Gardiner, M. J. and Radford, T. (1980) *Soil associations of Ireland and their land use potential: explanatory bulletin to soil map of Ireland 1980*, National Soil Survey of Ireland, An Foras Talúntais.

Gburek, W. J., Sharpley, A.N., Heathwaite, L. and Folmar, G.J. (2000) Phosphorus management at the watershed scale: a modification of the phosphorus index. *Journal of Environmental Quality*, **29**: 130-144.

Gibson, C. E., Foy, R. H. and Bailey-Watts, A. E. (1996) An analysis of the total phosphorus cycle in some temperate lakes: the response to enrichment. *Freshwater Biology*, **35**: 525-532.

Goodchild, M. F., Parks, B.O. and Steyaert, L.T. (1993) *Environmental modeling with GIS*, Oxford University Press, New York.

Grant, R., Laubel, A., Kronvang, B., Anderson, H. E., Svendsen, L. M. and Fuglsang, A. (1996) Loss of dissolved and particulate phosphorus from arable catchments by subsurface drainage. *Water Research*, **30(11)**: 2633-2642.

Gray, N. F. (1994) *Drinking water quality: problems and solutions*, John Wiley & Sons, Chichester.

Grobler, D. C. and Silberbauer, M. J. (1985) The combined effect of geology, phosphate sources and runoff on phosphate export from drainage basins. *Water Research*, **19(8)**: 975-981.

Groenenberg, J.E., Reinds, G.J. and Breeuwsma, A. (1996) *Simulation of phosphate leaching in catchments with phosphate- saturated soils in the Netherlands*. Wagenin (The Netherlands), DLO Winand Staring centre. Report 116, 78pp.

GSI. (1962) *Geological Map of Ireland*. Geological Survey of Ireland.

GSI. (1984) *Mineral Deposits Map of Ireland*. Geological Survey of Ireland.

Hamilton, P. A. and Helsel, D. R. (1995) Effects of agriculture on groundwater quality in five regions of the United States. *Groundwater*, **33(2)**: 217-226.

Haygarth, P. M. and Jarvis, S. C. (1999) Transfer of phosphorus from agricultural soils. *Advances in Agronomy*, **66**: 195-249.

Haygarth, P. M. and Sharpley, A. N. (2000) Terminology for phosphorus transfer. *Journal of Environmental Quality*, **29(1)**: 10-15.

Haygarth, P.M., Condron, L.M., Butler, P.J. and Chisholm, J.S. (2001) *Proceedings of the International Phosphorus Transfer Workshop: Connecting phosphorus transfer from agriculture to impacts in surface waters*. Institute of Grassland and Environmental Research, Plymouth University, Devon.

Haygarth, P.M., Warwick, M.S. and House, W.A. (1997) Size distribution of colloidal molybdate reactive phosphorus in river waters and soil solution. *Water Research*, **31(3)**: 439-448.

Heathwaite, A. L., Johnes, P. J. and Peters, N. E. (1996) Trends in Nutrients. *Hydrolgical Processes*, **10(2)**: 263-293.

Heathwaite, A. L., Sharpley, A.N. and Gburek, W. (1998) Integrating phosphorus and nitrogen management at the catchment scale. *Practical and innovative measures for the control of agricultural phosphorus losses to water*, Proceedings of the Phosphorus Workshop 1998, Antrim, p21.

Heathwaite, L. and Sharpley, A. (1999) Evaluating measures to control the impact of agricultural phosphorus on water quality. *Water Science and Technology*, **39(12)**: 149-155.

Horne, J. A. and Goldman, C. R. (1994) *Limnology*, McGraw-Hill Inc., New York.

Isenbeck-Schröter, M., Döring, U., Möller, A., Schröter, J. and Mattheß, G. (1993) Experimental approach and simulation of the rentention processes limiting orthophosphate transport in groundwater. *Journal of Contaminant Hydrology*, **14**: 143-161.

Johnes, P. J. (1996) Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach. *Journal of Hydrology*, **183**: 323-349.

Johnson, L. B., Richards, C., Host, G. E. and Arthur, J. W. (1997) Landscape influences on water chemistry in midwestern stream ecosystems. *Freshwater Biology*, **37**: 193-208.

K.T. Cullen & Co. (1996) *Investigations at Pouladower Spring*. Report to Ennis Urban District Council.

Kilroy, K. C., Lawrence, S.J., Lico, M.S., Bevans, H.E. and Watkins, S.A. (1997) Water quality assessment of the Las Vegas Valley area and the Carson and Truckee river basins, Nevada and California - nutrients, pesticides, and suspended sediment, October 1969-April 1990. *97-4106*, U.S. Geological Survey, Carson City.

King, J. J. and O'Grady, M. F. (1994) Aspects of the limnology of Lough Gur, Co. Limerick. *Irish Fisheries Invesitgations Series A (Freshwater)*, **37**: 1-11.

Kløve, B. (2001) Characteristics of nitrogen and phosphorus loads in peat mining wastewater. *Water Research*, **35(10)**: 2353-2362.

Kotlash, A. R. and Chessman, B. C. (1998) Effects of water sample preservation and storage on nitrogen and phosphorus determinations: implications for the use of automated sampling equipment. *Water Research*, **32(12)**: 3731-3737.

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.

Kurz, E. (2000). Phosphorus exports from agricultural grassland with overland flow and drainage water. In: H. Tunney, (ed.) *Quantification of phosphorus loss from soil to water*, Environmental Protection Agency.

Leahy, P. P., Ryan, B.J. and Johnson, A.I. (1993) An introduction to the U.S. Geological Survey's National Water Quality Assessment Program. *Water Resources Bulletin*, **29**: 529-532.

Lennox, S. D., Foy, R. H., Smith, R. V. and Jordan, C. (1997). Estimating the contribution from agriculture to the phosphorus load in surface water. In: H. Tunney, O. T. Carton, P. C. Brookes, and A. E. Johnston, (eds.) *Phosphorus Loss from Soil to Water*, CAB International, Walingford, 55-75.

Lloyd, J. W. and Heathcote, J. A. (1985) *Natural inorganic hydrochemistry in relation to groundwater*, Clarendon Press, Oxford.

Loftis, J. C. (1996) Trends in groundwater quality. *Hydrological Processes*, **10**: 335-355.

Lucey, J., Bowman, J. J., Clabby, K. J., Cunningham, P., Lehane, M., MacCárthaigh, M., McGarrigle, M. L. and Toner, P. F. (1999) *Water Quality in Ireland 1995 - 1997*, Environmental Protection Agency, Wexford.

MacCárthaigh, M. (1994) *Groundwater Monitoring Programme and Index of Representative Groundwater Monitoring Points*. Environmental Protection Agency, Wexford.

MacCárthaigh, M. (1996). Groundwater in Ireland. In: EurAqua, (ed.) *Optimizing freshwater data monitoring networks including links with modelling*, European Network of Freshwater Research Organisations, Koblenz, pp111-126.

McGarrigle, M. L. (1998). Impact of eutrophication on Irish river water quality. Eutrophication in Irish Waters, J. G. Wilson, ed., Royal Irish Academy, Dublin, 82-90.

McGarrigle, M. L., Champ, W. S. T., Norton, R., Moore, M. and Larkin, P. (1993) *The Trophic Status of Lough Conn.* Mayo County Council.

McGuckin, S. O., Jordan, C. and Smith, R. V. (1999) Deriving phosphorus export coefficients for CORINE land cover types. *Water Science and Technology*, **39(12)**: 47-53.

McKenszie, J. M., Siegel, D. I., Patterson, W., and McKenzie, D. J. (2001) A geochemical survey of spring water from the main Ethiopian rift valley, southern Ethiopia: implications fro well-head protection. *Hydrogeology Journal*, **9**, 265-272.

Merot, P. and Durand, P. (1995) Assessing the representativity of catchments according to their size from hydrochemical observations. *Effects of scale on interpretation and management of sediment and water quality (Proceedings of a Boulder Symposium, July 1995)*, 105-112.

Miztal, M., Smal, H. and Górniak, A. (1992) Groundwater inflow of nutrients to a lake from differently utilised catchments. *Water Research*, **26(9)**: 1237-1242.

Morgan, M. A. and O'Toole, P. (1992). Recent changes in farming in Ireland: implications for the environment. In: J. Feehan, (ed.) *Environment and Development in Ireland*, Environment Institute, University College Dublin, Dublin, 368-376.

Muldoon, M. A., Madison, F. W. and Johnson, M. D. (1990) Soils, geologic, and hydrogeologic influences on water quality in northwestern Wisconsin. Wisconsin Geological and Natural History Survey, Madison.

Murphy, J. and Riley, J.P. (1962) A modified single solution method for the determination of phosphate in natural waters. *Analtytica Chimica Acta*, **27**: 31-36.

Nolan, B. T. and Stoner, J. D. (2000) Nutrients in groundwaters of the conterminous United States 1992-1995. *Environmental Science and Technology*, **34(7)**: 1156-1165.

Notholt, A. J. G. and Highley, D. E. (1979) Raw materials research and development dossiers IV phosphate. *XII/1292/78*, Commission of the European Communities.

NSAI (National Standards Authority of Ireland) (1991) Septic tank systems – recommendations for domestic effluent disposal from a single dwelling house, **SR6**: 1991, EOLAS, Dublin, 30pp.

O'Brien, M. W. (1952) Phosphatic horizons in the Upper Carboniferous of Ireland. *19th International Geological Congress*, Algiers, 135-143.

O'Kiely, P. (1985). Silage in Ireland. In: Irish National Committee for the IHP (ed.) *Impact of Agriculture on Groundwater in Ireland*, Dublin.

Omernik, J.M. (1987) Ecoregions of the counterminous United states. *Annals of the Association of American Geologists*, **77**, 118-125.

O'Raghallaigh, C., Feely, M., McArdle, P., MacDermot, C., Geoghegan, M. and Keary, R. (1997) *Mineral localities in the Galway Bay area.* **RS97/1**, Geological Survey of Ireland.

O'Sullivan, G. (1994) *CORINE Land Cover Project (IRELAND)*. Prepared for the CEC. Natural Resources Development Centre, Trinity College Dublin.

Otzuki, A. and Wetzel, R.G. (1972) Co-precipitation of phosphate with carbonates on a marl lake. *Limnology and Oceanography*, **17**: 763-767.

Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N. (1985) *PHREEQE – A computer program for geochemical calculations*. USGS Water Resources Investigation 80-96.

Pionke, H. B., Gburek, W. J., Schnabel, R. R., Sharpley, A. N. and Elwinger, G. F. (1999) Seasonal flow, nutrient concentrations and loading patterns in stream flow draining an agricultural hill-land watershed. *Journal of Hydrology*, **220**: 62-73.

Pionke, H. B., Gburek, W. J., Sharpley, A. N. and Zollweg, J. A. (1997). Hydrological and chemical controls on phosphorus loss from catchments. In: H. Tunney, O. T. Carton, P. C.

Brookes, and A. E. Johnston, (eds.) *Phosphorus Loss from Soil to Water*, CAB International, Walingford, 225-242.

Pote, D. H., Daniel, T. C., Sharpley, A. N., Moore, J., P.A., Edwards, D. R. and Nichols, D. J. (1996) Relating extractable soil phosphorus to phosphorus losses in runoff. *Soil Science Society of America Journal*, **60**: 855-859.

Ptacek, C. J. (1998) Geochemistry of a septic-system plume in a coastal barrier bar, Point Pelee, Ontario, Canada. *Journal of Contaminant Hydrology*, **33**: 293-312.

Rao, N. and Prasad, P. (1996) Phosphate pollution in the groundwater of the lower Vamsadhara river basin, India. *Environmental Geology*, **31(1/2)**: 117-122.

Roberts, G. (1987) Nitrogen inputs and outputs in a small agricultural catchment in the eastern part of the UK. *Soil Use and Management*, **3**: 148-154.

Robertson, W. D. (1995) Development of steady-state phosphate concentrations in septic system plumes. *Journal of Contaminant Hydrology*, **19**: 289-305.

Robertson, W. D., Schiff, S. L. and Ptacek, C. J. (1998) Review of phosphate mobility and persistence in 10 septic system plumes. *Ground Water*, **36(6)**: 1000-1010.

Rodgers, K. and de Barra, R. (2000) *An environmental appraisal and review of the main factors contributing to the decline of the River Robe as a salmonid fishery.* The Western Regional Fisheries Board. Occasional Report Series, **2000/1**.

Ryan, M. (1998) Water movement in a structured soil in the south-east of Ireland: preliminary evidence for preferential flow. *Irish Geography*, **31(2)**: 124-137.

Ryden, J. C., Syers, J. K. and Harris, R. F. (1973) Phosphorus in runoff and streams. *Advances in Agronomy*, **25**: 1-45.

Sharpley, A. N., Chapra, S. C., Wedepohl, R., Sims, J. T., Daniel, T. C. and Reddy, K. R. (1994) Managing agricultural phosphorus for the protection of surface waters: issues and options. *Journal of Environmental Quality*, **23**: 437-451.

Sharpley, A. N., Hedley, M. J., Sibbesen, E., Hillbricht-Ilkowska, A., House, W. A. and Ryszkowski, L. (1995). Phosphorus transfers from terrestrial to aquatic ecosystems. In: H. Tiessen, (ed.) *Phosphorus in the Global Environment*, SCOPE, John Wiley & Sons Ltd., 171-199.

Sharpley, A., Foy, R. and Withers, P. (2000) Practical and innovative measures for the control of agricultural phosphorus losses to water: an overview. *Journal of Environmental Quality*, **29(1)**: 1-9.

Shaw, E.M. (1988) *Hydrology in Practice.* 2nd Edition. Chapman & Hall, London.

Shuster, E. T. and White, W. B. (1971) Seasonal fluctuations in the chemistryof limestone springs: a possible means fro characterizing carbonate aquifers. *Journal of Hydrology*, **14**: 93-128.

Sims, J. T., Simard, R. R. and Joern, B. C. (1998) Phosphorus loss in agricultural drainage: historical perspective and current research. *Journal of Environmental Quality*, **27**: 277-293.

Spruill, T. B., Harned, D.A., Ruhl, P.M., Eimers, J.L., McMahon, G., Smith, K.E., Galeone, D.R. and Woodside, M.D. (1998) Water quality in the Albemarle-Pamlico drainage basin, North Carolina and Virginia, 1992-95. *1157*, U.S. Geological Survey.

Stamm, C., Flühler, H., Gächter, R., Leuenberger, J. and Wunderli, H. (1998) Preferential transport of phosphorus in drained grassland soils. *Journal of Environmental Quality*, **27**: 515-522.

Stapleton, L., Lehane, M. and Toner, P. (2000) *Ireland's Environment: A Millennium Report.* Environmental Protection Agency, Johnstown Castle Estate, Co. Wexford.

Stevens, R.J. (1979) Evaluation of an enzymatic method for orthophosphate determination in freshwaters. *Water Research*, **13**: 763-770.

Takatert, N., Sánchez-Pérez, J. and Trémolières, M. (1999) Spatial and temporal variations of nutrient concentration in the groundwater of a floodplain: effect of hydrology, vegetation and substrate. *Hydrological Processes*, **13**: 1511-1526.

Thorn, R. (1995) *Groundwater vulnerability assessments and groundwater studies and the development of aquifer protection plans for counties Galway, Mayo and Roscommon.* Project funded under the environment sub-programme- measure III- of the STRIDE (Science and technology for regional innovation and development in Europe) programme and the department of the Environment.

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., Carton, O.T., Brookes, P.C. and Johnston, A.E. (1997) *Phosphorus loss from soil to water*, CAB International, Walingford.

Tunney, H., Foy, R. H. and Carton, O. T. (1998). Phosphorus inputs to water from diffuse agricultural sources. In: J. G. Wilson, (ed.) *Eutrophication in Irish Waters*, Royal Irish Academy, Dublin, 25-39.

Velleman, P.F. (1993) *Learning data analysis with Data Desk*. W.H. Freeman and Company, New York.

Vollenweider, R. A. (1968) *Scientific fundamentals of the eutrophication of lakes and flowing waters with particular reference to nitrogen and phosphorus as factors in eutrophication*. OECD, Paris.

Walsh, M. (1975) Soils of the Lough Mask and River Robe catchment area and estimation of increase in agricultural production from the damaged soils following arterial drainage and reclamation. , Office of Public Works.

Walsh, M. and Burke, P. (1980) Soils of East Mayo. *Farm and Food Research*, **11(5)**: 145-147.

Ward, R.C. and Robinson, M. (1989) *Principles of Hydrology*. 3rd Edtion. McGraw-Hill, London.

Webber, J. and Wadsworth, G. A. (1976). Nitrate and phosphate in borehole, well and stream waters. In: Ministry of Agriculture and Forestry (ed.) *Agriculture and water quality*. Technical Bulletin 32, London, 237-251.

Zhang, R., Hamerlinck, J.D., Gloss, S.P. and Munn, L. (1996) Determination of nonpoint-source pollution using GIS and numerical models. *Journal of Environmental Quality*, **25**: 411-418.

Zhu, B. a. A., A.K. (1994) The effect of gypsum amendment on transport of phosphorus in a sandy soil. *Water, Air and Soil Pollution*, **78**: 375-382.

# APPENDIX A

# SITE CHARACTERISTICS

**Table A.1 Fergus catchment site details and codes with related studies.**

| *Code* | *Lakes, Bridges & reported names* | *Site Type* | *Catchment* | *Eastings* | *Northings* |
|---|---|---|---|---|---|
| FB01 | | Borehole | Fergus | 133800 | 183350 |
| FB02 | | Borehole | Fergus | 132250 | 188150 |
| FB03 | | Borehole | Fergus | 131800 | 189900 |
| FB04 | | Borehole | Fergus | 134900 | 182350 |
| FB05 | | Borehole | Fergus | 134143 | 183350 |
| FB06 | | Borehole | Fergus | 133200 | 186600 |
| FB07 | | Borehole | Fergus | 117250 | 192150 |
| FB08 | | Borehole | Fergus | 133750 | 190250 |
| FB09 | | Borehole | Fergus | 134000 | 190750 |
| FB10 | | Borehole | Fergus | 133450 | 185300 |
| FB11 | | Borehole | Fergus | 122500 | 190000 |
| FB12 | | Borehole | Fergus | 131500 | 189100 |
| FB13 | | Borehole | Fergus | 136200 | 189150 |
| FB14 | | Borehole | Fergus | 131000 | 185600 |
| FB16 | | Borehole | Fergus | 133450 | 187650 |
| FB15 | | Borehole | Fergus | 123400 | 188450 |
| FB17 | | Borehole | Fergus | 123350 | 188400 |
| FD01 | | Dug Well | Fergus | 131750 | 182500 |
| FD02 | | Dug Well | Fergus | 135400 | 190200 |
| FD03 | | Dug Well | Fergus | 131400 | 185450 |
| FD04 | | Dug Well | Fergus | 126100 | 189400 |
| FD05 | | Dug Well | Fergus | 128177 | 191340 |
| FD06 | | Dug Well | Fergus | 122600 | 189400 |
| FD07 | | Dug Well | Fergus | 122505 | 189990 |
| FD08 | | Dug Well | Fergus | 123400 | 188500 |
| FK01 | | Karst Window | Fergus | 133750 | 184450 |
| FK02 | S9[1] | Karst Window | Fergus | 133750 | 182950 |
| FL01 | L. Collaun | Lake | Fergus | 132050 | 190600 |
| FL02 | L. Dromore | Lake | Fergus | 135300 | 186200 |
| FL03 | L. Inchquin | Lake | Fergus | 126600 | 189100 |
| FL04 | Lough Ballycullinan | Lake | Fergus | 129450 | 186150 |
| FL05 | L. George | Swallow | Fergus | 134000 | 190800 |
| FL06 | L. Keogh | Swallow | Fergus | 132095 | 188273 |
| FL07 | Carron Turlough | Turlough | Fergus | 128292 | 198054 |
| FR01 | An Clab[1] | Swallow | Fergus | 123480 | 191923 |
| FR02 | Cross Bridge | River | Fergus | 126071 | 191887 |
| FR03 | Poplar Bridge | River | Fergus | 127162 | 191136 |
| FR04 | | River | Fergus | 113100 | 198185 |

(1) Coxon (1995)
(2) Drew (1988)
(3) Drew (1996)

**Table A.1(continued) Fergus catchment site details and codes with related studies.**

| *Code* | *Lakes, Bridges & reported names* | *Site Type* | *Catchment* | *Eastings* | *Northings* |
|---|---|---|---|---|---|
| FS01 | | Spring | Fergus | 132200 | 182900 |
| FS02 | | Spring | Fergus | 131400 | 185500 |
| FS03 | Buntober[2] | Spring | Fergus | 125930 | 192306 |
| FS04 | | Spring | Fergus | 134246 | 185873 |
| FS05 | Elmvale Group [2] (spring 1) | Spring | Fergus | 125744 | 191798 |
| FS06 | Elmvale Group [2] (spring 2) | Spring | Fergus | 125850 | 191750 |
| FS07 | Elmvale [2] before confluence | Spring | Fergus | 125917 | 191700 |
| FS08 | Fergus Rive Cave[2] | Spring | Fergus | 125201 | 192295 |
| FS09 | KIlnaboy Spring[2] | Spring | Fergus | 128013 | 191483 |
| FS10 | | Spring | Fergus | 134758 | 189314 |
| FS11 | | Spring | Fergus | 135221 | 186431 |
| FS12 | L. Shandangan Spring[2] | Spring | Fergus | 130050 | 191050 |
| FS13 | LD1[1] | Spring | Fergus | 133665 | 185914 |
| FS14 | LD2[1] | Spring | Fergus | 133655 | 185585 |
| FS15 | Iron well[3] | Spring | Fergus | 113500 | 198300 |
| FS16 | Magnesium well[3] | Spring | Fergus | 113501 | 198301 |
| FS17 | Poulnaboe[2] | Spring | Fergus | 124369 | 191831 |
| FS18 | S2[1] | Spring | Fergus | 133495 | 181550 |
| FS19 | St Brendans Well[3] | Spring | Fergus | 114600 | 198350 |
| FS20 | Twin wells[3] | Spring | Fergus | 113100 | 198150 |
| FS21 | | Spring | Fergus | 113100 | 198180 |

(1) Coxon (1995)
(2) Drew (1988)
(3) Drew (1996)

**Table A.2 Robe catchment site details and codes with related studies.**

| *Code* | *Bridges & reported names* | *Site Type* | *Catchment* | *Eastings* | *Northings* |
|---|---|---|---|---|---|
| RB01 | | Borehole | Robe | 122250 | 261200 |
| RB02 | H19[1] | Borehole | Robe | 124500 | 262100 |
| RB03 | H23[1] | Borehole | Robe | 122400 | 261150 |
| RB04 | H26[1] | Borehole | Robe | 122200 | 265400 |
| RB05 | H28[1] | Borehole | Robe | 124450 | 267150 |
| RB06 | H29a[1] | Borehole | Robe | 125450 | 267750 |
| RB07 | H29b[1] | Borehole | Robe | 125350 | 267850 |
| RB08 | H30[1] | Borehole | Robe | 125500 | 266600 |
| RB09 | | Borehole | Robe | 129250 | 268150 |
| RB10 | | Borehole | Robe | 122150 | 264800 |
| RB11 | | Borehole | Robe | 124400 | 262150 |
| RD01 | | Dug Well | Robe | 129250 | 261650 |
| RD02 | | Dug Well | Robe | 129900 | 261250 |
| RR01 | Crossboyne Bridge | River | Robe | 133750 | 271000 |
| RR02 | Foxhill Bridge | River | Robe | 123750 | 268200 |
| RS01 | Ballina[1, 3] | Spring | Robe | 125950 | 266000 |
| RS02 | Ballindine[2] | Spring | Robe | 136200 | 269800 |
| RS03 | Bunnadober[1,3] | Spring | Robe | 116750 | 262550 |
| RS04 | Cregduff[1,3] | Spring | Robe | 122250 | 263300 |
| RS05 | Fountainhill[1,3] | Spring | Robe | 124200 | 257450 |
| RS06 | Kilrush[1,3] | Spring | Robe | 127550 | 267550 |

(1) Coxon (1986)
(2) Doak (1995)
(3) Drew and Daly (1993)

**Table A.3 Limerick catchments site details and codes with related studies.**

| *Code* | *Public (WS) and Group water schemes (GWS)* | *Site Type* | *Catchment* | *Eastings* | *Northings* |
|---|---|---|---|---|---|
| LB01 | Athlacca WS | Borehole | Limerick | 155350 | 134050 |
| LB02 | Ballagh #1 GWS | Borehole | Limerick | 127300 | 124650 |
| LB03 | Ballagh #2 GWS | Borehole | Limerick | 126750 | 124750 |
| LB04 | Ballyagran-Castletown WS | Borehole | Limerick | 147010 | 128080 |
| LB05 | Ballyanders WS | Borehole | Limerick | 177850 | 123800 |
| LB06 | Banoge WS | Borehole | Limerick | 151750 | 136700 |
| LB07 | Broadford WS | Borehole | Limerick | 133350 | 121750 |
| LB08 | Bruff WS | Borehole | Limerick | 162880 | 136230 |
| LB09 | Bruree WS | Borehole | Limerick | 154670 | 130510 |
| LB10 | Cappagh 1 GWS | Borehole | Limerick | 139250 | 146400 |
| LB11 | Cappagh 2 GWS | Borehole | Limerick | 136200 | 144100 |
| LB12 | Carrickerry WS | Borehole | Limerick | 122250 | 138880 |
| LB13 | Clouncagh WS | Borehole | Limerick | 137080 | 134480 |
| LB14 | Coolcappa GWS | Borehole | Limerick | 128200 | 141300 |
| LB15 | Croom WS | Borehole | Limerick | 150800 | 141180 |
| LB16 | Fedamore WS | Borehole | Limerick | 159290 | 144530 |
| LB17 | Galbally WS | Borehole | Limerick | 179450 | 128200 |
| LB18 | Glenastar GWS | Borehole | Limerick | 125500 | 139100 |
| LB19 | Glin WS | Borehole | Limerick | 114210 | 146190 |
| LB20 | Herbertstown GWS | Borehole | Limerick | 168190 | 140870 |
| LB21 | Hospital #1 WS | Borehole | Limerick | 170600 | 136300 |
| LB22 | Hospital #2 WS | Borehole | Limerick | 170510 | 136360 |
| LB23 | Kilcornan GWS | Borehole | Limerick | 140150 | 151650 |
| LB24 | Kilfinane WS | Borehole | Limerick | 166000 | 121780 |
| LB25 | Knocklong WS | Borehole | Limerick | 172450 | 131100 |
| LB26 | Lough Gur WS | Borehole | Limerick | 165650 | 140800 |
| LB27 | Martinstown GWS | Borehole | Limerick | 170300 | 126450 |
| LB28 | Murroe Borehole WS | Borehole | Limerick | 172550 | 156150 |
| LB29 | New Pallasgrean WS | Borehole | Limerick | 177230 | 146730 |
| LB30 | Newbridge GWS | Borehole | Limerick | 131600 | 145350 |
| LD01 | Ardagh WS | Dug Well | Limerick | 127300 | 139770 |
| LD02 | Ballingarry WS | Dug Well | Limerick | 141650 | 136320 |
| LS01 | Ballagh Spring GWS | Spring | Limerick | 127150 | 124200 |
| LS02 | Ballinloughane GWS | Spring | Limerick | 121900 | 136850 |
| LS03 | Cappamore/Faileen WS | Spring | Limerick | 181720 | 156770 |
| LS04 | Castlemahon WS | Spring | Limerick | 131950 | 130800 |
| LS05 | Murroe Springs WS | Spring | Limerick | 172330 | 156380 |
| LS06 | Old Pallasgrean WS | Spring | Limerick | 176800 | 144600 |
| LS07 | Rathkeale-Kilcolman WS | Spring | Limerick | 136030 | 136970 |
| LS08 | Tobergall WS | Spring | Limerick | 131630 | 127860 |

**Table A.4 Hydrogeological characteristics of the Fergus catchment sites.**

| *Code* | *Site Type* | *SWL* | *Mean TP(µg l$^{-1}$)* | *Aquifers* | *Bedrock* | *Bedrock notes* | *Subsoils* | *Subsoils notes* | *DTB (m)* | *DTB notes* | *Vulnerability* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| FB01 | Borehole | | 69.4 | Rkc | TU | | Rck | Tls nearby | Shallow Rock | | Extreme |
| FB02 | Borehole | 2.46 | 32.3 | Rkc | BUaw | | Rck | Tls nearby | SR | | Extreme |
| FB03 | Borehole | 5.07 | 1290.5 | Rkc | TU | | Rck | Some Tls to N | SR | | Extreme |
| FB04 | Borehole | 18.60 | 11.3 | Rkc | TU | | Tls | Stoney till | | no data | High |
| FB05 | Borehole | 5.92 | 12.7 | Rkc | TU | | Tls | | 2 | 100m away | High |
| FB06 | Borehole | 7.55 | 97.7 | Rkc | BU | | Tls | Rck to N | | 1,7,12 in Ruan | High |
| FB07 | Borehole | 12.00 | 3.9 | LI | GL | | TNSSs | | 3 | 50m away | High |
| FB08 | Borehole | 13.92 | 27.1 | Rkc | TU | Close to BU | Tls | | | no data | Extreme |
| FB09 | Borehole | 4.61 | 9.1 | Rkc | TU | | Rck | Tls nearby | 2 | 1km away | Extreme |
| FB10 | Borehole | 9.37 | 28.1 | Rkc | TU | | Rck | Tls to N | SR | | Extreme |
| FB11 | Borehole | 41.53 | 54.9 | LI | GL | | TNSSs | | 3 | 50m away | Low |
| FB12 | Borehole | 14.25 | 3.6 | Rkc | TU | | Rck | Tls nearby | SR | | Extreme |
| FB13 | Borehole | 4.86 | 5.9 | Rkc | TU | | Rck | Tls nearby | 2 | 1km away | Extreme |
| FB14 | Borehole | 11.02 | 144.8 | Rkc | BUaw | Close to BUbc | Tls | | SR | | High |
| FB15 | Borehole | 10.93 | 7.7 | LI | GL | | TNSSs | | SR | | Low |
| FB16 | Borehole | 25.37 | 6.1 | Rkc | BU | | Tls | | | 1,7,12 in Ruan | High |
| FB17 | Borehole | 4.48 | 3.0 | LI | GL | | TNSSs | | SR | | Extreme |
| FD01 | Dug Well | | 27.1 | Rkc | BU | | Tls | Stony/sandy till | 9 | 1km away | High |
| FD02 | Dug Well | | 9.9 | Rkc | TU | | Tls | | SR | | Low |
| FD03 | Dug Well | | 32.7 | Rkc | BUmc | | Rck | Alv nearby | SR | | Extreme |
| FD04 | Dug Well | 0.68 | 14.8 | Rkc | GL | Close to CS | TNSSs | | SR | | Extreme |
| FD05 | Dug Well | | 91.3 | Rkc | BUaw | Close to SL | Tls | Rck nearby | | Outcrop | High |
| FD06 | Dug Well | | 5.6 | LI | GL | | TNSSs | | | no data | Low |
| FD07 | Dug Well | | 16.1 | LI | GL | | TNSSs | | 3 | 50m away | Low |
| FD08 | Dug Well | | 8.5 | LI | GL | | TNSSs | | | no data | Low |
| FS01 | Spring | | 22.1 | Rkc | BU | Close to BUbd | Tls | Stony till | 9 | 1km away | Extreme |
| FS02 | Spring | | 26.8 | Rkc | BUmc | Close to BU | Rck | Alv nearby | SR | | Extreme |
| FS03 | Spring | | 20.8 | Rkc | SL | | Tls | Rck nearby | SR | | Extreme |
| FS04 | Spring | | 28.9 | Rkc | TU | Close to BU | Tls | Alv nearby | SR | | Extreme |

**Table A.4 (continued) Hydrogeological characteristics of the Fergus catchment sites.**

| *Code* | *Site Type* | *SWL* | *Mean TP (µg l$^{-1}$)* | *Aquifers* | *Bedrock* | *Bedrock notes* | *Subsoils* | *Subsoils notes* | *DTB(m)* | *DTB notes* | *Vulnerability* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| FS05 | Spring | | 57.0 | Rkc | SL | | Tls | Alv nearby | Shallow Rock | | Extreme |
| FS06 | Spring | | 37.4 | Rkc | SL | | Tls | Alv nearby | SR | | Extreme |
| FS07 | Spring | | 49.4 | Rkc | SL | | Alv | Tls nearby | SR | | Extreme |
| FS08 | Spring | | 22.8 | Rkc | SL | | Tls | Rck nearby | SR | | Extreme |
| FS09 | Spring | | 58.2 | Rkc | BUaw | | Rck | Tls nearby | | Outcrop | High |
| FS10 | Spring | | 30.4 | Rkc | TU | | Tls | Rck nearby | SR | | Extreme |
| FS11 | Spring | | 19.6 | Rkc | TU | | Rck | Tls nearby | | Outcrops surround lake | Extreme |
| FS12 | Spring | | 5.8 | Rkc | BUaw | | Rck | | SR | | Extreme |
| FS13 | Spring | | 33.9 | Rkc | BU | | Tls | Alv nearby | | no data | High |
| FS14 | Spring | | 33.7 | Rkc | TU | | Tls | Alv nearby | | no data | Extreme |
| FS17 | Spring | | 78.6 | Rkc | SL | | Tls | | | >9m 1km due west | Extreme |
| FS18 | Spring | | 28.7 | Rkc | TU | | Tls | | | 1m close to spring | High |
| FR01 | Swallow | | 67.8 | PU | CS | | Tls | | | >9 300m N, 2 1km W | Low |
| FL05 | Swallow | | 7.0 | Rkc | TU | | Rck | Tls nearby | SR | | Extreme |
| FL06 | Swallow | | 32.7 | Rkc | BU | | Alv | Rck nearby | | no data | Extreme |
| FL07 | Turlough | | 13.4 | Rkc | BUaw | | Pt | | Outcrop | Turlough | High |
| FK01 | Karst Window | | 20.9 | Rkc | TU | | Rck | | SR | | Extreme |
| FK02 | Karst Window | | 29.3 | Rkc | TU | | Tls | | SR | SR upgradient | High |
| FL01 | Lake | | 10.5 | Rkc | TU | Half of lake in BU | Tls | Tls to S, Pt to N | | Outcrop nearby | Moderate |
| FL02 | Lake | | 20.2 | Rkc | TU | | Alv | | | Outcrops surround lake | Extreme |
| FL03 | Lake | | 23.8 | Rkc | SL | | Tls | | SR | | Extreme |
| FL04 | Lake | | 24.2 | Rkc | BUaw | West half of lake in SL | Rck | Rck to N | | Outcrops on north side | Extreme |
| FR02 | River | | 38.9 | Rkc | SL | | Alv | Tls nearby | SR | | Extreme |
| FR03 | River | | 46.9 | Rkc | SL | | Alv | | | Outcrop | High |
| FS19 | Spring | | 31.8 | PU | GL | | TNSSs | | | no data | Extreme |
| FS20 | Spring | | 5.9 | PU | GL | | TNSSs | | | no data | Extreme |
| FS21 | Spring | | 94.8 | PU | GL | | TNSSs | | | no data | Extreme |
| FS15 | Spring | | 23.2 | PU | GL | | TNSSs | | | no data | Extreme |
| FS16 | Spring | | 6.3 | PU | GL | | TNSSs | | | no data | Extreme |

**Table A.5 Hydrogeological characteristics of the Robe catchment sites.**

| *Code* | *Site Type* | *Mean TP ($\mu g\ l^{-1}$)* | *Subsoils* | *Vulnerability* |
|---|---|---|---|---|
| RB01 | Bore | 115.0 | Till (und.) | Extreme |
| RB02 | Bore | 300.4 | Till (und.) | High |
| RB03 | Bore | 2.9 | Till (und.) | High |
| RB04 | Bore | 12.9 | Till (und.) | High |
| RB05 | Bore | 20.7 | Till (und.) | High |
| RB06 | Bore | 32.3 | Raised Bog | Moderate |
| RB07 | Bore | 652.0 | Raised Bog | Moderate |
| RB08 | Bore | 4.9 | Blanket Bog | Extreme |
| RB09 | Bore | 20.1 | Raised Bog | Low |
| RB10 | Bore | 18.0 | Till (und.) | High |
| RD01 | Dug well | 32.7 | Till (und.) | High |
| RD02 | Dug well | 3.0 | Raised Bog | Moderate |
| RR01 | River | 48.5 | | High |
| RR02 | River | 43.9 | | Low |
| RS01 | Spring | 47.1 | Till (und.) | Moderate |
| RS02 | Spring | 13.9 | Till (und.) | High |
| RS03 | Spring | 32.4 | Till (und.) | Moderate |
| RS04 | Spring | 31.0 | Till (und.) | High |
| RS05 | Spring | 16.4 | Till (und.) | High |
| RS06 | Spring | 108.4 | Rock outcrop | Extreme |

**Table A.6 Hydrogeological characteristics of the Limerick catchments sites.**

| *Code* | *Site Type* | *Mean TP ($\mu g\ l^{-1}$)* | *Abs Rate ($m^3 d^{-1}$)* | *SWL (bgl)* | *SWL* | *AQUIFER* | *BEDROCK* | *SUBSOILS* | *SUBSOIL notes* | *DTB (m)* | *VULNERABILITY* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LB01 | Borehole | 3.9 | | | 6.78 | LI | BA | Tls | Rck nearby | 3 | Extreme |
| LB02 | Borehole | 13.1 | | | | LI | msl | Rck | close to Tls boundary | 1 | H - E |
| LB03 | Borehole | 14.0 | | | | LI | CF | Rck | Pt nearby | 1 | Extreme |
| LB04 | Borehole | 175.8 | 1080 | 7.35 | 12.67 | Rf | KT | TwG | Gvl nearby | 14 | High |
| LB05 | Borehole | 349.96 | | | 18.15 | LI | BN | TSs | Clayey/gravelly till | 10 | High |
| LB06 | Borehole | 2.1 | | | 19.03 | Pu | BA | Rck | TwG nearby | 2 | Extreme |
| LB07 | Borehole | 38.0 | | | 30.99 | LI | msl | Tls | Rck close to N | 3 | H - E |
| LB08 | Borehole | 9.7 | 378 | 12.90 | 19.03 | LI | BA | Tls | Rck nearby | 3 | High |
| LB09 | Borehole | 36.9 | 500 | 1.24 | 2.20 | LI | ORS | Tls | Rck nearby | 3 | Extreme |
| LB10 | Borehole | 5.3 | | | 23.60 | RKc | WA | Rck | Tls dominant nearby | 3 | Extreme |
| LB11 | Borehole | 2.9 | | | 15.90 | RKc | WA | Rck | Tls dominant nearby | 2 | Extreme |
| LB12 | Borehole | 289.5 | 128 | 2.38 | 6.24 | Lg | CF | Gvl | | 13 | High |
| LB13 | Borehole | 19.5 | 590 | 4.68 | 13.30 | LI | MH | Tls | Some Gvl to S and SE | 15 | Low |
| LB14 | Borehole | 119.9 | | | 9.53 | Pu | CS | Rck | Tls in W, TwG to E | 3 | Extreme |
| LB15 | Borehole | 5.8 | 790 | 8.82 | | Rf | WA | TwG | Tls close to S | 18 | High |
| LB16 | Borehole | 80.0 | 333 | 9.46 | 25.20 | Rf | WA | TwG | Gravel pits nearby | 10 | High |
| LB17 | Borehole | 66.2 | | | 50.00 | Rf | KT | TSs | Rck nearby | 2 | Extreme |
| LB18 | Borehole | 7.3 | | | 36.40 | Pu | CS | Rck | Gvl close to W | 6 | Extreme |
| LB19 | Borehole | 9.6 | 406 | 7.00 | 50.00 | PI | NAMu | Rck | Tls close to S, Gvl close to W | 3 | H - E |
| LB20 | Borehole | 69.3 | 288 | 14.50 | 15.43 | Lm | KRf | Tls | Tls close to W | 1 | Extreme |
| LB21 | Borehole | 49.4 | 251 | 1.74 | 11.65 | LI | BA | Alv | Tls either nearby | 5 | High |
| LB22 | Borehole | 40.4 | 366 | 1.34 | 7.40 | LI | BA | Alv | Tls either nearby | 8 | High |
| LB23 | Borehole | 21.7 | | | | RKc | WA | Tls | | 4 | High |
| LB24 | Borehole | 79.3 | 414 | 16.07 | 31.30 | LI | ORS | TwG | Severah gravel pits close | 10 | H - E |
| LB25 | Borehole | 651.3 | | | | LI | AG | Tls | Clayey till | 17 | Extreme |

**Table A.6 (continued) Hydrogeological characteristics of the Limerick catchments sites.**

| *Code* | *Site Type* | *Mean TP ($\mu g\ l^{-1}$)* | *Abs Rate ($m^3 d^{-1}$)* | *SWL (bgl)* | *SWL* | *AQUIFER* | *BEDROCK* | *SUBSOILS* | *SUBSOIL notes* | *DTB (m)* | *VULNERABILITY* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LB26 | Borehole | 83.1 | | | 18.20 | Lm | KRf | Tls | Rck surrounds site | 4 | Extreme |
| LB27 | Borehole | 9.8 | | | 14.40 | LI | ORS | Tls | Surrouned by TwG | 24 | High |
| LB28 | Borehole | 161.5 | | | 4.20 | LI | CA | Tls | | 14 | High |
| LB29 | Borehole | 85.3 | 273 | 3.00 | 50.00 | Rf | HE | Tls | TSs boundary close | 5 | High |
| LB30 | Borehole | 28.52 | | | 1.21 | RKc | WA | Tls | Rck nearby | 3 | Extreme |
| LD01 | Dug Well | 161.2 | 327 | 1.40 | 2.05 | Lm | msl | TwG | | 3 | H - E |
| LD02 | Dug Well | 8.8 | 550 | 1.80 | 2.10 | Lg | KT | TwG | Tls close to W | 37 | High |
| LS01 | Spring | 5.8 | | | | LI | CF | Rck | Pt nearby | 1 | Extreme |
| LS02 | Spring | 3.7 | | | | PI | NAMu | Rck | Pt to S | 3 | Extreme |
| LS03 | Spring | 5.0 | | | 1.62 | Rf | WA | Alv | TwG nearby | | H - E |
| LS04 | Spring | 10.5 | 336 | | | Lg | HF | TwG | HIS & Tud upgradient | 3 | High |
| LS05 | Spring | 51.2 | 560 | | 2.87 | Lg | CA | TwG | TwG close to N | 14 | High |
| LS06 | Spring | 63.3 | | | 2.54 | Lm | KRf | Tls | Stoney/clayey till | 21 | High |
| LS07 | Spring | 10.8 | 1840 | | | Rf | KT | Tls | Large area of Tls | 20 | Low |
| LS08 | Spring | 5.4 | 1195 | | 1.20 | Rf | WA | Tls | | | Low |

# APPENDIX B

# GROUNDWATER PROTECTION SCHEMES

# AND SOURCE PROTECTION REPORTS

## LIMERICK GROUNDWATER PROTECION SCHEME

The Limerick groundwater protection scheme consists of a main report (Deakin *et al.*, 1998) and fourteen maps. The maps are listed in Table B.1 and are divided into two sets of seven, covering east and west Limerick. The east-west division in these maps is along easting 155,000. These maps were used in conjunction with source protection reports to provide the hydrogeological characteristics used in Chapter Five.

**Table B.1 Maps in the County Clare groundwater protection scheme (Deakin and Daly, 2001).**

| *MAP NUMBER* | *MAP DESCRIPTION* |
|---|---|
| Map 1 (E) | Bedrock Geology (East Limerick) |
| Map 1 (W) | Bedrock Geology (West Limerick) |
| Map 2 (E) | Quaternary Deposits (East Limerick) |
| Map 2 (W) | Quaternary Deposits (West Limerick) |
| Map 3 (E) | Depth to Bedrock (East Limerick) |
| Map 3 (W) | Depth to Bedrock (West Limerick) |
| Map 4 (E) | Hydrogeological Data (East Limerick) |
| Map 4 (W) | Hydrogeological Data (West Limerick) |
| Map 5 (E) | Aquifers (East Limerick) |
| Map 5 (W) | Aquifers (West Limerick) |
| Map 6 (E) | Groundwater Vulnerability (East Limerick) |
| Map 6 (W) | Groundwater Vulnerability (West Limerick) |
| Map 7 (E) | Groundwater Resource Protection (East Limerick) |
| Map 7 (W) | Groundwater Resource Protection(West Limerick) |

## SOURCE PROTECTION REPORTS

Eighteen source protection reports prepared by the Geological Survey of Ireland were available for Co. Limerick and were used in this research to augment information available in the protection scheme maps.

**Table B.2 Source protection reports for the Limerick groundwater drinking supplies.**

| *Source* | *Sampling code used in this Study* |
|---|---|
| Ardagh Public Supply | LD01 |
| Ballingarry Public Supply | LD02 |
| Ballyagran Public Supply | LB05 |
| Bruff Public Supply | LB08 |
| Bruree Public Supply | LB09 |
| Cappamore Faileen/Bilboa Public Supply | LS03 |
| Carrigkerry Public Supply | LB12 |
| Croom Public Supply | LB15 |
| Clouncagh Public Supply | LB13 |
| Fedamore Public Supply | LB16 |
| Glin Public Supply | LB19 |
| Herbertstown Public Supply | LB20 |
| Kilcoleman Public Supply | LS07 |
| Mortlestown Public Supply | LB24 |
| Hospital Public Supply | LB21/LB22 |
| Murroe Public Supply | LS05 |
| New Pallasgrean Public Supply | LB29 |
| Tobergal (SW Region) Public Supply | LS08 |

## CLARE GROUNDWATER PROTECTION SCHEME

The Clare Groundwater Protection Scheme consists of a main report and 21 maps (Deakin and Daly, 2001). These maps were used to identify the hydrogeological characteristics of each of the sampling locations in the Fergus catchment. The maps consist of three sets of seven maps representing the western, eastern and central area of Co. Clare (see Table B.2). The majority of the sites sampled in Co. Clare were located in the Central Clare group of maps.

**Table B.2 Maps in the County Clare groundwater protection scheme (Deakin and Daly, 2001).**

| *MAP NUMBER* | *MAP DESCRIPTION* |
|---|---|
| Map 1 (E) | Bedrock Geology (East Clare) |
| Map 1 (C) | Bedrock Geology (Central Clare |
| Map 1 (W) | Bedrock Geology (West Clare) |
| Map 2 (E) | Quaternary Deposits (East Clare) |
| Map 2 (C) | Quaternary Deposits (Central Clare) |
| Map 2 (W) | Quaternary Deposits (West Clare) |
| Map 3 (E) | Depth to Bedrock (East Clare) |
| Map 3 (C) | Depth to Bedrock (Central Clare) |
| Map 3 (W) | Depth to Bedrock (West Clare) |
| Map 4 (E) | Hydrogeological Data (East Clare) |
| Map 4 (C) | Hydrogeological Data (Central Clare) |
| Map 4 (W) | Hydrogeological Data (West Clare) |
| Map 5 (E) | Aquifers (East Clare) |
| Map 5 (C) | Aquifers (Central Clare) |
| Map 5 (W) | Aquifers (West Clare) |
| Map 6 (E) | Groundwater Vulnerability (East Clare) |
| Map 6 (C) | Groundwater Vulnerability (Central Clare) |
| Map 6 (W) | Groundwater Vulnerability (West Clare) |
| Map 7 (E) | Groundwater Resource Protection (East Clare) |
| Map 7 (C) | Groundwater Resource Protection (Central Clare) |
| Map 7 (W) | Groundwater Resource Protection(West Clare) |

# APPENDIX C

# ANALYTICAL METHODS

## PHOSPHORUS ANALYSIS (after Eisenreich *et al.*, 1975)

### Total phosphorus and total dissolved phosphorus

Organically bound phosphorus is completely oxidized by acid persulphate to dissolved phosphate at 120 °C. The phosphate which is formed is measured colorimetrically. For TP the digestion is performed on unfiltered samples, for TDP the digestion is performed on filtered samples (0.45μm pore).

Materials:
Digestion Reagent: 6.0g of $K_2S_2O_8$ is dissolved in a flask with ca. 80ml distilled water containing 10 ml of 3.6N $H_2SO_4$. The flask is placed in a sonicator to speed up dissolution. When dissolved, the mixture is made up to 100ml with distilled water.

Mixed reagent. This is prepared daily. Care is taken to mix well after each addition. The same graduated cylinder is used for all reagents and is not washed out between additions.

1. 13.5ml 3.6N $H_2SO_4$ is measured into a 100ml volumetric flask.
2. 25ml antimony stock is added and mixed (see below for making up of stock solution).
3. 25ml molybdate stock is addedand mixed (see below for making up of stock solution).
4. 0.2g ascorbic acid is added and dissolved, and made up to 100ml with distilled water.

Procedure:
1. 25mls of samples and standards is pipetted into digestion flasks.
2. 5mls of digestion reagent ia added, the caps are put on (leave tops slightly loose).
3. The sample plus bottle is weighed before and after autoclaving to check for weight loss by evaporation.
4. The samples are autoclaved for 30 min at 15 psi (103.35 kilopascals).
5. When cooled to room temperature the caps are removed and 5ml of digested sample is pipetted into a test tube. Add 1 ml of mixed reagent (see below for making up mixed reagent).
6. Measure absorbance at 882nm after 10 min. The standards are used to construct a calibration curve from which the sample absorbances are converted to concentrations.

**Dissolved reactive Phosphorus.**

Phosphate ions ($PO_4^{3-}$) react with sodium molybdate and antimony potassium tartrate; the resulting compound is reduced by ascorbic acid to "molybdenum blue" which is determined spectrophotometrically.

Stock solutions for Phosphate Analysis:
1. Antimony: Dissolve 0.37g $KSbO.C_4H_4O_6$ in DDW. Dilute to 500ml. Remove any precipitate formed by filtration.
2. Molybdate: Dissolve 10.84g of $Na_2MoO_4.2H_2O$ in about 500ml of distilled water and dilute to 1 litre.
3. 3.6 N $H_2SO_4$: Mix 100ml conc. $H_2SO_4$ with 500ml distilled water. Cool and dilute to 1 litre.
4. Standard $PO_4$-P solution. Dissolve 4.393g oven-dry (105 °C) $KH_2PO_4$ in distilled water and dilute to 1 litre. Store in fridge.

Reagents:
Mixed reagent: This is prepared daily. Care is taken to mix well after each addition. The same graduated cylinder is used for all reagents and is not washed out between additions.

1. 23.5ml 3.6N $H_2SO_4$ is measured into a 100ml volumetric flask.
2. 25ml antimony stock is added and mixed.
3. 25ml molybdate stock is added and mixed.
4. 0.2g ascorbic acid is added and dissolved, and made up to 100ml with distilled water.

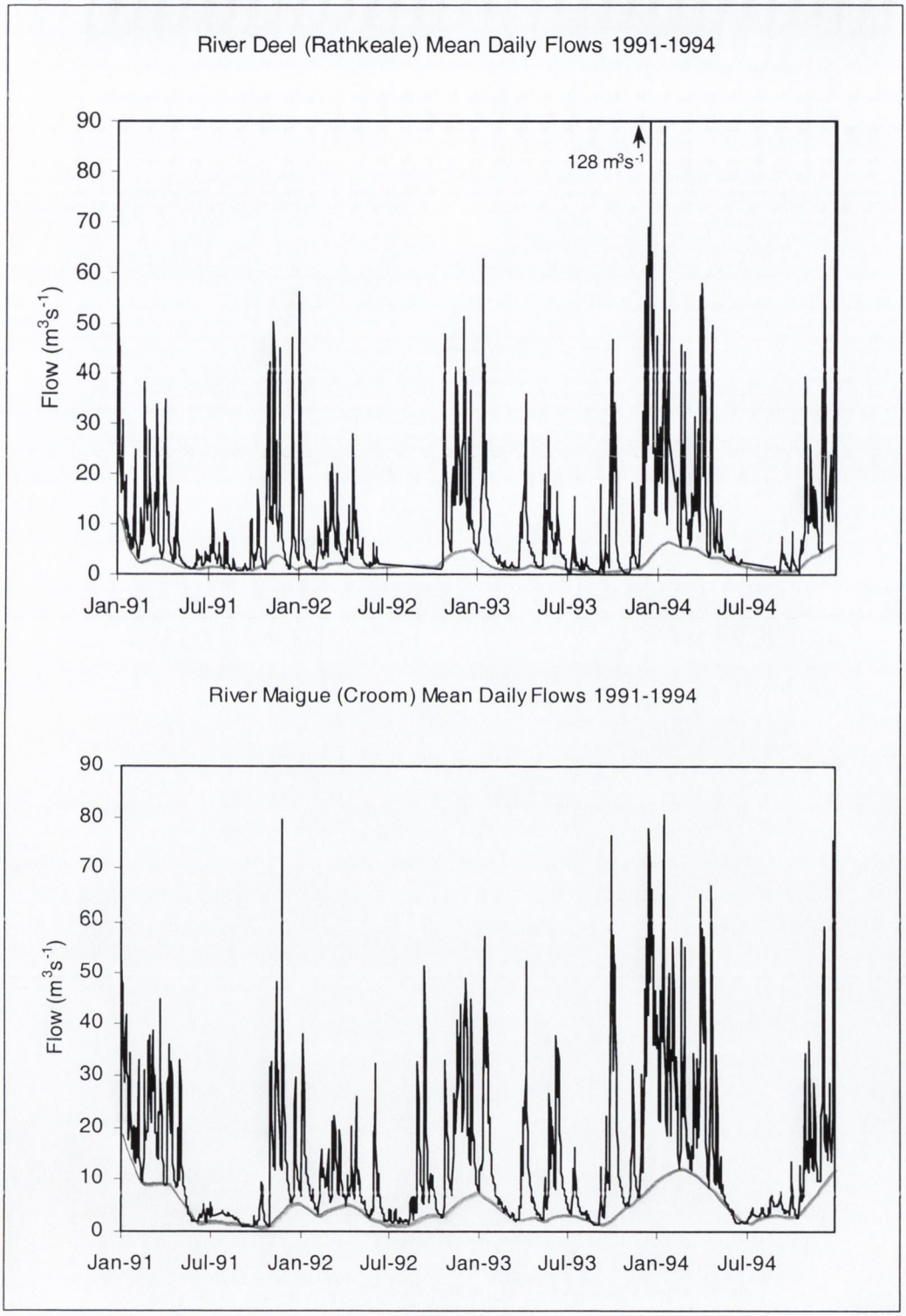
Procedure:
1. The samples are filtered through 0.45µm pore filter paper.
2. 5ml of samples and standards are pipetted into test tubes.
3. 1ml of mixed reagent is added and mixed well.
4. Absorbance is measured at 882nm after 15 min.

The standards are used to construct a calibration curve from which the sample absorbances are converted to concentrations.

**Table C.1 Variation of electrical conductivity at boreholes and springs of the Robe and Fergus catchments.**

| *Site Name* | *Catchment* | *Site Type* | *Average EC* | *Standard Dev.* | *Coeff of Var* | *Avg TP* |
|---|---|---|---|---|---|---|
| | | | ($\mu$S cm$^{-1}$) (x) | Of Avg EC (SD) | x/SD x 100 | ($\mu$g l$^{-1}$) |
| FB01 | Fergus | Borehole | 639 | 43 | 6.7% | 56 |
| FB02 | Fergus | Borehole | 546 | 121 | 22.1% | 35 |
| FB03 | Fergus | Borehole | 880 | 52 | 5.9% | 1186 |
| FB04 | Fergus | Borehole | 739 | 73 | 9.8% | 11 |
| FB06 | Fergus | Borehole | 709 | 40 | 5.6% | 71 |
| FB08 | Fergus | Borehole | 742 | 83 | 11.2% | 27 |
| FB09 | Fergus | Borehole | 401 | 111 | 27.7% | 10 |
| FB10 | Fergus | Borehole | 647 | 37 | 5.7% | 32 |
| FB12 | Fergus | Borehole | 691 | 133 | 19.3% | 4 |
| FB13 | Fergus | Borehole | 671 | 74 | 11.1% | 6 |
| FB15 | Fergus | Borehole | 422 | 224 | 53.0% | 8 |
| FB16 | Fergus | Borehole | 973 | 97 | 9.9% | 7 |
| FB17 | Fergus | Borehole | 462 | 55 | 11.8% | 3 |
| FS01 | Fergus | Spring | 477 | 61 | 12.8% | 21 |
| FS02 | Fergus | Spring | 442 | 42 | 9.5% | 29 |
| FS03 | Fergus | Spring | 384 | 48 | 12.5% | 21 |
| FS04 | Fergus | Spring | 464 | 49 | 10.6% | 26 |
| FS05 | Fergus | Spring | 459 | 81 | 17.5% | 52 |
| FS06 | Fergus | Spring | 447 | 65 | 14.6% | 37 |
| FS08 | Fergus | Spring | 419 | 8 | 1.9% | 21 |
| FS09 | Fergus | Spring | 412 | 81 | 19.7% | 58 |
| FS10 | Fergus | Spring | 426 | 102 | 23.9% | 30 |
| FS12 | Fergus | Spring | 434 | 76 | 17.4% | 8 |
| FS13 | Fergus | Spring | 399 | 37 | 9.3% | 32 |
| FS14 | Fergus | Spring | 404 | 41 | 10.2% | 37 |
| FS17 | Fergus | Spring | 430 | 117 | 27.2% | 79 |
| FS18 | Fergus | Spring | 405 | 47 | 11.6% | 26 |
| RB01 | Robe | Borehole | 703 | 70 | 10.0% | 115 |
| RB02 | Robe | Borehole | 732 | 28 | 3.9% | 300 |
| RB03 | Robe | Borehole | 659 | 28 | 4.2% | 3 |
| RB04 | Robe | Borehole | 819 | 13 | 1.5% | 13 |
| RB05 | Robe | Borehole | 825 | 36 | 4.4% | 21 |
| RB06 | Robe | Borehole | 727 | 50 | 6.8% | 35 |
| RB08 | Robe | Borehole | 811 | 21 | 2.6% | 5 |
| RB09 | Robe | Borehole | 763 | 60 | 7.9% | 20 |
| RB10 | Robe | Borehole | 690 | 10 | 1.5% | 19 |
| RS01 | Robe | Spring | 765 | 55 | 7.2% | 47 |
| RS02 | Robe | Spring | 763 | 15 | 1.9% | 14 |
| RS03 | Robe | Spring | 732 | 32 | 4.4% | 33 |
| RS04 | Robe | Spring | 749 | 41 | 5.4% | 31 |
| RS05 | Robe | Spring | 773 | 40 | 5.2% | 16 |
| RS06 | Robe | Spring | 759 | 71 | 9.3% | 124 |

**Figure C.1 Baseflow separation calculations for the Deel and Maigue Rivers.**




CALCULATIONS:

Rathkeale (Deel): Total flow for period = 12078 $m^3s^{-1}$ = $1.04 \times 10^9$ $m^3$
Volume under separation curve (baseflow) = $2.42 \times 10^8$ $m^3$
Therefore percentage baselow = [$(2.42 \times 10^8$ $m^3)/(1.04 \times 10^9$ $m^3)$] × 100 = 23%

Croom (Maigue) Total flow for period = 19209 $m^3s^{-1}$ = $1.66 \times 10^9$ $m^3$
Volume under separation curve (baseflow) = $6.79 \times 10^8$ $m^3$
Therefore percentage baselow = [$(6.79 \times 10^8$ $m^3)/(1.66 \times 10^9$ $m^3)$] × 100 = 41%

# APPENDIX D

# ANALYTICAL DATA

**Table D.1 Phosphorus and field data for the Fergus catchment sites.**

| Code | Date | TP | TDP ($\mu g\ l^{-1}$) | DRP | SWL (m) | pH | DO ($mg\ l^{-1}$) | Temp (°C) | EC ($\mu S\ cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| FB01 | 7/4/98 | 46 | | | | | | 17.1 | 664 |
| FB01 | 8/12/98 | 54 | 56 | 43 | | | | 14.4 | 575 |
| FB01 | 9/15/98 | 138 | | | | | | | 663 |
| FB01 | 2/15/99 | 60 | | | | 7.17 | 8.16 | | 660 |
| FB01 | 6/17/99 | 45 | | | | 7.09 | 5.43 | 12.5 | 680 |
| FB01 | 10/5/99 | 74 | | | | 7.15 | 8.31 | 10.9 | 617 |
| FB02 | 8/11/98 | 36 | | | 2.78 | | | 17.2 | 462 |
| FB02 | 9/15/98 | 23 | | | 1.80 | | | | 674 |
| FB02 | 2/15/99 | 33 | | | 2.30 | 6.89 | 3.70 | | 647 |
| FB02 | 6/15/99 | 37 | | | 4.20 | 7.07 | 3.56 | 12.4 | 651 |
| FB02 | 10/4/99 | 33 | | | 1.20 | 7.61 | 7.52 | 12.5 | 422 |
| FB03 | 7/3/98 | 1615 | | | | | | 15.0 | 927 |
| FB03 | 8/11/98 | 1632 | 1563 | 1327 | 6.20 | | | 13.3 | 893 |
| FB03 | 9/14/98 | 1814 | 1675 | 1669 | 4.60 | | | 13.2 | 2420 |
| FB03 | 2/14/99 | 1430 | | | 4.62 | 7.01 | 4.11 | | 925 |
| FB03 | 6/15/99 | 737 | | | 5.52 | 7.01 | 1.35 | 12.2 | 845 |
| FB03 | 10/6/99 | 515 | | | 4.42 | 6.98 | 2.97 | 12.1 | 808 |
| FB04 | 8/12/98 | 5 | | | | | | 16.7 | 655 |
| FB04 | 2/15/99 | 5 | | | 22.20 | 7.17 | 4.90 | | 781 |
| FB04 | 6/18/99 | 6 | | | 12.90 | 7.17 | 3.03 | 15.8 | 757 |
| FB04 | 10/6/99 | 24 | | | 15.00 | 7.22 | 5.72 | 13.4 | 781 |
| FB05 | 9/11/99 | 17 | | | | 7.28 | 5.39 | 12.6 | 541 |
| FB05 | 10/6/99 | 8 | | | 5.92 | 7.31 | 3.15 | 12.2 | 644 |
| FB06 | 7/4/98 | 31 | | | 11.80 | | | 12.7 | 727 |
| FB06 | 8/11/98 | 32 | 32 | 12 | 10.96 | | | 15.5 | 640 |
| FB06 | 9/15/98 | 230 | | | 4.60 | | | | 720 |
| FB06 | 2/15/99 | 69 | | | 9.02 | 7.19 | 3.41 | | 733 |
| FB06 | 6/17/99 | 50 | | | 5.20 | 7.11 | 1.40 | 13.4 | 735 |
| FB06 | 10/6/99 | 175 | | | 3.70 | 7.17 | 2.05 | 12.5 | 712 |
| FB07 | 6/16/99 | 4 | | | 12.00 | 6.86 | 2.32 | 11.8 | 724 |
| FB08 | 7/3/98 | 26 | | | | | | 12.3 | 780 |
| FB08 | 8/11/98 | 26 | | | 20.14 | | | 14.7 | 604 |
| FB08 | 9/15/98 | 27 | | | 12.68 | | | | 797 |
| FB08 | 2/13/99 | 47 | | | | 7.06 | 9.21 | | 739 |
| FB08 | 6/17/99 | 26 | | | | 6.99 | 7.20 | 13.6 | 823 |
| FB08 | 10/4/99 | 11 | | | 8.93 | 7.16 | 8.53 | 13.4 | 766 |
| FB09 | 7/3/98 | 3 | | | | | | | |
| FB09 | 8/11/98 | 4 | | | 5.58 | | | 19.5 | 350 |
| FB09 | 9/14/98 | 9 | | | 4.48 | | | 12.0 | 389 |
| FB09 | 2/13/99 | 7 | | | 4.58 | 7.66 | 7.29 | | 469 |
| FB09 | 6/15/99 | 23 | | | | 7.65 | 7.65 | 14.0 | 458 |
| FB09 | 10/4/99 | 9 | | | 3.80 | 7.66 | 2.80 | 15.3 | 499 |
| FB10 | 8/12/98 | 43 | | | | | | | |
| FB10 | 9/15/98 | 3 | | | 9.60 | | | | 661 |
| FB10 | 2/14/99 | 36 | | | | 7.22 | 5.67 | | 605 |
| FB10 | 6/17/99 | 33 | | | 10.50 | 7.03 | 3.71 | 16.8 | 672 |
| FB10 | 10/26/99 | 26 | | | 8.00 | 7.09 | 6.29 | 12.4 | 664 |
| FB11 | 8/13/98 | 29 | | | 16.10 | | | 15.1 | 571 |
| FB11 | 2/14/99 | 140 | | | 50.00 | 7.75 | 7.30 | | 604 |
| FB11 | 6/16/99 | 19 | | | 50.00 | 7.59 | 4.04 | 12.0 | 615 |
| FB11 | 10/5/99 | 32 | 32 | 32 | 50.00 | 6.94 | 5.55 | 12.2 | 593 |
| FB12 | 7/3/98 | 4 | | | | | | 12.0 | 748 |
| FB12 | 8/12/98 | 5 | | | 15.90 | | | 12.1 | 420 |
| FB12 | 9/14/98 | 1 | | | 13.12 | | | | |
| FB12 | 2/14/99 | 4 | | | 13.60 | 7.44 | 8.79 | | 739 |
| FB12 | 6/17/99 | 2 | | | 18.10 | 7.16 | 7.41 | 13.0 | 729 |
| FB12 | 10/4/99 | 3 | | | 11.85 | 7.28 | 8.82 | 12.3 | 755 |

**Table D.1 (cont'd) Phosphorus and field data for the Fergus catchment sites.**

| Code | Date | TP | TDP ($\mu g\ l^{-1}$) | DRP | SWL (m) | pH | DO ($mg\ l^{-1}$) | Temp (°C) | EC ($\mu S\ cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| FB13 | 8/11/98 | 8 | | | 5.72 | | | 15.1 | 568 |
| FB13 | 2/15/99 | 6 | | | 5.30 | 7.26 | 5.04 | | 722 |
| FB13 | 6/17/99 | 4 | | | 6.50 | 7.12 | 2.24 | 15.9 | 666 |
| FB13 | 10/4/99 | 6 | | | 1.91 | 7.24 | 2.83 | 13.1 | 729 |
| FB14 | 8/12/98 | 121 | | | | | | 14.3 | 665 |
| FB14 | 9/15/98 | 23 | | | | | | | 598 |
| FB14 | 2/15/99 | 74 | | | | 7.52 | 4.47 | | 535 |
| FB14 | 6/17/99 | 65 | | | 15.25 | 7.18 | 1.89 | 12.7 | 647 |
| FB14 | 10/5/99 | 441 | | | 6.78 | 6.45 | 2.99 | 11.9 | 615 |
| FB15 | 2/14/99 | 7 | | | 6.25 | 7.45 | 5.82 | | 541 |
| FB15 | 6/16/99 | 4 | | | 15.60 | 7.38 | 2.90 | 12.4 | 561 |
| FB15 | 10/5/99 | 12 | | | | 6.25 | 2.30 | 12.7 | 164 |
| FB16 | 7/3/98 | 2 | | | | | | 15.1 | 1072 |
| FB16 | 8/11/98 | 5 | | | | | | 18.3 | 925 |
| FB16 | 9/15/98 | 1 | | | 24.70 | | | | 1040 |
| FB16 | 2/13/99 | 20 | | | 25.10 | 6.76 | 4.40 | | 1072 |
| FB16 | 6/14/99 | 4 | | | 26.30 | 7.01 | 2.80 | 12.5 | 852 |
| FB16 | 10/4/99 | 4 | | | | 7.01 | 4.98 | 12.1 | 946 |
| FB17 | 2/14/99 | 3 | | | 5.28 | 6.88 | 6.42 | | 493 |
| FB17 | 6/16/99 | 4 | | | 6.63 | 7.20 | 1.40 | 14.7 | 494 |
| FB17 | 10/5/99 | 2 | | | 1.53 | 6.40 | 1.53 | 11.9 | 399 |
| FD01 | 8/10/98 | 26 | | | | | | 17.1 | 616 |
| FD01 | 9/15/98 | 31 | | | | | | | |
| FD01 | 2/15/99 | 30 | | | | 7.07 | 3.71 | | 731 |
| FD01 | 6/18/99 | 27 | | | | 6.87 | 1.77 | 13.5 | 722 |
| FD01 | 10/5/99 | 22 | | | | 7.46 | 5.86 | 11.1 | 761 |
| FD02 | 9/14/98 | 11 | | | | | | 13.7 | 289 |
| FD02 | 2/15/99 | 9 | | | | 7.73 | 9.04 | | 306 |
| FD02 | 6/17/99 | 11 | | | | 7.75 | 7.30 | 17.4 | 276 |
| FD02 | 10/4/99 | 9 | | | | 7.96 | 9.56 | 11.9 | 309 |
| FD03 | 7/4/98 | 25 | | | | | | 14.8 | 524 |
| FD03 | 8/12/98 | 37 | | | | | | | |
| FD03 | 9/15/98 | 32 | | | | | | | 488 |
| FD03 | 2/15/99 | 36 | | | | 7.46 | 6.85 | | 525 |
| FD04 | 8/11/98 | 31 | | | | | | | |
| FD04 | 9/12/98 | 11 | | | | | | | 135 |
| FD04 | 2/15/99 | 11 | | | | 6.48 | 8.34 | | 153 |
| FD04 | 6/15/99 | 12 | | | 1.10 | 6.37 | 8.32 | 13.5 | 164 |
| FD04 | 10/5/99 | 10 | | | 0.25 | 5.84 | 9.14 | 12.8 | 143 |
| FD05 | 8/10/98 | 76 | | | | | | | |
| FD05 | 6/14/99 | 106 | | | | 7.29 | 4.74 | 13.2 | 487 |
| FD06 | 8/13/98 | 6 | | | | | | 12.8 | 381 |
| FD06 | 9/15/98 | 3 | | | | | | | 551 |
| FD06 | 2/14/99 | 8 | | | | 6.92 | 4.19 | | 572 |
| FD06 | 6/16/99 | 5 | | | | 6.77 | 2.49 | 11.7 | 678 |
| FD06 | 10/5/99 | 6 | | | | 5.66 | 2.32 | 13.1 | 174 |
| FD07 | 8/13/98 | 11 | | | | | | 15.5 | 318 |
| FD07 | 9/15/98 | 11 | | | | | | | 586 |
| FD07 | 2/14/99 | 27 | | | | 7.07 | 4.05 | | 609 |
| FD08 | 8/13/98 | 9 | | | | | | 12.6 | |
| FD08 | 9/15/98 | 3 | | | | | | | |
| FD08 | 2/14/99 | 10 | | | | 6.61 | 5.68 | | 279 |
| FD08 | 6/16/99 | 9 | | | | 6.24 | 1.30 | 11.9 | 306 |
| FD08 | 10/5/99 | 11 | | | | 4.88 | 3.83 | 12.1 | 75 |
| FK01 | 7/4/98 | 10 | | | | | | | |
| FK01 | 8/12/98 | 21 | | | | | | 16.6 | 347 |
| FK01 | 9/14/98 | 29 | | | | | | | 421 |

**Table D.1 (cont'd) Phosphorus and field data for the Fergus catchment sites.**

| Code | Date | TP | TDP ($\mu g\ l^{-1}$) | DRP | SWL (m) | pH | DO ($mg\ l^{-1}$) | Temp (°C) | EC ($\mu S\ cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| FK01 | 2/14/99 | 19 | | | | 7.56 | 8.48 | | 461 |
| FK01 | 6/17/99 | 19 | | | | 7.62 | 6.23 | 15.2 | 376 |
| FK01 | 10/5/99 | 27 | | | | 7.48 | 7.46 | 12.2 | 440 |
| FK02 | 7/4/98 | 21 | | | | | | 16.1 | 395 |
| FK02 | 8/12/98 | 29 | | | | | | 17.4 | 341 |
| FK02 | 9/15/98 | 34 | | | | | | | 410 |
| FK02 | 2/15/99 | 22 | | | | 7.54 | 9.01 | | 449 |
| FK02 | 6/17/99 | 21 | | | | 7.58 | 6.60 | 14.9 | 352 |
| FK02 | 10/5/99 | 48 | | | | 7.46 | 7.46 | 12.1 | 428 |
| FL01 | 7/3/98 | 5 | | | | | | 17.2 | 358 |
| FL01 | 8/11/98 | 14 | | | | | | 20.1 | 231 |
| FL01 | 9/14/98 | 9 | | | | | | 16.0 | 354 |
| FL01 | 2/13/99 | 13 | | | | 7.88 | 11.09 | | 438 |
| FL01 | 6/15/99 | 8 | | | | 8.24 | 10.63 | 16.6 | 388 |
| FL01 | 10/4/99 | 15 | | | | 8.05 | 9.38 | 15.2 | 373 |
| FL02 | 7/4/98 | 11 | | | | | | 17.1 | 384 |
| FL02 | 8/11/98 | 23 | | | | | | 20.0 | 319 |
| FL02 | 9/15/98 | 21 | | | 1.53 | | | | 400 |
| FL02 | 2/14/99 | 21 | | | | 8.00 | 10.36 | | 474 |
| FL02 | 6/14/99 | 17 | | | | 8.40 | 11.30 | 17.9 | 410 |
| FL02 | 10/26/99 | 28 | | | | 7.87 | 10.63 | 12.1 | 425 |
| FL03 | 7/3/98 | 15 | | | | | | 16.5 | 360 |
| FL03 | 8/10/98 | 29 | | | | | | 18.7 | 376 |
| FL03 | 9/12/98 | 38 | | | | | | 14.0 | 372 |
| FL03 | 2/13/99 | 33 | | | | 7.93 | 9.76 | | 410 |
| FL03 | 6/15/99 | 10 | | | | 8.43 | 11.48 | 15.8 | 391 |
| FL03 | 7/14/99 | 14 | 6 | 1 | | 8.42 | 10.30 | 18.9 | 378 |
| FL03 | 9/6/99 | 26 | 9 | 3 | | 8.38 | 3.65 | 18.4 | 382 |
| FL04 | 7/4/98 | 24 | | | | | | | |
| FL05 | 7/3/98 | 10 | | | | | | 17.9 | 407 |
| FL05 | 8/11/98 | 7 | | | | | | | 292 |
| FL05 | 9/14/98 | 5 | | | | | | 15.7 | 399 |
| FL05 | 2/13/99 | 7 | | | | 8.11 | 10.19 | | 428 |
| FL05 | 6/15/99 | 5 | | | | 8.40 | 11.24 | 18.7 | 427 |
| FL05 | 10/4/99 | 8 | | | | 8.25 | 10.07 | 14.6 | 383 |
| FL06 | 7/4/98 | 20 | | | | | | 16.4 | 374 |
| FL06 | 8/11/98 | 31 | | | | | | 20.1 | 243 |
| FL06 | 9/14/98 | 34 | | | | | | | 369 |
| FL06 | 2/14/99 | 32 | | | | 7.24 | 8.33 | | 101 |
| FL06 | 6/15/99 | 30 | | | | 8.55 | 12.36 | 17.4 | 321 |
| FL06 | 10/4/99 | 48 | | | | 7.98 | 9.62 | 12.4 | 376 |
| FL07 | 9/15/98 | 17 | | | | | | | 318 |
| FL07 | 2/15/99 | 6 | | | | 8.13 | 8.61 | | 372 |
| FL07 | 10/26/99 | 17 | 4 | 1 | | 7.90 | 11.41 | 11.2 | 410 |
| FR01 | 7/3/98 | 61 | | | | | | 15.6 | 393 |
| FR01 | 8/10/98 | 70 | 53 | 21 | | | | 17.8 | 345 |
| FR01 | 9/11/98 | 106 | 90 | 61 | | | | 12.3 | 298 |
| FR01 | 2/13/99 | 55 | 35 | | | 7.62 | 13.71 | 6.1 | 334 |
| FR01 | 6/14/99 | 52 | | | | 7.82 | 9.45 | 15.7 | 409 |
| FR01 | 7/13/99 | 58 | 35 | 13 | | 7.45 | 7.88 | 18.5 | 395 |
| FR01 | 9/6/99 | 73 | 39 | 21 | | 7.21 | 7.19 | 18.4 | 425 |
| FR02 | 9/11/98 | 68 | | | | | | 12.9 | 383 |
| FR02 | 2/13/99 | 31 | | | | 7.61 | | 8.8 | 434 |
| FR02 | 6/18/99 | 27 | | | | 7.63 | 11.51 | 14.3 | 497 |
| FR02 | 7/13/99 | 22 | 15 | 9 | | 7.98 | 12.07 | 13.7 | 492 |
| FR02 | 9/6/99 | 46 | 31 | 23 | | 7.65 | 10.64 | 13.5 | 464 |
| FR03 | 9/11/98 | 62 | | | | | | 12.5 | 383 |

**Table D.1 (cont'd) Phosphorus and field data for the Fergus catchment sites.**

| Code | Date | TP | TDP ($\mu g\ l^{-1}$) | DRP | SWL (m) | pH | DO ($mg\ l^{-1}$) | Temp (°C) | EC ($\mu S\ cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| FR03 | 2/13/99 | 34 | | | | 7.72 | | | 435 |
| FR03 | 6/15/99 | 30 | | | | 7.74 | 12.21 | 13.1 | 513 |
| FR03 | 7/14/99 | 38 | 33 | 27 | | 6.82 | 8.52 | 13.3 | 501 |
| FR03 | 9/6/99 | 70 | 48 | 39 | | 7.43 | 9.34 | 13.3 | 479 |
| FR04 | 10/26/99 | 33 | | | | 8.06 | 10.62 | 9.9 | 351 |
| FS01 | 7/5/98 | 22 | | | | | | | |
| FS01 | 8/12/98 | 19 | | | | | | 16.0 | 399 |
| FS01 | 9/15/98 | 27 | | | | | | | 466 |
| FS01 | 2/15/99 | 23 | | | | 7.61 | 6.61 | | 502 |
| FS01 | 6/18/99 | 23 | | | | 7.46 | 4.38 | 13.9 | 542 |
| FS01 | 10/5/99 | 19 | | | | 7.42 | 6.37 | 11.9 | 464 |
| FS02 | 7/4/98 | 13 | | | | | | 16.1 | 439 |
| FS02 | 8/12/98 | 34 | | | | | | | 391 |
| FS02 | 9/15/98 | 17 | | | | | | | 434 |
| FS02 | 2/15/99 | 35 | | | | 7.63 | 7.62 | | 463 |
| FS02 | 6/17/99 | 42 | | | | 7.62 | 6.37 | 15.9 | 500 |
| FS02 | 10/5/99 | 20 | | | | 7.63 | 10.25 | 10.6 | 416 |
| FS03 | 7/2/98 | 66 | | | | | | | 349 |
| FS03 | 8/10/98 | 9 | | | | | | 13.6 | 411 |
| FS03 | 9/11/98 | 7 | | | | | | 12.6 | 451 |
| FS03 | 2/13/99 | 9 | 11 | | | 7.62 | 12.80 | 9.6 | 424 |
| FS03 | 6/14/99 | 10 | | | | 7.48 | 8.91 | 12.5 | 423 |
| FS03 | 7/13/99 | 11 | 7 | 4 | | 7.71 | 10.75 | 13.2 | 422 |
| FS03 | 9/6/99 | 34 | 19 | 13 | | 7.36 | 9.94 | 13.8 | 352 |
| FS04 | 8/16/98 | 28 | | | | | | | |
| FS04 | 9/15/98 | 37 | | | | | | | 420 |
| FS04 | 2/15/99 | 26 | | | | 7.59 | 6.35 | | 493 |
| FS04 | 6/17/99 | 22 | | | | 7.53 | 5.88 | 15.2 | 407 |
| FS04 | 10/25/99 | 30 | 25 | 22 | | 7.40 | 4.75 | 11.5 | 491 |
| FS05 | 7/3/98 | 45 | | | | | | 11.8 | 475 |
| FS05 | 8/10/98 | 59 | 50 | 24 | | | | 12.8 | 329 |
| FS05 | 9/11/98 | 78 | | | | | | 12.7 | 356 |
| FS05 | 2/13/99 | 48 | 44 | | | 7.35 | 6.10 | 8.5 | 420 |
| FS05 | 5/30/99 | | | 36 | | 7.59 | 8.82 | 13.3 | 409 |
| FS05 | 6/18/99 | 26 | 22 | | | 7.37 | 5.97 | 12.7 | 517 |
| FS05 | 6/30/99 | 49 | 45 | 36 | | 7.32 | 7.95 | 11.9 | 417 |
| FS05 | 7/13/99 | 50 | 48 | 46 | | 7.37 | 5.68 | 12.0 | 523 |
| FS05 | 8/4/99 | 52 | 49 | 46 | | 7.24 | 5.03 | 11.9 | 552 |
| FS05 | 8/20/99 | 50 | 48 | 43 | | 7.08 | 6.41 | 12.6 | 540 |
| FS05 | 9/6/99 | 66 | 57 | 48 | | 7.29 | 5.40 | 12.0 | 500 |
| FS05 | 9/18/99 | 53 | 45 | 39 | | 7.49 | 8.23 | 12.5 | 467 |
| FS05 | 10/7/99 | 47 | 42 | 42 | | 7.29 | 7.56 | 11.5 | 469 |
| FS05 | 10/26/99 | 50 | 44 | 42 | | 7.47 | 5.32 | 12.4 | 480 |
| FS05 | 11/28/99 | 95 | 65 | 48 | | | 4.90 | 11.7 | 259 |
| FS05 | 12/28/99 | 45 | 38 | 38 | | 7.01 | 11.08 | 7.3 | 436 |
| FS05 | 1/29/00 | 107 | 63 | 36 | | 7.05 | 2.75 | 9.1 | 320 |
| FS05 | 3/4/00 | 50 | 41 | 35 | | 7.50 | 10.40 | 8.6 | 388 |
| FS06 | 7/3/98 | 24 | | | | | | 11.6 | 455 |
| FS06 | 8/10/98 | 39 | | | | | | 12.5 | 318 |
| FS06 | 9/11/98 | 50 | | | | | | 12.3 | 412 |
| FS06 | 2/13/99 | 29 | | | | 7.48 | 7.95 | 8.7 | 443 |
| FS06 | 6/18/99 | 48 | | | | 7.31 | 4.37 | 11.4 | 530 |
| FS06 | 6/30/99 | 34 | | | | 7.45 | 9.62 | 11.9 | 427 |
| FS06 | 7/13/99 | 31 | | | | 7.54 | 8.38 | 12.3 | 504 |
| FS06 | 9/6/99 | 43 | 40 | 33 | | 7.31 | 7.60 | 12.9 | 485 |
| FS07 | 7/13/99 | 40 | 35 | 31 | | 7.53 | 7.99 | 12.3 | 506 |
| FS07 | 9/6/99 | 59 | 48 | 40 | | 7.43 | 7.32 | 12.5 | 489 |

**Table D.1 (cont'd) Phosphorus and field data for the Fergus catchment sites.**

| Code | Date | TP | TDP ($\mu g\ l^{-1}$) | DRP | SWL (m) | pH | DO ($mg\ l^{-1}$) | Temp (°C) | EC ($\mu S\ cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| FS08 | 7/3/98 | 12 | | | | | | 12.4 | 412 |
| FS08 | 8/10/98 | 21 | | | | | | 13.9 | 412 |
| FS08 | 9/11/98 | 27 | 23 | 18 | | | | | |
| FS08 | 2/13/99 | 18 | 19 | | | 7.70 | 13.20 | 8.8 | 431 |
| FS08 | 5/30/99 | | | 15 | | 7.68 | 10.30 | 12.0 | 418 |
| FS08 | 6/30/99 | 45 | 41 | 38 | | 7.58 | 9.89 | 13.1 | 423 |
| FS08 | 7/13/99 | | | | | | | | |
| FS08 | 9/18/99 | 21 | 18 | 17 | | 7.68 | 10.06 | 11.6 | 412 |
| FS08 | 10/6/99 | 18 | 14 | 13 | | 7.55 | 10.49 | 11.3 | 426 |
| FS08 | 10/25/99 | 12 | 10 | 8 | | 7.76 | 9.62 | 11.0 | 415 |
| FS08 | 11/28/99 | 42 | 21 | 19 | | | 10.20 | 11.0 | 322 |
| FS08 | 12/28/99 | 20 | 17 | 17 | | 7.18 | 12.29 | 8.0 | 437 |
| FS08 | 1/29/00 | 23 | 18 | 15 | | 7.07 | 6.76 | 9.1 | 355 |
| FS08 | 3/4/00 | 16 | 14 | 11 | | 7.52 | 11.76 | 9.0 | 388 |
| FS09 | 9/12/98 | 5 | | | | | | 13.6 | 483 |
| FS09 | 2/13/99 | 6 | | | | 7.44 | 10.08 | 8.4 | 433 |
| FS09 | 6/14/99 | 15 | | | | 7.45 | 9.48 | 16.3 | 446 |
| FS09 | 7/14/99 | 19 | 10 | 6 | | 7.26 | 7.75 | 16.9 | 431 |
| FS09 | 9/6/99 | 39 | 19 | 9 | | 7.46 | 6.23 | 13.5 | 428 |
| FS10 | 7/3/98 | 94 | | | | | | 14.8 | 455 |
| FS10 | 8/11/98 | 19 | | | | | | 14.3 | 380 |
| FS10 | 9/14/98 | 23 | | | | | | 14.3 | 448 |
| FS10 | 2/13/99 | 9 | | | | 7.69 | 9.36 | | 516 |
| FS10 | 6/18/99 | 23 | | | | 6.92 | 3.10 | 14.5 | 525 |
| FS10 | 10/4/99 | 15 | | | | 7.52 | 6.98 | 12.4 | 431 |
| FS11 | 6/14/99 | 25 | | | | 7.04 | 2.12 | 11.1 | 670 |
| FS11 | 10/26/99 | 15 | | | | 7.16 | 2.92 | 10.6 | 650 |
| FS12 | 7/3/98 | 5 | | | | | | 13.7 | 430 |
| FS12 | 8/10/98 | 4 | | | | | | 14.3 | 347 |
| FS12 | 9/15/98 | 3 | | | | | | | 463 |
| FS12 | 2/15/99 | 2 | | | | 7.52 | 7.25 | | 504 |
| FS12 | 6/18/99 | 15 | | | | 7.26 | 3.30 | 13.6 | 468 |
| FS12 | 10/5/99 | 6 | | | | 6.65 | 7.54 | 12.1 | 486 |
| FS13 | 7/4/98 | 40 | | | | | | 15.7 | 401 |
| FS13 | 8/12/98 | 29 | 28 | 16 | | | | 16.5 | 322 |
| FS13 | 9/15/98 | 30 | | | | | | | |
| FS13 | 2/14/99 | 32 | | | | 7.73 | 9.40 | | 452 |
| FS13 | 5/30/99 | | | 12 | | 7.58 | 7.83 | 14.2 | 411 |
| FS13 | 6/18/99 | 13 | 10 | | | 7.54 | 4.91 | 14.4 | 397 |
| FS13 | 6/30/99 | 23 | 19 | 12 | | 7.59 | 7.42 | 14.6 | 360 |
| FS13 | 8/4/99 | 24 | 20 | 14 | | 7.55 | 4.54 | 11.9 | 393 |
| FS13 | 8/20/99 | 27 | 22 | 21 | | 7.42 | 3.82 | 16.6 | 415 |
| FS13 | 9/12/99 | 59 | 45 | 30 | | 7.37 | | 14.1 | 421 |
| FS13 | 9/18/99 | 36 | 30 | 23 | | 7.36 | 8.93 | 14.2 | 371 |
| FS13 | 10/6/99 | 41 | 30 | 24 | | 7.45 | 7.44 | 12.8 | 428 |
| FS13 | 10/25/99 | 26 | 23 | 18 | | 7.43 | 7.09 | 10.7 | 430 |
| FS13 | 11/28/99 | 50 | 34 | 29 | | | 13.14 | 11.6 | 440 |
| FS13 | 12/28/99 | 44 | 35 | 30 | | 7.17 | 11.05 | 6.7 | 500 |
| FS13 | 1/29/00 | 32 | 22 | 18 | | 7.36 | 10.43 | 8.0 | 395 |
| FS13 | 3/4/00 | 35 | 24 | 19 | | 7.50 | 9.85 | 8.2 | 412 |
| FS14 | 7/4/98 | 36 | | | | | | 15.1 | 415 |
| FS14 | 8/12/98 | 15 | | | | | | | |
| FS14 | 9/15/98 | 40 | | | | | | | |
| FS14 | 2/14/99 | 23 | | | | 7.50 | 8.99 | | 454 |
| FS14 | 6/18/99 | 26 | | | | 7.65 | 7.30 | 16.3 | 356 |
| FS14 | 9/12/99 | 62 | 43 | 30 | | 7.49 | | 14.9 | 391 |
| FS15 | 6/16/99 | 23 | | | | 6.78 | 1.96 | 12.3 | 829 |

**Table D.1 (cont'd) Phosphorus and field data for the Fergus catchment sites.**

| Code | Date | TP | TDP ($\mu g\ l^{-1}$) | DRP | SWL (m) | pH | DO ($mg\ l^{-1}$) | Temp (°C) | EC ($\mu S\ cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| FS16 | 6/16/99 | 6 | | | | 7.03 | 4.43 | 14.3 | 902 |
| FS17 | 7/3/98 | 44 | | | | | | 12.1 | 477 |
| FS17 | 8/10/98 | 65 | 56 | 32 | | | | 13.2 | 243 |
| FS17 | 9/11/98 | 125 | 86 | 65 | | | | 12.7 | 301 |
| FS17 | 2/13/99 | 52 | | | | 7.32 | 8.91 | 8.2 | 424 |
| FS17 | 6/14/99 | 163 | | | | 7.50 | 7.51 | 15.3 | 491 |
| FS17 | 7/13/99 | 47 | 46 | 41 | | 7.33 | 6.68 | 12.1 | 564 |
| FS17 | 9/6/99 | 53 | 49 | 42 | | 7.20 | 4.96 | 13.1 | 510 |
| FS18 | 7/5/98 | 24 | | | | | | 15.4 | 408 |
| FS18 | 8/12/98 | 34 | 25 | 17 | | | | 16.0 | 306 |
| FS18 | 9/15/98 | 34 | | | | | | | 425 |
| FS18 | 2/15/99 | 21 | | | | 7.15 | 7.66 | | 491 |
| FS18 | 5/30/99 | | | 6 | | 7.23 | 6.61 | 13.1 | 402 |
| FS18 | 6/18/99 | 15 | 8 | | | 7.47 | 5.95 | 14.3 | 392 |
| FS18 | 6/30/99 | 20 | 17 | 13 | | 7.52 | 5.78 | 14.6 | 378 |
| FS18 | 8/4/99 | 22 | 18 | 13 | | 7.48 | 3.79 | 16.4 | 403 |
| FS18 | 8/20/99 | 25 | 22 | 17 | | 7.45 | 3.78 | 16.4 | 421 |
| FS18 | 9/12/99 | 40 | 33 | 24 | | 7.43 | | 14.9 | 412 |
| FS18 | 9/18/99 | 33 | 28 | 23 | | 7.34 | 6.07 | 14.3 | 369 |
| FS18 | 10/6/99 | 34 | 22 | 19 | | 7.30 | 6.47 | 12.5 | 441 |
| FS18 | 10/25/99 | 23 | 18 | 15 | | 7.52 | 5.65 | 11.7 | 438 |
| FS18 | 11/28/99 | 54 | 27 | 23 | | | | 12.1 | 416 |
| FS18 | 12/28/99 | 33 | 27 | 23 | | 7.13 | 10.10 | 6.8 | 412 |
| FS18 | 1/29/00 | 23 | 18 | 15 | | 7.40 | 11.15 | 8.5 | 461 |
| FS18 | 3/4/00 | 25 | 17 | 14 | | 7.13 | 9.48 | 8.5 | 423 |
| FS19 | 6/16/99 | 35 | | | | 7.05 | 8.00 | 12.0 | 453 |
| FS19 | 10/26/99 | 29 | | | | 7.66 | 9.69 | 10.9 | 400 |
| FS20 | 6/16/99 | 6 | | | | 7.61 | 13.90 | 11.7 | 728 |
| FS20 | 10/26/99 | 6 | | | | 7.66 | 6.51 | 11.5 | 739 |
| FS21 | 6/16/99 | 146 | | | | 7.78 | 7.78 | 11.4 | 457 |
| FS21 | 10/26/99 | 44 | | | | 7.91 | 9.42 | 10.5 | 366 |

**Table D.2 Phosphorus and field data for the Robe catchment sites.**

| Code | Date | TP ($\mu g\ l^{-1}$) | TDP ($\mu g\ l^{-1}$) | DRP ($\mu g\ l^{-1}$) | SWI (m) | pH | DO ($mg\ l^{-1}$) | Temp (°C) | EC ($\mu S\ cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| RB01 | 8/8/98 | 82 | | | 9.90 | | | 14.4 | 663 |
| RB01 | 2/20/99 | 108 | | | 7.80 | 7.41 | 3.85 | 8.5 | 807 |
| RB01 | 6/12/99 | 103 | | | 8.62 | 7.54 | 1.75 | 13.2 | 661 |
| RB01 | 10/2/99 | 167 | | | 7.24 | 7.55 | 3.37 | 10.8 | 679 |
| RB02 | 8/7/98 | 449 | | | 6.40 | | | 15.9 | 689 |
| RB02 | 9/8/98 | 748 | 712 | 712 | 5.98 | | | 14.8 | 730 |
| RB02 | 2/20/99 | 86 | 86 | | 7.80 | 7.35 | 8.23 | 8.2 | 766 |
| RB02 | 6/12/99 | 89 | | | 6.50 | 7.26 | 9.02 | 12.2 | 727 |
| RB02 | 10/2/99 | 130 | | | | 7.26 | 8.25 | 11.9 | 746 |
| RB03 | 8/8/98 | 6 | | | 6.62 | | | 12.9 | 658 |
| RB03 | 9/10/98 | 1 | | | 7.80 | | | 11.9 | 620 |
| RB03 | 6/12/99 | 4 | | | 7.00 | 7.38 | 3.15 | 14.2 | 677 |
| RB03 | 10/2/99 | 1 | | | 5.00 | 7.49 | 3.97 | 12.0 | 681 |
| RB04 | 8/6/98 | 7 | | | 11.12 | | | 15.4 | 819 |
| RB04 | 9/9/98 | 1 | | | 12.40 | | | 14.9 | 800 |
| RB04 | 2/19/99 | 21 | | | 11.83 | 7.36 | 4.61 | 8.8 | 835 |
| RB04 | 6/11/99 | 26 | | | 13.00 | 7.17 | 5.84 | 11.7 | 817 |
| RB04 | 10/2/99 | 10 | | | 10.46 | 7.37 | 6.25 | 12.0 | 822 |
| RB05 | 8/6/98 | 35 | | | 9.73 | | | 12.6 | 781 |
| RB05 | 9/8/98 | 7 | | | 9.40 | | | 12.6 | 801 |
| RB05 | 2/19/99 | 11 | | | 8.64 | 7.45 | 5.40 | 9.6 | 866 |
| RB05 | 6/11/99 | 32 | | | 10.42 | 7.27 | 4.17 | 11.6 | 821 |
| RB05 | 10/2/99 | 19 | | | 8.14 | 7.21 | 8.71 | 11.2 | 857 |
| RB06 | 9/8/98 | 25 | | | 7.63 | | | | |
| RB06 | 2/19/99 | 16 | | | 6.28 | 8.08 | 10.23 | 8.8 | 670 |
| RB06 | 6/11/99 | 39 | | | 7.62 | 7.57 | 6.95 | 10.2 | 750 |
| RB06 | 10/2/99 | 50 | | | 6.40 | 7.48 | 7.65 | 10.9 | 761 |
| RB07 | 9/8/98 | 489 | | | | | | 14.0 | 907 |
| RB07 | 2/19/99 | 843 | | | 2.30 | 7.55 | 3.07 | 8.9 | 905 |
| RB07 | 6/11/99 | 624 | | | 3.60 | 7.20 | 5.75 | 12.0 | 954 |
| RB07 | 10/2/99 | | | | 2.40 | | | | |
| RB08 | 8/6/98 | 6 | | | 13.50 | | | 12.4 | 796 |
| RB08 | 9/8/98 | 3 | | | 13.30 | | | 13.5 | 812 |
| RB08 | 2/19/99 | 4 | | | 6.88 | 7.16 | 8.19 | | 792 |
| RB08 | 6/11/99 | 7 | | | 13.03 | 7.42 | 9.45 | 14.4 | 808 |
| RB08 | 10/2/99 | 5 | | | 7.10 | 7.19 | 7.61 | 12.0 | 845 |
| RB09 | 8/7/98 | 22 | | | | | | 10.9 | 731 |
| RB09 | 9/8/98 | 21 | | | | | | 11.4 | 803 |
| RB09 | 2/19/99 | 13 | | | | 7.20 | 4.46 | 9.7 | 672 |
| RB09 | 6/12/99 | 24 | | | | 6.99 | 3.76 | 11.2 | 796 |
| RB09 | 10/2/99 | 21 | | | | 6.84 | 5.69 | 10.8 | 813 |
| RB10 | 8/6/98 | 28 | | | 6.96 | | | 13.7 | 698 |
| RB10 | 9/8/98 | 15 | | | 8.57 | | | | |
| RB10 | 6/11/99 | 16 | | | 8.53 | 7.04 | 1.45 | 11.7 | 678 |
| RB10 | 10/2/99 | 14 | | | 6.48 | 7.33 | 2.45 | 11.1 | 693 |
| RB11 | 2/20/99 | 38 | | | 5.49 | 7.34 | 4.85 | 9.4 | 704 |
| RB11 | 6/12/99 | | | | 7.60 | | | | |
| RD01 | 8/8/98 | 28 | | | | | | 15.5 | 791 |
| RD01 | 9/9/98 | 48 | | | | | | 15.3 | 732 |
| RD01 | 2/20/99 | 22 | | | | 7.10 | 7.96 | 9.8 | 777 |
| RD02 | 8/8/98 | 4 | | | | | | 10.9 | 813 |
| RD02 | 9/9/98 | 1 | | | | | | 11.1 | 773 |
| RD02 | 2/20/99 | 2 | | | | 6.99 | 3.03 | 9.9 | 848 |
| RD02 | 6/12/99 | 5 | | | | 7.02 | 2.04 | 11.3 | 832 |
| RD02 | 10/3/99 | 4 | | | | 6.96 | 3.74 | 11.0 | 854 |

**Table D.2 (cont'd) Phosphorus and field data for the Robe catchment sites.**

| Code | Date | TP | TDP | DRP | SWL | pH | DO | Temp | EC |
|---|---|---|---|---|---|---|---|---|---|
| | | | ($\mu g\ l^{-1}$) | | (m) | | ($mg\ l^{-1}$) | (°C) | ($\mu S\ cm^{-1}$) |
| RR01 | 7/8/98 | 30 | | | 0.70 | | | 15.3 | 674 |
| RR01 | 8/7/98 | 64 | | | 1.03 | | | 15.8 | 558 |
| RR01 | 9/8/98 | 44 | | | 0.76 | | | 15.8 | 658 |
| RR01 | 2/19/99 | 55 | | | | 8.08 | 10.48 | 8.5 | 646 |
| RR01 | 6/11/99 | 27 | | | | 8.38 | 12.50 | 14.1 | 674 |
| RR01 | 10/3/99 | 71 | | | | 7.81 | 10.01 | 11.0 | 537 |
| RR02 | 7/8/98 | 29 | | | 4.85 | | | 15.3 | 696 |
| RR02 | 8/6/98 | 68 | | | | | | 16.7 | 607 |
| RR02 | 9/8/98 | 38 | | | | | | 15.9 | 667 |
| RR02 | 2/19/99 | 40 | | | | 8.04 | 10.42 | 8.9 | 645 |
| RR02 | 6/11/99 | 23 | | | | 8.26 | 11.99 | 14.4 | 685 |
| RR02 | 10/3/99 | 65 | | | | 7.81 | 9.20 | 11.0 | 625 |
| RS01 | 7/7/98 | 29 | | | | | | 11.3 | 762 |
| RS01 | 8/7/98 | 52 | | | | | | 11.2 | 797 |
| RS01 | 9/9/98 | 57 | | | | | | 13.6 | 698 |
| RS01 | 2/20/99 | 18 | | | | 7.31 | 5.07 | 8.4 | 661 |
| RS01 | 5/30/99 | | | 24 | | 6.97 | 2.56 | 10.7 | 756 |
| RS01 | 6/12/99 | 35 | | | | 7.17 | 3.90 | 11.1 | 789 |
| RS01 | 6/29/99 | 102 | 20 | 12 | | 7.00 | 4.95 | 12.4 | 800 |
| RS01 | 7/17/99 | | | | | | | | |
| RS01 | 8/21/99 | 62 | 14 | 9 | | 7.08 | 4.94 | 13.2 | 812 |
| RS01 | 9/4/99 | 37 | 37 | 24 | | 7.08 | | 12.2 | 855 |
| RS01 | 9/19/99 | 66 | 51 | 47 | | 6.97 | 8.58 | 11.3 | 768 |
| RS01 | 10/6/99 | 27 | 22 | 24 | | 6.72 | 5.45 | 11.3 | 732 |
| RS01 | 10/25/99 | 30 | 24 | 24 | | 6.94 | 2.46 | 10.7 | 737 |
| RS01 | 11/27/99 | 102 | 88 | 66 | | 6.77 | 3.26 | 10.0 | 741 |
| RS01 | 12/29/99 | 36 | 23 | 22 | | 7.14 | 17.84 | 8.0 | 598 |
| RS01 | 1/30/00 | 23 | 18 | 15 | | | 6.04 | 8.2 | 595 |
| RS01 | 3/4/00 | 29 | 25 | 19 | | 6.81 | 6.01 | 8.2 | 622 |
| RS02 | 8/7/98 | 20 | | | | | | 10.6 | 752 |
| RS02 | 9/8/98 | 11 | | | 0.30 | | | 11.0 | 763 |
| RS02 | 2/19/99 | 5 | | | | 7.05 | 3.78 | 9.0 | 747 |
| RS02 | 6/11/99 | 16 | | | | 7.09 | 2.08 | 10.7 | 769 |
| RS02 | 10/3/99 | 18 | | | | 6.99 | 3.43 | 11.5 | 784 |
| RS03 | 8/6/98 | 39 | | | | | | 11.2 | 733 |
| RS03 | 9/8/98 | 34 | 30 | 19 | | | | 11.1 | 734 |
| RS03 | 2/19/99 | 13 | | | | 7.24 | 5.40 | 9.1 | 652 |
| RS03 | 5/30/99 | | | 21 | | 7.17 | 3.27 | 11.1 | 692 |
| RS03 | 6/12/99 | 26 | | | | 7.01 | 3.30 | 10.8 | 735 |
| RS03 | 6/29/99 | 30 | 27 | 26 | | 7.04 | 3.44 | 10.5 | 751 |
| RS03 | 7/17/99 | 44 | 39 | 37 | | 6.98 | 1.97 | 11.5 | 726 |
| RS03 | 8/3/99 | 34 | 31 | 28 | | 7.02 | 3.29 | 12.7 | 767 |
| RS03 | 8/21/99 | 42 | 37 | 33 | | 7.00 | 2.04 | 12.1 | 761 |
| RS03 | 9/4/99 | 51 | 39 | 35 | | 6.98 | | 12.3 | 769 |
| RS03 | 9/19/99 | 37 | 30 | 29 | | 7.03 | 5.43 | 11.2 | 719 |
| RS03 | 10/6/99 | 28 | 25 | 28 | | 6.80 | 4.38 | 11.2 | 735 |
| RS03 | 10/25/99 | 25 | 21 | 21 | | 6.97 | 2.69 | 11.1 | 702 |
| RS03 | 11/27/99 | 26 | 20 | 18 | | 6.07 | 5.08 | 10.4 | 508 |
| RS03 | 12/29/99 | 35 | 29 | 29 | | 6.75 | 9.24 | 9.5 | 619 |
| RS03 | 1/30/00 | 23 | 21 | 20 | | | 7.28 | 9.1 | 572 |
| RS03 | 3/4/00 | 32 | 26 | 23 | | 6.77 | 8.50 | 9.4 | 610 |

**Table D.2 (cont'd) Phosphorus and field data for the Robe catchment sites.**

| Code | Date | TP | TDP | DRP | SWL | pH | DO | Temp | EC |
|---|---|---|---|---|---|---|---|---|---|
| | | | ($\mu g\ l^{-1}$) | | (m) | | ($mg\ l^{-1}$) | (°C) | ($\mu S\ cm^{-1}$) |
| RS04 | 7/8/98 | 22 | | | | | | 11.5 | 734 |
| RS04 | 8/6/98 | 41 | 42 | 21 | | | | 11.3 | 750 |
| RS04 | 9/10/98 | 31 | 30 | 31 | | | | 10.6 | 705 |
| RS04 | 2/20/99 | 22 | 17 | | | 7.35 | 5.35 | 8.7 | 834 |
| RS04 | 5/30/99 | | | 21 | | 6.94 | 2.46 | 12.8 | 628 |
| RS04 | 6/12/99 | 32 | | | | 7.18 | 2.19 | 11.4 | 692 |
| RS04 | 6/29/99 | 27 | 25 | 23 | | 7.05 | 3.03 | 11.6 | 709 |
| RS04 | 7/17/99 | 28 | 24 | 23 | | 7.05 | 3.10 | 13.5 | 754 |
| RS04 | 8/3/99 | 32 | 28 | 22 | | 7.03 | 3.59 | 11.9 | 784 |
| RS04 | 8/21/99 | 35 | 32 | 28 | | 7.04 | 3.07 | 11.9 | 773 |
| RS04 | 9/4/99 | 43 | 40 | 31 | | 7.08 | | 11.4 | 791 |
| RS04 | 9/19/99 | 37 | 28 | 27 | | 7.00 | 6.38 | 11.1 | 758 |
| RS04 | 10/6/99 | 29 | 22 | 24 | | 6.78 | 4.29 | 11.1 | 741 |
| RS04 | 10/25/99 | 22 | 25 | 18 | | 7.12 | 5.30 | 11.3 | 706 |
| RS04 | 11/27/99 | 34 | 23 | 21 | | 5.40 | 3.54 | 10.0 | 706 |
| RS04 | 12/29/99 | 33 | 22 | 21 | | 7.10 | 9.80 | 9.4 | 653 |
| RS04 | 1/30/00 | 25 | 18 | 16 | | | 6.44 | 8.8 | 576 |
| RS04 | 3/4/00 | 35 | 24 | 20 | | 6.72 | 6.45 | 8.9 | 630 |
| RS05 | 7/8/98 | 18 | | | | | | 11.1 | 754 |
| RS05 | 8/7/98 | 18 | | | | | | 11.5 | 762 |
| RS05 | 9/10/98 | 9 | | | | | | 10.4 | 726 |
| RS05 | 2/20/99 | 20 | | | | 7.16 | 6.61 | 9.5 | 791 |
| RS05 | 6/12/99 | 17 | | | | 7.12 | 6.53 | 10.6 | 832 |
| RS06 | 7/7/98 | 5 | | | | | | 12.1 | 732 |
| RS06 | 8/6/98 | 44 | | | | | | 11.6 | 743 |
| RS06 | 9/8/98 | 29 | 20 | 18 | | | | 11.5 | 760 |
| RS06 | 2/19/99 | 24 | 21 | | | 7.37 | 4.75 | 9.1 | 674 |
| RS06 | 5/30/99 | | | 21 | | 7.11 | 3.45 | 10.9 | 705 |
| RS06 | 6/12/99 | 27 | | | | 7.05 | 1.17 | 10.9 | 740 |
| RS06 | 6/29/99 | 30 | 25 | 23 | | 6.79 | 1.35 | 11.5 | 781 |
| RS06 | 7/17/99 | 38 | 27 | 26 | | 6.89 | 1.68 | 12.9 | 814 |
| RS06 | 8/3/99 | 181 | 13 | 3 | | 6.94 | 1.47 | 13.4 | 838 |
| RS06 | 8/21/99 | 123 | 7 | 1 | | 6.94 | 1.92 | 12.2 | 802 |
| RS06 | 9/4/99 | 956 | 10 | 8 | | 7.00 | | 11.8 | 826 |
| RS06 | 9/19/99 | 91 | 63 | 51 | | 6.82 | 4.49 | 11.5 | 595 |
| RS06 | 10/6/99 | 31 | 26 | 24 | | 6.59 | 5.70 | 11.5 | 841 |
| RS06 | 10/25/99 | 26 | 20 | 18 | | 6.77 | 2.87 | 10.5 | 719 |
| RS06 | 11/27/99 | 112 | 59 | 50 | | 6.87 | 4.17 | 9.5 | 629 |
| RS06 | 12/29/99 | 48 | 39 | 38 | | 6.90 | 7.68 | 9.2 | 647 |
| RS06 | 1/30/00 | 32 | 25 | 19 | | | 4.05 | 8.8 | 583 |
| RS06 | 3/4/00 | 45 | 31 | 22 | | 7.10 | 5.98 | 9.0 | 626 |
| RS06 | 7/26/99 | 122 | | | | | | | |

**Table D.3 Phosphorus and field parameter data for the Limerick sites.**

| Code | Date | TP | TDP ($\mu g\ l^{-1}$) | DRP | SWL (m) | pH | DO ($mg\ l^{-1}$) | Temp (°C) | EC ($\mu S\ cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| LB01 | 8/20/98 | 8 | | | | | | | |
| LB01 | 9/24/98 | 1 | | | | | | | |
| LB01 | 9/2/99 | 3 | 3 | 4 | 6.78 | 7.12 | 4.70 | 12.9 | 668 |
| LB02 | 10/26/99 | 13 | 8 | 9 | | 6.50 | 6.99 | 10.3 | 705 |
| LB03 | 10/26/99 | 14 | 4 | 7 | | 6.86 | 1.19 | 10.7 | 225 |
| LB04 | 8/20/98 | 27 | | | | | | | |
| LB04 | 9/24/98 | 403 | | | | | | | |
| LB04 | 3/2/99 | 239 | 233 | 109 | 6.88 | 7.31 | 5.05 | 11.0 | 692 |
| LB04 | 7/19/99 | 33 | 32 | 32 | 18.45 | 7.29 | 6.07 | 11.9 | 672 |
| LB05 | 9/24/98 | 5 | | | | | | | |
| LB05 | 3/2/99 | 6 | 6 | 7 | | 7.29 | 6.65 | 10.0 | 413 |
| LB05 | 7/19/99 | 1039 | 1007 | 18 | 18.15 | 7.51 | 7.22 | 13.0 | 405 |
| LB06 | 9/24/98 | 3 | | | | | | | |
| LB06 | 7/28/99 | 2 | 4 | 2 | 19.03 | 7.25 | 1.46 | 13.9 | 721 |
| LB07 | 8/20/98 | 32 | | | | | | | |
| LB07 | 9/24/98 | 23 | | 24 | | | | | |
| LB07 | 3/4/99 | 33 | 31 | 27 | 30.99 | 7.16 | 7.78 | 9.6 | 658 |
| LB07 | 9/1/99 | 64 | 59 | 26 | | 7.00 | 8.66 | 11.9 | 640 |
| LB08 | 8/20/98 | 11 | | | | | | | |
| LB08 | 9/24/98 | 5 | | | | | | | |
| LB08 | 3/2/99 | 13 | 12 | 12 | 19.03 | 7.08 | 3.94 | 10.5 | 878 |
| LB08 | 7/19/99 | 11 | 11 | 11 | | 7.02 | 7.02 | 12.6 | 837 |
| LB09 | 9/24/98 | 21 | | | | | | | |
| LB09 | 3/2/99 | 43 | | | | 7.19 | 4.75 | 11.0 | 707 |
| LB09 | 7/19/99 | 47 | 47 | 19 | 2.20 | 6.89 | 5.08 | 12.5 | 664 |
| LB10 | 9/24/98 | 3 | | | 22.30 | | | 14.5 | 816 |
| LB10 | 10/7/99 | 2 | 2 | 5 | 24.90 | 7.19 | 9.10 | 13.1 | 836 |
| LB11 | 9/24/98 | 3 | | | 15.90 | | | 15.6 | 851 |
| LB11 | 10/7/99 | 3 | 2 | 7 | | 7.09 | 2.54 | 13.2 | 896 |
| LB12 | 9/24/98 | 839 | | | | | | | |
| LB12 | 3/4/99 | 13 | | | 3.82 | 7.29 | 8.41 | 9.2 | 722 |
| LB12 | 9/1/99 | 17 | 13 | 14 | 8.66 | 6.94 | 6.51 | 11.9 | 695 |
| LB13 | 7/27/99 | 20 | 21 | 22 | 13.30 | 7.12 | 5.66 | 12.2 | 650 |
| LB14 | 9/25/98 | 27 | | | 10.40 | | | 13.7 | 474 |
| LB14 | 10/7/99 | 213 | 2 | 4 | 8.65 | 6.60 | 2.10 | 12.1 | 505 |
| LB15 | 8/20/98 | 11 | | | | | | | |
| LB15 | 9/24/98 | 5 | | | | | | | |
| LB15 | 7/27/99 | 2 | 3 | 3 | | 7.26 | 7.02 | 12.7 | 805 |
| LB16 | 8/20/98 | 208 | | | | | | | |
| LB16 | 9/24/98 | 21 | | 6 | | | | | |
| LB16 | 7/27/99 | 11 | 12 | 6 | 25.20 | 7.18 | 6.79 | 13.9 | 847 |
| LB17 | 9/24/98 | 80 | | | | | | | |
| LB17 | 3/2/99 | 54 | | | 50.00 | 6.20 | 5.79 | 10.6 | 192 |
| LB17 | 7/19/99 | 64 | 64 | 55 | 50.00 | 6.14 | 4.48 | 12.4 | 167 |
| LB18 | 9/25/98 | 5 | | | 36.40 | | | 14.9 | 287 |
| LB18 | 10/26/99 | 13 | 5 | 8 | | 7.27 | | | 341 |
| LB19 | 9/24/98 | 11 | | | | | | | |
| LB19 | 3/4/99 | 9 | | | | 7.25 | 1.85 | | 471 |
| LB19 | 9/1/99 | 9 | 8 | 10 | 50.00 | 7.37 | 2.84 | 15.4 | 484 |
| LB20 | 8/20/98 | 68 | | | | | | | |
| LB20 | 9/24/98 | 72 | | 42 | | | | | |
| LB20 | 3/2/99 | 69 | | | 12.91 | 7.24 | 5.80 | 11.0 | 518 |
| LB20 | 7/19/99 | 67 | 66 | 66 | 17.95 | 6.89 | 4.29 | 12.5 | 526 |
| LB21 | 8/20/98 | 42 | | | | | | | |
| LB21 | 9/24/98 | 38 | | | | | | | |
| LB21 | 3/2/99 | 79 | 73 | 71 | 6.22 | 7.29 | 7.62 | 11.2 | 872 |
| LB21 | 7/19/99 | 39 | 38 | 39 | 17.08 | 7.17 | 4.68 | 12.2 | 858 |

**Table D.3 (cont'd) Phosphorus and field data for the Limerick sites.**

| Code | Date | TP | TDP ($\mu g\ l^{-1}$) | DRP | SWL (m) | pH | DO ($mg\ l^{-1}$) | Temp (°C) | EC ($\mu S\ cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| LB22 | 8/20/98 | 38 | | | | | | | |
| LB22 | 9/24/98 | 34 | | | | | | | |
| LB22 | 3/2/99 | 50 | | | 2.60 | 7.08 | 4.50 | 10.6 | 735 |
| LB22 | 7/19/99 | 39 | 38 | 38 | 12.20 | 7.21 | 4.29 | 12.3 | 766 |
| LB23 | 9/24/98 | 21 | | | | | | 15.1 | 849 |
| LB23 | 10/7/99 | 23 | 21 | 25 | | 6.94 | 3.30 | 13.7 | 860 |
| LB24 | 8/20/98 | 80 | | | | | | | |
| LB24 | 9/24/98 | 82 | | 72 | | | | | |
| LB24 | 3/2/99 | 77 | | | 29.92 | 6.81 | 9.34 | 10.9 | 508 |
| LB24 | 7/19/99 | 78 | 78 | 78 | 32.67 | 7.26 | 9.24 | 12.5 | 478 |
| LB25 | 9/24/98 | 539 | | | | | | | |
| LB25 | 3/2/99 | 219 | | | | 7.23 | 3.21 | 11.4 | 648 |
| LB25 | 7/19/99 | 1196 | 1200 | 355 | | 7.33 | 3.93 | 13.1 | 641 |
| LB26 | 8/20/98 | 86 | | | | | | | |
| LB26 | 9/24/98 | 82 | | | | | | | |
| LB26 | 7/28/99 | 81 | 81 | 81 | 18.20 | 7.20 | 5.83 | 13.1 | 576 |
| LB27 | 8/20/98 | 11 | | | | | | | |
| LB27 | 9/24/98 | 7 | | | | | | | |
| LB27 | 7/27/99 | 12 | 11 | 12 | 14.40 | 7.15 | 8.93 | 12.7 | 361 |
| LB28 | 3/1/99 | 180 | | | 4.20 | 7.51 | 3.40 | 11.2 | 483 |
| LB28 | 7/5/99 | 143 | 124 | 114 | | 7.40 | 6.48 | 13.6 | 476 |
| LB29 | 3/1/99 | 9 | | | 50.00 | 7.72 | 7.12 | 11.6 | 717 |
| LB29 | 7/5/99 | 161 | 159 | 12 | 50.00 | 7.46 | 6.20 | 13.4 | 685 |
| LB30 | 9/24/98 | 17 | | | 1.40 | | | | 903 |
| LB30 | 10/7/99 | 41 | 42 | 44 | 1.02 | 7.10 | 7.46 | 13.6 | 796 |
| LD01 | 9/25/98 | 84 | | | | | | | |
| LD01 | 3/4/99 | 180 | 177 | 91 | 1.69 | 7.09 | 3.78 | 9.4 | 808 |
| LD01 | 9/1/99 | 220 | 217 | 84 | 2.40 | 7.01 | 3.96 | 12.9 | 755 |
| LD02 | 8/20/98 | 12 | | | | | | | |
| LD02 | 9/24/98 | 5 | | | | | | | |
| LD02 | 7/27/99 | 10 | 9 | 8 | 2.10 | 7.24 | 8.30 | 14.6 | 580 |
| LS01 | 10/26/99 | 6 | 6 | 8 | | 6.15 | 10.07 | 9.8 | 111 |
| LS02 | 9/25/98 | 3 | | | | | | 13.7 | 88 |
| LS02 | 9/25/98 | 3 | | | | | | 13.7 | 88 |
| LS02 | 10/26/99 | 6 | 4 | 5 | | 6.27 | 5.96 | 9.8 | 107 |
| LS03 | 3/1/99 | 11 | | | | 6.55 | 10.52 | | 159 |
| LS03 | 7/5/99 | 10 | 9 | 9 | | 7.12 | 8.53 | 12.5 | 159 |
| LS04 | 9/24/98 | 5 | | | | | | | |
| LS04 | 3/4/99 | 5 | | | 1.50 | 7.31 | 4.34 | 9.9 | 1297 |
| LS04 | 9/1/99 | 4 | 5 | 4 | 1.74 | 6.87 | 5.18 | 12.9 | 740 |
| LS05 | 3/1/99 | 60 | 7 | | | 7.49 | 7.80 | 10.9 | 583 |
| LS05 | 7/5/99 | 42 | 43 | 21 | 2.87 | 7.26 | 7.98 | 14.9 | 562 |
| LS06 | 3/1/99 | 20 | | | | 7.17 | 4.80 | 11.2 | 674 |
| LS06 | 7/5/99 | 106 | 24 | 25 | 2.54 | 7.16 | 5.13 | 13.1 | 669 |
| LS07 | 8/20/98 | 13 | | | | | | | |
| LS07 | 9/24/98 | 13 | | | | | | | |
| LS07 | 7/27/99 | 7 | 9 | 8 | | 6.93 | 8.62 | 13.0 | 548 |
| LS08 | 8/20/98 | 3 | | | | | | | |
| LS08 | 9/24/98 | 5 | | | | | | | |
| LS08 | 3/4/99 | 9 | 6 | 9 | 1.20 | 7.25 | 2.32 | 11.9 | 611 |
| LS08 | 9/1/99 | 6 | 7 | 7 | | 7.38 | 3.65 | 14.8 | 573 |

**Table D.4 Ion data (mg $l^{-1}$) for Limerick public supply sites (after Deakin, 1994).**

| *Site Name* | *Geology* | *Year* | *EC* | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $Cl^{-}$ | $SO_4^{2-}$ | $CaCO_3$ | $NO_3^{-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LB05 | Silurian | 1994 | 385 | 52 | 15 | 8.4 | 0.6 | 14.4 | 7.1 | 179 | 6.1 |
| LS03 | Silurian | 1994 | 168 | 17 | 4 | 8 | 0.5 | 13.6 | 7 | 52 | 3.8 |
| LB24 | Old Red Sandstone | 1993 | 468 | 63 | 10.6 | 9.5 | 0.8 | 18.6 | 7.3 | 191 | 18.7 |
| LB27 | Old Red Sandstone | 1994 | 381 | 59 | 8 | 8.3 | 0.6 | 17 | 6.9 | 164 | 18.4 |
| LB09 | Old Red Sandstone | 1994 | 682 | 112 | 14 | 15.7 | 3.5 | 30.1 | 14 | 294 | 24.5 |
| LS05 | Old Red Sandstone | 1994 | 541 | 96 | 6 | 11.8 | 1.2 | 25.4 | 11.5 | 219 | 20.6 |
| LD02 | Kiltorcan | 1994 | 610 | 99 | 12 | 12.5 | 1.4 | 29.7 | 10.5 | 243 | 29.1 |
| LB04 | Kiltorcan | 1994 | 226 | 32 | 4 | 7.8 | 0.4 | 15.4 | 7.3 | 79 | 8.1 |
| LB17 | Kiltorcan | 1994 | 169 | 17 | 6 | 8.5 | 0.8 | 15.4 | 5.1 | 57 | 4.7 |
| LB01 | Mellon House Beds | 1993 | 645 | 95 | 19.3 | 18.3 | 2.5 | 23.7 | 23.1 | 301 | 5 |
| LB13 | Mellon House Beds | 1994 | 620 | 101 | 10 | 15.9 | 1.3 | 25.3 | 14 | 270 | 16.5 |
| LB08 | Ballysteen Limestones | 1993 | 818 | 140 | 12.6 | 16.8 | 3.5 | 34.6 | 29.7 | 339 | 22.2 |
| LB06 | Ballysteen Limestones | 1994 | 685 | 93 | 28 | 16.7 | 1.7 | 25.2 | 23 | 319 | 2.1 |
| LB22 | Ballysteen Limestones | 1994 | 848 | 136 | 17 | 22.9 | 9.2 | 36.8 | 41.6 | 347 | 26.5 |
| LB21 | Ballysteen Limestones | 1994 | 683 | 123 | 11 | 13.8 | 2.7 | 27.5 | 21.6 | 290 | 30.5 |
| LS07 | Ballysteen Limestones | 1994 | 578 | 90 | 11 | 15 | 1.1 | 27.9 | 15.3 | 245 | 14.7 |
| LB25 | Waulsortian Limestone | 1993 | 652 | 73 | 28.8 | 14.3 | 3.8 | 18.8 | 17.3 | 300 | 14.7 |
| LS04 | Waulsortian Limestone | 1994 | 700 | 107 | 25 | 15.1 | 1.2 | 28.2 | 12.3 | 333 | 8.3 |
| LB15 | Waulsortian Limestone | 1994 | 793 | 124 | 22 | 15.1 | 2.1 | 34.2 | 18.3 | 348 | 17.2 |
| LB16 | Waulsortian Limestone | 1994 | 828 | 131 | 25 | 15.9 | 3.3 | 33.8 | 18.3 | 371 | 22.5 |
| LB26 | Waulsortian Limestone | 1994 | 480 | 78 | 8 | 14.8 | 1 | 21.3 | 12.3 | 202 | 17.2 |
| LS08 | Waulsortian Limestone | 1994 | 541 | 70 | 20 | 13.5 | 0.8 | 19.6 | 11.5 | 256 | 4.2 |
| LS06 | Volcanics | 1993 | 630 | 110 | 20.7 | 13 | 2.5 | 20.8 | 15.1 | 290 | 10.6 |
| LB29 | Herbertstown Limestones | 1994 | 638 | 95 | 21 | 14.7 | 2.5 | 20.8 | 15.2 | 294 | 9.3 |
| LD01 | Muddy Shelf Limestones | 1994 | 738 | 136 | 9.7 | 14.5 | 1.7 | 29.9 | 29.9 | 340 | 11.9 |
| LB07 | Muddy Shelf Limestones | 1994 | 644 | 119 | 7 | 15.6 | 2.8 | 29.3 | 16.7 | 280 | 15.8 |
| LB12 | Namurian | 1994 | 568 | 21 | 10 | 96.1 | 3.1 | 19.7 | 9.2 | 279 | 0 |
| LB19 | Namurian | 1994 | 471 | 33 | 12 | 52.8 | 1.5 | 31.9 | 11.8 | 214 | 0.5 |

**Table D.5 Major ions data and field parameters and phosphorus fractions for Fergus catchment sites in February and June 1999.**

| Site Name | Sampled | Catchment | Site Type | DO | pH | Temp | EC | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $Cl^{-}$ | $NO_3^{-}$ | $SO_4^{2-}$ | $HCO_3^{-}$ | TP | TDP | DRP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | (°C) | (mg $l^{-1}$) | | (°C) | (µS $cm^{-1}$) | | | | | | (mg $l^{-1}$) | | | | | |
| FR01 | 13/02/99 | Fergus | Sink | 13.71 | 7.62 | 6.1 | 334 | 45.6 | 15.9 | 3.08 | 1.75 | 29.069 | 1.386 | 5.223 | 70.8 | 0.055 | 0.035 | |
| FS17 | 13/02/99 | Fergus | Spring | 8.91 | 7.32 | 8.2 | 424 | 67.4 | 13.9 | 2.85 | 1.82 | 29.771 | 3.379 | 7.002 | 98.2 | 0.052 | | |
| FS08 | 13/02/99 | Fergus | Spring | 13.2 | 7.7 | 8.8 | 431 | 71 | 11.5 | 2.11 | 1.12 | 29.113 | 3.871 | 5.961 | 99.1 | 0.018 | 0.019 | |
| FS03 | 13/02/99 | Fergus | Spring | 12.8 | 7.62 | 9.6 | 424 | 67.6 | 12.7 | 1.98 | 0.85 | 27.340 | 3.490 | 5.804 | 96.7 | 0.009 | 0.011 | |
| FS05 | 13/02/99 | Fergus | Spring | 6.1 | 7.35 | 8.6 | 420 | 51.4 | 13.6 | 2.84 | 1.51 | 29.370 | 3.583 | 6.229 | 73.9 | 0.048 | 0.044 | |
| FS06 | 13/02/99 | Fergus | Spring | 7.95 | 7.48 | 8.7 | 443 | 55.1 | 11.7 | 2.89 | 0.975 | 29.320 | 3.795 | 6.015 | 76.8 | 0.029 | | |
| FS09 | 13/02/99 | Fergus | Spring | 10.08 | 7.44 | 8.4 | 433 | 71.5 | 11.9 | 1.99 | 1.326 | 25.423 | 3.472 | 5.690 | 103.7 | 0.006 | | |
| FR01 | 13/07/99 | Fergus | Sink | 7.88 | 7.45 | 18.5 | 395 | 62 | 15.3 | 4.74 | 1.89 | 26.026 | 0.675 | 6.222 | 101.7 | 0.058 | 0.035 | 0.013 |
| FS17 | 13/07/99 | Fergus | Spring | 6.68 | 7.33 | 12.1 | 564 | 88.8 | 13 | 3.44 | 1.47 | 20.808 | 2.699 | 7.574 | 138.5 | 0.047 | 0.046 | 0.041 |
| FS03 | 13/07/99 | Fergus | Spring | 10.75 | 7.71 | 13.3 | 422 | 77.3 | 11.8 | 2.6 | 0.75 | 16.239 | 3.614 | 4.632 | 122.1 | 0.011 | 0.007 | 0.004 |
| FS05 | 13/07/99 | Fergus | Spring | 5.68 | 7.37 | 12 | 523 | 90.3 | 13 | 3.57 | 1.51 | 21.351 | 3.220 | 7.774 | 140.3 | 0.050 | 0.048 | 0.046 |
| FS07 | 13/07/99 | Fergus | Spring | 7.99 | 7.53 | 12.3 | 506 | 89.3 | 12.9 | 3.57 | 1.51 | 20.416 | 3.284 | 7.453 | 139.7 | 0.040 | 0.035 | 0.031 |
| FR02 | 13/07/99 | Fergus | River | 12.07 | 7.98 | 13.7 | 492 | 87.4 | 12.7 | 3.3 | 1.36 | 19.773 | 3.822 | 6.964 | 136.3 | 0.022 | 0.015 | 0.009 |
| FS09 | 14/07/99 | Fergus | Spring | 7.75 | 7.26 | 16.9 | 431 | 75 | 11.1 | 2.33 | 1.39 | 15.575 | 4.482 | 5.743 | 116.9 | 0.019 | 0.010 | 0.006 |
| FR03 | 14/07/99 | Fergus | River | 8.52 | 6.82 | 13.3 | 501 | 90 | 13.1 | 3.58 | 1.52 | 21.468 | 3.120 | 7.541 | 140.1 | 0.038 | 0.033 | 0.027 |
| FL03 | 14/07/99 | Fergus | Lake | 10.3 | 8.42 | 18.9 | 378 | 61.1 | 12.3 | 2.89 | 1.23 | 22.343 | 1.971 | 5.986 | 93.8 | 0.014 | 0.006 | 0.001 |
| Blank | 14/07/99 | | QC | | | | | 1.3 | 0.3 | 0.1 | 0.05 | 0.958 | 0.000 | 0.546 | 1.5 | | | |

**Table D.6 Major ions, field parameters and phosphorus fractions for Fergus and Robe catchment sites in September 1999.**

| Site Name | Sampled | Catchment | Site Type | DO ($mg\ l^{-1}$) | pH | Temp (°C) | EC ($\mu S\ cm^{-1}$) | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $Cl^{-}$ | $NO_3^{-}$ ($mg\ l^{-1}$) | $SO_4^{2-}$ | $HCO_3^{-}$ | TP | TDP | DRP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FB11 | 05/10/99 | Fergus | Borehole | | 6.94 | 12.2 | 593 | 54.9 | 62 | 15.18 | 1.14 | 26.941 | 0.326 | 7.027 | 177.6 | 0.032 | 0.03 | 0.032 |
| FR01 | 06/09/99 | Fergus | Sink | 7.19 | 7.19 | 17.9 | 425 | 61.15 | 15.1 | 4.55 | 2.615 | 27.171 | 1.040 | 8.862 | 95.9 | 0.073 | 0.039 | 0.021 |
| FS17 | 06/09/99 | Fergus | Spring | 4.96 | 7.20 | 13.1 | 510 | 90.1 | 11.6 | 3.52 | 1.5 | 19.770 | 5.361 | 7.373 | 134.0 | 0.053 | 0.049 | 0.042 |
| FS03 | 06/09/99 | Fergus | Spring | 9.94 | 7.36 | 13.8 | 352 | 55.6 | 8.8 | 2.05 | 1.23 | 11.689 | 3.120 | 3.682 | 91.7 | 0.034 | 0.019 | 0.013 |
| FS05 | 06/09/99 | Fergus | Spring | 5.4 | 7.29 | 12.0 | 500 | 87.5 | 12.1 | 3.435 | 1.57 | 20.237 | 5.605 | 8.093 | 134.2 | 0.066 | 0.057 | 0.048 |
| FS06 | 06/09/99 | Fergus | Spring | 7.6 | 7.43 | 12.5 | 489 | 86.1 | 11.5 | 3.29 | 1.45 | 19.499 | 4.991 | 7.708 | 131.0 | 0.043 | 0.040 | 0.033 |
| FS07 | 06/09/99 | Fergus | Spring | 7.32 | 7.43 | 12.5 | 489 | 85.9 | 12.1 | 3.4 | 1.54 | 19.686 | 5.281 | 7.877 | 132.4 | 0.059 | 0.048 | 0.040 |
| FR02 | 06/09/99 | Fergus | River | 10.64 | 7.65 | 13.5 | 464 | 80.1 | 11.4 | 3.13 | 1.5 | 18.478 | 4.395 | 7.239 | 124.4 | 0.046 | 0.031 | 0.023 |
| FS09 | 06/09/99 | Fergus | Spring | 6.23 | 7.46 | 13.5 | 428 | 77.55 | 9.9 | 2.295 | 1.765 | 14.608 | 11.381 | 7.002 | 111.5 | 0.217 | 0.019 | 0.009 |
| FR03 | 06/09/99 | Fergus | River | 9.34 | 7.43 | 13.3 | 479 | 84.2 | 11.9 | 3.35 | 1.86 | 19.270 | 4.635 | 7.656 | 130.3 | 0.070 | 0.048 | 0.039 |
| FL03 | 06/09/99 | Fergus | Lake | 3.65 | 8.38 | 18.2 | 382 | 61.6 | 11.8 | 2.9 | 1.35 | 21.183 | 1.745 | 6.288 | 97.4 | 0.026 | 0.009 | 0.003 |
| FS13 | 12/09/99 | Fergus | Spring | | 7.37 | 14.1 | 421 | 66 | 11.8 | 3.35 | 1.92 | 26.273 | 3.738 | 7.198 | 99.8 | 0.059 | 0.045 | 0.030 |
| FS14 | 12/09/99 | Fergus | Spring | | 7.49 | 14.9 | 391 | 63.35 | 11.85 | 3.215 | 2.015 | 20.276 | 3.600 | 7.185 | 94.7 | 0.062 | 0.043 | 0.030 |
| FS18 | 12/09/99 | Fergus | Spring | | 7.43 | 14.9 | 412 | 67.8 | 11.8 | 3.77 | 1.83 | 21.084 | 3.099 | 6.723 | 103.9 | 0.040 | 0.033 | 0.024 |
| RS06 | 04/09/99 | Robe | Spring | | 7.00 | 11.8 | 826 | 142.9 | 11.9 | 8.04 | 3.86 | 26.988 | 0.078 | 7.537 | 237.9 | 0.956 | 0.010 | 0.008 |
| RS01 | 04/09/99 | Robe | Spring | | 7.08 | 12.2 | 855 | 146.5 | 11.8 | 10.42 | 6.67 | 28.517 | 3.899 | 11.210 | 237.2 | 0.037 | 0.037 | 0.024 |
| RS04 | 04/09/99 | Robe | Spring | | 7.08 | 11.4 | 791 | 140.9 | 11.2 | 9.27 | 3.91 | 27.697 | 5.751 | 9.625 | 229.8 | 0.043 | 0.040 | 0.031 |
| RS03 | 04/09/99 | Robe | Spring | | 6.98 | 12.3 | 769 | 137.5 | 11.5 | 9.51 | 3.81 | 27.784 | 5.518 | 9.656 | 219.8 | 0.051 | 0.039 | 0.035 |
| Blank | 06/09/99 | | QC | | | | | 0.6 | 0.3 | 0.1 | 0.05 | 0.000 | 0.000 | 0.000 | | | | |

**Table D.7 Ion balance for Co. Limerick public supply wells (after Deakin, 1994). All parameters expressed as milliequivalents per litre.**

| Site Name | Geology | Year | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $Cl^{-}$ | $SO_4^{2-}$ | $CaCO_3$ | $NO_3^{-}$ | Sum Cations | Sum Anions | Ion Balance (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LB05 | Silurian | 1994 | 2.60 | 1.25 | 0.37 | 0.02 | 0.41 | 0.15 | 3.58 | 0.44 | 4.23 | 4.57 | -3.85 |
| LS03 | Silurian | 1994 | 0.85 | 0.33 | 0.35 | 0.01 | 0.38 | 0.15 | 1.04 | 0.27 | 1.54 | 1.84 | -8.76 |
| LB24 | Old Red Sandstone | 1993 | 3.15 | 0.88 | 0.41 | 0.02 | 0.52 | 0.15 | 3.82 | 1.34 | 4.47 | 5.83 | -13.25 |
| LB27 | Old Red Sandstone | 1994 | 2.95 | 0.67 | 0.36 | 0.02 | 0.48 | 0.14 | 3.28 | 1.31 | 3.99 | 5.22 | -13.29 |
| LB09 | Old Red Sandstone | 1994 | 5.60 | 1.17 | 0.68 | 0.09 | 0.85 | 0.29 | 5.88 | 1.75 | 7.54 | 8.77 | -7.55 |
| LS05 | Old Red Sandstone | 1994 | 4.80 | 0.50 | 0.51 | 0.03 | 0.72 | 0.24 | 4.38 | 1.47 | 5.84 | 6.81 | -7.61 |
| LD02 | Kiltorcan | 1994 | 4.95 | 1.00 | 0.54 | 0.04 | 0.84 | 0.22 | 4.86 | 2.08 | 6.53 | 7.99 | -10.08 |
| LB04 | Kiltorcan | 1994 | 1.60 | 0.33 | 0.34 | 0.01 | 0.43 | 0.15 | 1.58 | 0.58 | 2.28 | 2.74 | -9.18 |
| LB17 | Kiltorcan | 1994 | 0.85 | 0.50 | 0.37 | 0.02 | 0.43 | 0.11 | 1.14 | 0.34 | 1.74 | 2.02 | -7.34 |
| LB01 | Mellon House Beds | 1993 | 4.75 | 1.61 | 0.80 | 0.06 | 0.67 | 0.48 | 6.02 | 0.36 | 7.22 | 7.53 | -2.09 |
| LB13 | Mellon House Beds | 1994 | 5.05 | 0.83 | 0.69 | 0.03 | 0.71 | 0.29 | 5.40 | 1.18 | 6.61 | 7.58 | -6.87 |
| LB08 | Ballysteen Limestone | 1993 | 7.00 | 1.05 | 0.73 | 0.09 | 0.97 | 0.62 | 6.78 | 1.59 | 8.87 | 9.96 | -5.78 |
| LB06 | Ballysteen Limestone | 1994 | 4.65 | 2.33 | 0.73 | 0.04 | 0.71 | 0.48 | 6.38 | 0.15 | 7.75 | 7.72 | 0.22 |
| LB22 | Ballysteen Limestone | 1994 | 6.80 | 1.42 | 1.00 | 0.24 | 1.04 | 0.87 | 6.94 | 1.89 | 9.45 | 10.74 | -6.38 |
| LB21 | Ballysteen Limestone | 1994 | 6.15 | 0.92 | 0.60 | 0.07 | 0.77 | 0.45 | 5.80 | 2.18 | 7.74 | 9.20 | -8.66 |
| LS07 | Ballysteen Limestone | 1994 | 4.50 | 0.92 | 0.65 | 0.03 | 0.79 | 0.32 | 4.90 | 1.05 | 6.10 | 7.05 | -7.28 |
| LB25 | Waulsortian Limestone | 1993 | 3.65 | 2.40 | 0.62 | 0.10 | 0.53 | 0.36 | 6.00 | 1.05 | 6.77 | 7.94 | -7.96 |
| LS04 | Waulsortian Limestone | 1994 | 5.35 | 2.08 | 0.66 | 0.03 | 0.79 | 0.26 | 6.66 | 0.59 | 8.12 | 8.30 | -1.11 |
| LB15 | Waulsortian Limestone | 1994 | 6.20 | 1.83 | 0.66 | 0.05 | 0.96 | 0.38 | 6.96 | 1.23 | 8.74 | 9.53 | -4.32 |
| LB16 | Waulsortian Limestone | 1994 | 6.55 | 2.08 | 0.69 | 0.08 | 0.95 | 0.38 | 7.42 | 1.61 | 9.41 | 10.36 | -4.81 |
| LB26 | Waulsortian Limestone | 1994 | 3.90 | 0.67 | 0.64 | 0.03 | 0.60 | 0.26 | 4.04 | 1.23 | 5.24 | 6.12 | -7.83 |
| LS08 | Waulsortian Limestone | 1994 | 3.50 | 1.67 | 0.59 | 0.02 | 0.55 | 0.24 | 5.12 | 0.30 | 5.77 | 6.21 | -3.65 |
| LS06 | Volcanics | 1993 | 5.50 | 1.73 | 0.57 | 0.06 | 0.59 | 0.31 | 5.80 | 0.76 | 7.85 | 7.46 | 2.59 |
| LB29 | Herbertstown Limestone | 1994 | 4.75 | 1.75 | 0.64 | 0.06 | 0.59 | 0.32 | 5.88 | 0.66 | 7.20 | 7.45 | -1.66 |
| LD01 | Muddy Shelf Limestone | 1994 | 6.80 | 0.81 | 0.63 | 0.04 | 0.84 | 0.62 | 6.80 | 0.85 | 8.28 | 9.12 | -4.79 |
| LB07 | Muddy Shelf Limestone | 1994 | 5.95 | 0.58 | 0.68 | 0.07 | 0.83 | 0.35 | 5.60 | 1.13 | 7.28 | 7.90 | -4.07 |
| LB12 | Namurian | 1994 | 1.05 | 0.83 | 4.18 | 0.08 | 0.55 | 0.19 | 5.58 | 0.00 | 6.14 | 6.33 | -1.49 |
| LB19 | Namurian | 1994 | 1.65 | 1.00 | 2.30 | 0.04 | 0.90 | 0.25 | 4.28 | 0.04 | 4.98 | 5.46 | -4.56 |

**Table D.8 Ion balance for Fergus and Robe sites sampled in September 1999. All parameters expressed as milliequivalents per litre.**

| *Site Name* | *Catchment* | *Sampled* | *Ca* | *Na* | *Mg* | *K* | *Cl* | *$NO_3$* | *$SO_4$* | *$CACO_3$* | *Sum Cations* | *Sum Anions* | *Ion Balance (%)* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FR01 | Fergus | 06/09/99 | 3.06 | 0.66 | 0.38 | 0.07 | 0.77 | 0.02 | 0.18 | 3.14 | 4.16 | 4.11 | 0.60 |
| FS17 | Fergus | 06/09/99 | 4.51 | 0.50 | 0.29 | 0.04 | 0.56 | 0.09 | 0.15 | 4.39 | 5.34 | 5.19 | 1.44 |
| FS03 | Fergus | 06/09/99 | 2.78 | 0.38 | 0.17 | 0.03 | 0.33 | 0.05 | 0.08 | 3.01 | 3.36 | 3.46 | -1.46 |
| FS05 | Fergus | 06/09/99 | 4.38 | 0.53 | 0.29 | 0.04 | 0.57 | 0.09 | 0.17 | 4.40 | 5.23 | 5.23 | -0.01 |
| FS06 | Fergus | 06/09/99 | 4.31 | 0.50 | 0.27 | 0.04 | 0.55 | 0.08 | 0.16 | 4.30 | 5.12 | 5.09 | 0.29 |
| FR02 | Fergus | 06/09/99 | 4.01 | 0.50 | 0.26 | 0.04 | 0.52 | 0.07 | 0.15 | 4.08 | 4.80 | 4.82 | -0.23 |
| FS09 | Fergus | 06/09/99 | 3.88 | 0.43 | 0.19 | 0.05 | 0.41 | 0.18 | 0.15 | 3.66 | 4.54 | 4.40 | 1.65 |
| FR03 | Fergus | 06/09/99 | 4.21 | 0.52 | 0.28 | 0.05 | 0.54 | 0.07 | 0.16 | 4.27 | 5.05 | 5.05 | 0.05 |
| FL03 | Fergus | 06/09/99 | 3.08 | 0.51 | 0.24 | 0.03 | 0.60 | 0.03 | 0.13 | 3.19 | 3.87 | 3.95 | -1.01 |
| FS13 | Fergus | 12/09/99 | 3.30 | 0.51 | 0.28 | 0.05 | 0.74 | 0.06 | 0.15 | 3.27 | 4.14 | 4.22 | -0.97 |
| FS14 | Fergus | 12/09/99 | 3.17 | 0.52 | 0.27 | 0.05 | 0.57 | 0.06 | 0.15 | 3.10 | 4.00 | 3.88 | 1.51 |
| FS18 | Fergus | 12/09/99 | 3.39 | 0.51 | 0.31 | 0.05 | 0.59 | 0.05 | 0.14 | 3.41 | 4.26 | 4.19 | 0.85 |
| RS06 | Robe | 04/09/99 | 7.15 | 0.52 | 0.67 | 0.10 | 0.76 | 0.00 | 0.16 | 7.80 | 8.43 | 8.72 | -1.68 |
| RS01 | Robe | 04/09/99 | 7.33 | 0.51 | 0.87 | 0.17 | 0.80 | 0.06 | 0.23 | 7.78 | 8.88 | 8.88 | 0.01 |
| RS04 | Robe | 04/09/99 | 7.05 | 0.49 | 0.77 | 0.10 | 0.78 | 0.09 | 0.20 | 7.54 | 8.40 | 8.61 | -1.20 |
| RS03 | Robe | 04/09/99 | 6.88 | 0.50 | 0.79 | 0.10 | 0.78 | 0.09 | 0.20 | 7.21 | 8.26 | 8.28 | -0.10 |