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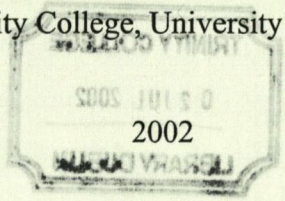
The relationship between catchment characteristics and lake chemistry in the Republic of Ireland

Volume I of II

By

Gary N. Free, B.A. (Mod.)

Thesis submitted in fulfilment for the degree of Doctor in Philosophy to Trinity College, University of Dublin.



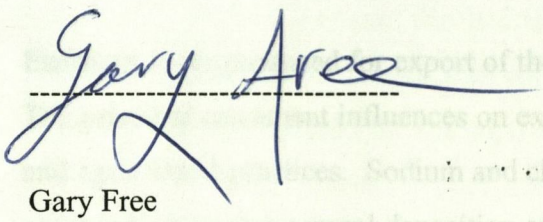
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Summary

The purpose of this thesis was to examine the relationships between catchment characteristics and lake chemistry in the Republic of Ireland. Additional aims were to examine the seasonal variation in water chemistry and, where possible, variation over a period of years. The impetus for this research came from draft work on the European Union's Water Framework Directive which currently requires catchment information to be used for the definition of lake types, risk assessment, and the design of monitoring programmes.

Thirty-one lakes were sampled monthly or approximately quarterly during 1996 and 1997. This sample contained a wide range of the types of catchments and lakes found in Ireland. In addition, a more limited suite of information on 189 lakes and catchments was examined.

Estimates were produced for export of the major ions Na^+, Cl^-, K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-}. The principal catchment influences on export were rock type, deposition of marine salts and agricultural practices. Sodium and chloride had a curvilinear decline from the west coast indicating that aerosol deposition of sea-salts was an important factor. Examining export rates led to the discovery of a good curvilinear fit whereas previous work that used concentration found only an approximate trend. A highly significant relationship between K^+ fertiliser application and non-marine K^+ export indicted that agricultural practices were an important controlling factor. The similarity of the Cl^- to SO_4^{2-} ratio between atmospheric deposition and export indicated that SO_4^{2-} inputs and outputs were in balance with the exception of lakes in Cavan and Monaghan where SO_4^{2-} export was substantially higher than atmospheric deposition. This was attributed to a higher soil organic S pool and increased mineralisation in this region following the drought of 1995. The amount of chemical weathering in catchments located on resistant rock types was investigated by calculating the export of non-marine base cations (C_B). Catchment area (m^2) divided by mean catchment relief explained 94% of the variation in C_B ($r^2 = 0.94$, $p \leq 0.0001$, $n = 13$).

Colour was found to be highest in lakes with peatland catchments, short residence times and few upstream lakes. In addition, lakes receiving high rainfall (> 1800 mm) in peatland catchments typically had low colour. This may suggest that there is a finite 'store' of colour available for release in catchments and that high rainfall dilutes this store resulting

in low colour. Examination of 10 years of data on colour and rainfall in Lough Pollaphuca revealed that the variation in colour was mainly caused by variation in rainfall with no obvious influence of dry periods in the summer as found in England. Negative relationships were found between colour and sunshine hours and sheep density. Colour was found to significantly reduce transparency and in certain cases decrease the dissolved oxygen concentration.

In contrast to national trends, no increase in TP concentration was found in three lakes in County Clare since 1981. Catchment characteristics that described agriculture (mainly pasture) were the most strongly correlated with TP export and concentration in both the 31 and 189 lake data-sets. Wet soils tended to export more TP than dry soils. Two published export coefficient models were used to predict TP export. Overall, the performances of the models were not adequate for them to be used as predictive tools. However, coefficients applied to a subset of six lakes that had agricultural catchments resulted in the explanation of 93% of the variation between observed and predicted export. However, the export was substantially overestimated but the significant relationship indicated that the model might be useful if the magnitude of the coefficients were reduced.

The seasonal variation in the concentration and fractional composition of nitrogen was examined. An 81 - 105% increase in TN, mainly in the NO_3^- fraction, was found between 1981-2 and 1996-7 in four Clare lakes. This was attributed to increased fertiliser application although higher mineralisation following a drought in 1995 may also have been responsible. Multiple regression explained 83% of the variation in TN and indicated that concentrations were highest in catchments that received large amounts of N fertiliser, low precipitation and where lakes were a small proportion of the catchment area.

Factors that were important throughout the thesis included the influence of drought, effect of elevated summer rainfall, and the unique behaviour of lake chemistry in limestone catchments.

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1 INTRODUCTION

1.1 Research rational and background

The chemistry of lake water is a result of many interacting processes. These may be viewed in the context of the hydrologic cycle acting at catchment level where the quality and quantity of precipitation is modified by chemical, physical and biological processes in the drainage area before being further modified within the lake (Gower, 1980).

The chemistry of lakes has long been recognised to be highly influenced by the nature of their catchments. As a result, there now exists a large body of literature that examines the relationships between catchment characteristics and freshwater chemistry. These studies either focus on a particular element such as phosphorus (Kirchner, 1975) or nitrogen (Arheimer *et al.*, 1996) or use a broader approach focusing on several elements (Close & Davies-Colley, 1990; Herlihy *et al.*, 1998).

These works, and others, underline that the catchment is the appropriate unit of study to achieve an understanding of freshwater chemistry. Such understanding is necessary for effective water quality management. This has now been recognised by the European Union through the production of the Water Framework Directive (Council of the European Communities, 2000) that requires a catchment approach to be used in several ways. For example, it:

- acknowledges the catchment as the unit of study through definition of 'river basin districts' (Article 2, paragraph 15);
- separates lakes into types based on several catchment characteristics such as altitude, geology, latitude, longitude and air temperature (Annex 2, paragraph 1.2);
- establishes type specific reference conditions of physicochemistry that may be based on modelling which would most likely involve information on catchment characteristics (Annex 2, paragraph 1.3);
- requires the identification of pressures, including diffuse sources, which can be assessed by "Estimation of land use patterns, including identification of main

urban, industrial and agricultural areas and, where relevant, fisheries and forests." (Annex 2, paragraph 1.4);

- identification of pressures, along with past monitoring data, is used to assess whether a lake will meet its water quality objectives (Annex 2, paragraph 1.5);
- those lakes identified to be at risk of not meeting their water quality objectives by utilising the catchment information and past monitoring data may be further characterised to optimise the design of both a monitoring programme and a programme of measures (Annex 2, paragraph 1.5); and
- promotes an understanding of catchment-lake relationships as the causes of a possible failure to meet water quality objectives must be investigated (Article 11, paragraph 5).

Some countries have already adopted a catchment approach to manage their water quality. The Swedish Environmental Protection Agency[†], in the absence of historical records or undisturbed catchments of a similar type, defines a river's reference total phosphorus (TP) and total nitrogen (TN) load by using one of a series of equations based on catchment characteristics and conservative chemical elements. For example, export of TP from a river in reference condition may be hindcasted by using an equation based on either the percentage of lake area in the drainage area, discharge, 'export' of chemical oxygen demand, export of silica or both discharge and colour.

The controls that a catchment exerts on lake chemistry are the subject of this thesis, but a corollary of this is that a lake can be used to indicate the nature and 'health' of its catchment. The Irish Environmental Protection Agency has used riverine TP load, TN load, NO_3^- concentration and the trophic state of lakes, amongst others, as key indicators of national environmental 'health' (Lehane, 1999). This reflects a need to find a true measure of national progress, one that reflects sustainable development rather than purely economic indicators such as gross domestic product.

Owing to the inherent link between a lake and its catchment, lake monitoring may be an effective way of monitoring the effects of climate change on the terrestrial environment. Warm, dry summers can result in higher NO_3^- (Smith and Stewart, 1989; Ferrier *et al.*,

[†] http://www.internat.environ.se/index.php3?main=/documents/legal/assess/assedoc/lakedoc/nutri1.htm

1995) and colour in freshwater (Mitchell & McDonald, 1992); these variables may be easier to monitor than changes in the drainage area of which they are indicative. The Water Framework Directive may achieve this, as one of its objectives is to assess long-term changes in natural conditions as separate from those caused by anthropogenic activity (Annex 5, sub-paragraph 1.3.1).

In contrast to other countries, little work has been done in Ireland on the controls that a catchment exerts on lake chemistry. This thesis addresses this deficiency. Some of the factors that make Ireland a unique location for study include the low acid deposition inputs, particularly in the west (Jordan, 1997; Dalton, 1999), wide range in trophic status of lakes (Foy & Bailey-Watts, 1998; Lucey *et al.*, 1999), diversity of lake types and a dominance of grasslands and peat bogs with less extensive arable farming than in the rest of Europe (Stanners & Bourdeau, 1995). Accordingly, the Water Framework Directive recognises that geographic areas have unique properties by defining lake types by 'ecoregion' as well altitude, mean depth, surface area and catchment geology in System A (Annex 2, paragraph 1.2.2).

This work formed part of a project entitled 'The Ecological Assessment of Irish Lakes' which was instigated as a result of the preparatory work and draft publications on the Water Framework Directive (e.g. Commission of the European Communities, 1994). The project generated an extensive amount of limnological data both directly and indirectly, through student theses. The project's final report (Irvine *et al.*, 2001) contains information on phytoplankton, profundal invertebrates, catchment characteristics, hindcasting of lake chemistry and vertebrate populations. The project produced Ph.D. theses on zooplankton (Caroni, 2000), littoral macroinvertebrates (White, 2001) and cydorids (De Eyto, 1999). Additional work was done on macrophytes (Lennon, 1997), rapid chemical assessment techniques (Kennelly, 1997; Day, 1997), sediment chemistry (Findlay, 1996) and palaeo-cydorid communities (Keaney, 1997) for the partial fulfilment of M.Sc. or B.A. degrees.

1.2 Research objectives

The primary objective of this thesis was to examine the relationships between catchment characteristics and lake chemistry across a diverse series of lakes in the Republic of Ireland. The aim was to produce models that adequately predict lake chemistry using catchment characteristics. These models will then be interpreted to identify key process in the catchment that control lake chemistry. An additional aim was to examine how changes in lake chemistry over the last 16 to 24 years yield an insight into the mechanisms in a catchment that control lake chemistry. To meet these objectives it was necessary to construct a through and detailed description of each of the 31 lake's chemistry and catchment. In this context an additional objective of the thesis was to document the seasonal chemistry of the lakes and to provide confidence in the results through incorporating quality control and quality assurance concepts. Additional aims were to produce export estimates where possible as these are lacking from Irish literature and also to provide information on the general limnology of the lakes. Other, more specific aims are detailed in the introduction to Chapter 4, Chapter 5, Chapter 6 and Chapter 7.

1.3 Research methodology

There are many ways to examine the relationships between catchments and lake chemistry (Table 1.1). The method chosen was a multi-lake study (n = 31) on a national scale. This method was considered the most suitable given the need to be representative of the lake and catchment types in Ireland. Multi-lake national studies have been employed in other countries such as Finland (Kortelainen, 1993) and New Zealand (Close & Davies-Colley, 1990) and allow a wide range in natural conditions to be examined. Therefore, the conclusions produced often have correspondingly wide applicability.

The 31 lakes are a small sample on a national scale as the Republic of Ireland has in excess of 5500 lakes (Irvine *et al.*, 2001). In order to address this, limited data on the summer chemistry of 189 lakes was obtained from Kennelly (1997), Day (1997) and through additional sampling. A limited suite of catchment characteristics for these lakes was supplied by Paul Mills (Compass Informatics) and through additional work. The

focus of this thesis is on the 31 lakes sampled seasonally with the less extensive data on the 189 lakes playing an auxiliary role.

1.4 Thesis outline

Chapter 2 introduces the Irish environment, the rational behind the choice of catchment characteristics and methods used. Some important inter-relationships between the catchment characteristics are highlighted. Chapter 3 describes the general limnology of the 31 lakes, providing information on thermal stratification, acid status, trophic status and summer phytoplankton composition. A grouping of the lakes based on acid and nutrient status follows this. The thesis is then structured by the chemical elements of interest: Chapter 4 on the major ions (Na^+, Cl^-, SO_4^{2-}, K^+, Mg^{2+}, Ca^{2+} and SiO_2), Chapter 5 on colour, Chapter 6 on phosphorus and Chapter 7 on nitrogen. Chapter 8 is a general discussion focusing on themes common to all the chapters ending with an assessment of the limitations and strengths of the thesis. Chapter 9 summarises the preceding chapters and highlights the key contributions of the thesis as well as providing suggestions for future research.

Table 1.1 Different experimental approaches to studying the relationships between catchments and lake chemistry.

Experimental Approach	Benefits	Limitations
Single plot (e.g. Kurz, 2000)	Ability to control many parameters which allows significance of some catchment characteristics (e.g. nutrient application, soil moisture) to be isolated.	Results are only applicable to similar sites, problems with scaling conclusions up to catchment level.
Single catchments (e.g. McGarrigle *et al.*, 1994)	Resources can be focused to obtain detailed catchment and chemical information. Ideal for application to lakes of high conservation value.	Results are only applicable to similar sites, generally done over a limited time period and conclusions may not take climatic variability into account.
Experimental catchments (e.g. Gjessing, 1994)	Ability to control a few parameters which allows their importance to be identified. Results are more applicable to 'natural' conditions. Ideal when threats are well defined such as acidification.	Conclusions only apply to similar catchments and numerous uncontrolled natural factors may complicate conclusions. Very costly experiments.
Time series of a catchment (e.g. Smith and Stewart, 1989)	Allows changes in a catchment to be related to those in lake chemistry. Changes can be attributed to a few important factors. Very relevant as similar lakes types may face similar pressures. Easy to model.	Very costly. Limited applicability of conclusions. Little or no control of experimental conditions.
Type-specific multi-catchment study (e.g. forested catchments) (e.g. Arheimer *et al.*, 1996)	Allows resources to be focused on the most relevant set of catchment characteristics for determining lake chemistry (e.g. age of forestry, drainage, felled areas). Ideal for focusing on specific impacts such as forestry or peat harvesting.	Results only applicable to a single catchment type. A limited time period may restrict conclusions to similar climatic conditions. If the chemical variation is small then very detailed and accurate catchment information may be required to explain it.
Regional study (Herlihy *et al.*,1998)	Reduces variation owing to geographic factors such as climate, soils and type of agriculture.	Limited applicability. Only a small range of catchment characteristics may be present in the sample (e.g. slope).
National study (e.g. Kortelainen, 1993)	Wide applicability of conclusions.	Logistical problems, expensive. Generally limited temporal intensity. Extensive suite of catchment characteristics needed owing to catchment diversity.
International study (e.g. Henriksen *et al.*, 1998)	Fundamental process and basis of ecosystem functioning may be isolated.	Logistical problems, expensive. Conclusions may be too broad. Often applied to data previously collected with resultant data incompatibility.

2 CATCHMENT CHARACTERISTICS

2.1 Introduction

A catchment may be defined as an area including a river or lake and its associated drainage area (Gower, 1980). A catchment characteristic is an environmental descriptor relating to a specific catchment attribute such as slope, drainage density, rock-type, and so on.

This chapter provides a brief introduction to the Irish environment and the parameters used to describe catchments. The parameters used to describe the 31 catchments are tabulated. Limited information on a further 158 catchments is summarised. Some implications and interrelationships of the catchment characteristics are discussed.

2.1.1 Introduction to the Irish environment

Ireland is located in Western Europe between 51.5° to 55.5° latitude and 5.5° to 10.5° longitude. The Republic of Ireland has an area of 70,282 km^2 and the entire island has an area of 84,421 km^2. The population in 1991 was 3.52 million (Stapleton, 1996).

The climate of Ireland is strongly influenced by the westerly atmospheric circulation in middle latitudes and the proximity of the North Atlantic Ocean. Precipitation in the east of Ireland ranges from 750 to 1000 mm, while in the west it ranges from 1000 to 1250 mm reaching 1500 mm in some coastal areas. In mountain districts, rainfall can be in excess of 2000 mm (Rohan, 1986). Approximate average annual runoff ranges from 200 to 400 mm in the east to 800 to 1000 mm in the west. This is generally high for non-mountainous areas in Europe (Stanners & Bourdeau, 1995). Temperature is strongly influenced by the proximity to the Atlantic Ocean. In coastal areas temperatures are warmer in winter and colder in summer than in the midlands. Mean daily minimum temperature in January ranges from 3.5 to 6.5°C. Mean daily maximum air temperature in July ranges from 14 to 16°C (Rohan, 1986). Sunshine hours is a measure of duration of sunshine of a certain intensity and is lowest in the north-east (annual average of 2.5 hours per day) and highest in the south-east (annual average of 3.0 hours per day). Sunshine hours increase as latitude decreases in Europe to greater than 5 hours in Sicily (Palz, 1979).

The geology of Ireland is diverse. Most of the centre of Ireland is low-lying and is dominated by Carboniferous limestone while coastal areas are frequently hilly with variable geology (Figure 2.1). Granite occurs in five major outcroppings in Ireland (the Leinster, Galway, Foxford, Donegal and Newry granites) (Figure 2.1) (Herries Davies & Stephens, 1978). Sandstone occurs in the south mainly as the Old Red Sandstone series which forms the Macgillycuddy's Reeks mountains in Killarney (Figure 2.1) (Geological Survey, 1985). Shale and sandstone mainly occur in the south-west in counties Limerick and Clare where they border Carboniferous limestone. Gneiss, schist and quartzite are found along the Galway coast (west Ireland) to Donegal in the north-west. Major outcroppings of basalt are confined to Northern Ireland. The last major rock type is the Silurian and Ordovician strata which run south-west from the north-east coast of Ireland (Figure 2.1) (Geological Survey, 1985).

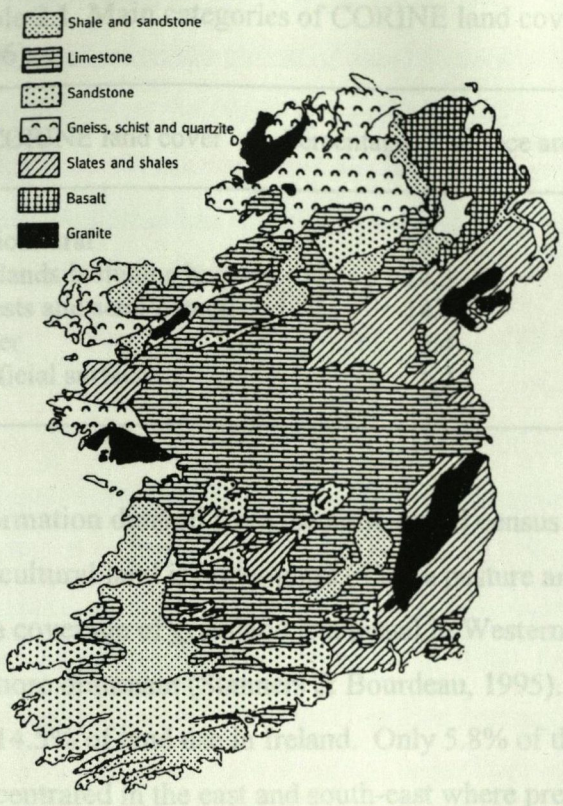


Figure 2.1 Generic rock types in Ireland (Collins & Cummins, 1996).

Most of Ireland lies at low altitudes. Goodale *et al.* (1998) have estimated that 87% of Ireland is below 200 m and 95% is below 300 m. Information about land cover in Ireland has been obtained through remote sensing by satellites. This information is stored in the co-ordination of information on the environment (CORINE) database and can be used to divide Ireland into five principal land cover types (Table 2.1). Agricultural land usage dominates, accounting for 68.1% of land cover where agriculture areas are defined as those consisting of arable land, permanent crops, pastures and heterogeneous agricultural areas (O'Sullivan, 1992). The wetlands category which includes bogs is the next most abundant, accounting for 14.3% of the surface area. The forests and semi-natural category account for 14.0%. Water and artificial surfaces account for 2.4 and 1.2% respectively.

Table 2.1 Main categories of CORINE land cover in the Republic of Ireland (Stapleton, 1996).

CORINE land cover	Percentage of surface area
Agricultural	68.1
Wetlands including bogs	14.3
Forests and semi-natural	14.0
Water	2.4
Artificial surfaces	1.2

Information derived from the agricultural census of 1988 indicates that the majority of agricultural land is under grass (43.5% pasture and 18.8% hay and silage, Table 2.2). This high coverage of grassland is unusual in Western Europe where arable agriculture tends to be more dominant (Stanners & Bourdeau, 1995). Rough grazing is estimated to account for 14.5% of land use in Ireland. Only 5.8% of the land is used for crops and this is concentrated in the east and south-east where precipitation is low and the soils are free draining (Department of Agriculture and Food, 1989).

Table 2.2 Land use in the Republic of Ireland in 1988 (Department of Agriculture and Food, 1989).

Land use (1988)	Percentage of surface area
Pasture	43.5
Hay and silage	18.8
Crops	5.8
Rough grazing	14.5
Other land uses	17.4

Irish agriculture is mainly cattle-based. Production is mainly based on grass. Dairy and cattle production are almost of equal economic importance, but cattle farmed for meat are more numerous than those farmed for milk (5.6 and 1.5 million respectively in June 1995) (Table 2.3). These numbers have been relatively stable since 1970. In contrast, the total sheep population has more than doubled to over eight million in 1995 (Figure 2.2), mainly because of a change in the EC common policy on sheep-meat in 1980. This dramatic increase may have a substantial impact on semi-natural areas in Ireland as a large proportion are kept on hills and mountains (45% in 1988) (Department of Agriculture and Food, 1989; Department of Agriculture, Food and Forestry, 1997). In the west of Ireland, Whelan *et al.* (1998) have associated peatland erosion with high sheep densities. The number of pigs totalled over 1.5 million in 1995 (Table 2.3). Pig production is mainly concentrated in the south and north-east of Ireland. Pig production is intensive: 95% of pig production came from just 900 units in 1988. Poultry production takes place in specialised units and output in 1988 was 37 million broilers. Other poultry present in 1988 included 3.2 million turkeys and 1.9 million hens (Department of Agriculture and food, 1989).

Table 2.3 Livestock numbers for June 1995 (Department of Agriculture, Food and Forestry, 1997).

Livestock	Numbers in 1995
Dairy cattle	1,511,100
Other cattle	5,611,100
Total sheep	8,369,500
Total pigs	1,550,400

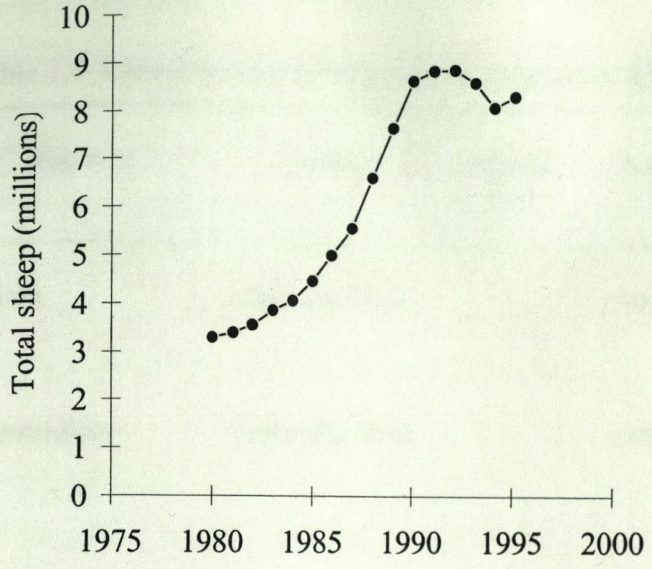


Figure 2.2 Total sheep numbers (millions) in Ireland in June 1980 to 1995 (Department of Agriculture, Food and Forestry, 1997).

After agriculture the CORINE database identified wetlands (such as bogs) as being the next most important land cover (14.3%) (Table 2.1). Other estimates of peatland cover range from 11 to 17% (Duggan, 1996; Sheehy Skeffington & O'Connell 1998). Most peatlands are found along the western coast of Ireland or at high altitudes. This is because the distribution of peatland is partly dependent on precipitation. High precipitation is important in providing the waterlogged anaerobic conditions which inhibit decay and thereby allow peatland development (O'Connell, 1987; Sheehy Skeffington & O'Connell, 1998). Precipitation is also important in determining the type of bog. Schouten (1984) noted that differences in bog morphology were closely related to annual precipitation (Table 2.4). Raised bogs occur in isolated depressions where the rainfall is 800 to 1100 mm. Blanket bogs cover large areas and occur where precipitation is greater than 1300 mm. Intermediate bogs occur where precipitation ranges between 1100 and 1300 mm.

Forests and semi-natural vegetation account for 14.0% of the surface area of Ireland (Table 2.1). About 6 - 8% of this is forestry, which is the lowest percentage coverage in Europe. Forest coverage is increasing by about 1% of surface area every three years. Forestry consists mainly of Western North American conifers with about 10% of broadleaf species (Stapleton, 1996; Stanners & Bourdeau, 1995).

Table 2.4 Characteristics of bog type as detailed in Schouten (1984).

Bog type	Location	Altitude (m)	Precipitation (mm)	Macro-morphology
Raised	East and West		800 - 1100	Isolated in topographic depressions, depth >8 m and domed surface.
Intermediate	Generally West		1100 - 1300	Raised bogs, which extend over the edges of the depressions in which they developed. Has some blanket bog characteristics.
Blanket (lowland)	West	0 - 150	> 1300	Cover extensive parts of the landscape. Follows the topography, depth 2 - 8 m.
Blanket (highland)	West	150 - 300	> 1300	
Blanket (mountain)	West and East	> 300	> 1300	

2.1.2 Factors used to describe catchments

The necessity and usefulness of many factors used to describe catchments is self-evident. It is obvious that an adequate description of the catchment must include information on catchment area, lake area, geology, soils, slope, land cover, density of farm animals and climatic data. Additional catchment characteristics that may be useful in explaining lake chemistry are described below or in later chapters.

One useful descriptor is the catchment to lake area ratio which indicates the size of a lake relative to its catchment. A low value indicates that a lake is a substantial proportion of its catchment. It would be expected that such lakes would have long residence times and nutrient chemistry would be strongly influenced by internal processes. In addition, if the surface area of the lake is large enough, precipitation may make up a considerable proportion of lake volume (Schindler, 1971; Engstrom, 1987). In contrast, lakes with high catchment to lake area ratios would typically have short residence times and the effect of internal processes would be expected to be lower, except in summer when flushing is low. Therefore, water chemistry in these lakes will be more strongly influenced by their

drainage area than internal processes compared to other lakes with a low catchment to lake area ratio.

Upstream lakes in catchments certainly influence the chemistry of downstream lakes. This can occur by upstream nutrient loss to lake sediments or increases in particulate fractions of some elements (Zhou *et al.*, 2000). In addition, seasonal fluctuations in lake chemistry may be muted by the presence of upstream lakes (Rasmussen *et al.*, 1989). There are several ways of indicating the relative importance of these processes. The first is the upstream lake area itself. However, the importance of upstream lake area will depend on its area relative to that of a downstream lake. An indication of the relative importance of upstream lakes may be obtained by calculating the ratio of upstream lake area to that of the downstream lake. If upstream lakes have a similar area as the sampled lake then this indicates that substantial alteration of chemical parameters may take place even before water reaches the sampled lake. However, the area of upstream lakes may be a function of catchment area, larger catchments would have more upstream lakes. One way of taking this into account is to express upstream lake area as a proportion of catchment area.

Further consideration shows that the position of upstream lakes in the catchment relative to the sampled lake is also important. For example, if upstream lakes are located relatively high in the catchment they will have less influence on the chemistry of the sampled lake than if they were located immediately upstream. One method used by Rasmussen *et al.* (1989) which circumvents this problem is to calculate the proportion of the catchment which flows into upstream lakes. This may give an indication of the extent to which catchment runoff is altered by upstream lakes. Thus, sampled lakes with lakes directly upstream would have a large proportion of their catchment flowing into upstream lakes. Finally it is true that some chemical qualities will be the result of alterations in both upstream lakes and in the sampled lake itself. The proportion of total lake area in the catchment may be useful in describing the importance of internal lake processes in all lakes in the catchment. An ideal approach would take retention time in all lakes into account but a lack of information on lake bathymetry generally prevents this.

Slope is frequently included in descriptions of catchments (Rasmussen *et al.*, 1989; Houle *et al.*, 1995; Mitchell & McDonald, 1995). Catchments with steep slopes will tend to have faster runoff which may increase erosion of soil particulates (Strahler, 1964). Steep slopes

tend to have thin stony soils that are well drained. Such soils may have less organic matter, carbon and nitrogen. Thus, slope can be related to soil depth, texture, moisture content and nutrient status (Young, 1972).

Measures of altitude and relief (a difference in elevation between two points) are useful in describing catchments. Measures of altitude such as lake altitude, mean catchment altitude and mean catchment boundary altitude may be used to infer several things about a catchment. For example, high altitudes are associated with high precipitation and low temperature (Black, 1996; Goodale *et al.*, 1998). In Ireland, a high altitude also implies a non-limestone geology as limestone mainly occurs in low-lying areas in the midlands (Geological survey, 1985). A high lake altitude may also mean that the lake is located close to the head of a catchment and that the catchment area is likely to be small.

Maximum catchment relief is the difference in height between the catchment outflow and the highest point on the catchment boundary. However, high summits may give misleading results. Therefore, measuring relief as the difference in height between mean catchment boundary height and catchment outflow may be better (Strahler, 1964). The measures of relief differ from those of altitude in that they are more indicative of the potential energy (owing to height) in a defined catchment (Strahler, 1964). Measures of relief may be divided by a horizontal distance to give a relief ratio (Strahler, 1964).

Drainage density is of fundamental importance as a catchment descriptor (Gregory & Walling, 1973). It is derived by dividing the total river channel length by the total catchment area (Strahler, 1964). A high drainage density means that there is a long length of river channel per unit area in the catchment. A high drainage density is often associated with low infiltration, low groundwater storage and a flashier hydrograph. A high drainage density is also associated with a high sediment yield (Knighton 1984, cited in Gordon *et al.*, 1992). Estimates of drainage density are dependent on map scale, watershed shape, relief, climate, geology, soils and vegetation (Gordon *et al.*, 1992; Black, 1996; Strahler, 1964).

The ruggedness number (dimensionless) is calculated as the product of maximum catchment relief (km) and drainage density (km^{-1} km^2) (Strahler, 1964). Catchments with a high maximum relief will give precipitation a high potential energy. If this is coupled with

a high drainage density (i.e. a high ruggedness number) runoff may be rapid. Therefore, such catchments may be expected to have higher amounts of physical erosion. Hydrographs from catchments with a high ruggedness number may be expected to show sharp peaks.

Another parameter that attempts to express several properties of catchments is the flow path index used by Houle *et al.* (1995). This index is calculated as the natural logarithm of drainage area divided by shoreline length divided by catchment slope. Higher flow path values tend to be associated with large catchments that have a low slope and a small lake perimeter.

Catchment shape is also important in describing catchments because it affects hydrograph shape; long rectangular shaped catchments may take longer to drain than circular catchments that drain faster and have peaked hydrographs (Black, 1996). Two methods may be used to quantify shape. The first is the compactness coefficient which compares the catchment boundary length with that of a circle of the same area as the catchment (Gravelius cited in Wisler and Brater, 1959). The closer the catchment boundary length is to that of a circle (compactness coefficient = 1) the more compact the catchment is. Another measure of catchment shape is the crenulation of the catchment perimeter which is calculated by dividing the length of the catchment boundary (km) by the catchment area (km^2) (Miller, 1953, cited in Mitchell & McDonald, 1995).

2.2 Materials and methods

Thirty-one catchments and lakes were selected in the Republic of Ireland (Figure 2.3). They were selected to represent the diversity of catchments and lakes, to enable comparison with previous studies and for ease of sampling. The names of the lakes, counties where they are located, national grid references and national lake codes are presented in Table 2.5. Grid references are for the centre of the lake where samples were taken and were obtained using a Garmin GPS 38, the stated accuracy of which was ± 100 m. Lough Leane, Muckross and Caragh were sampled from the shoreline but the grid reference refers to the centre of the lake. The national lake code details a lakes hydrometric area, river catchment code, lake order (ordered on distance from the river mouth) and sub-basin where this is relevant (Irvine *et al.*, 2001).

A further 158 lakes were sampled once during the summer of 1996 or 1997 (Figure 2.4). Data from the 31 lakes (June 1997) was combined with the 158 lakes to give a total sample size of 189. A less extensive suite of catchment characteristics were determined for these lakes.

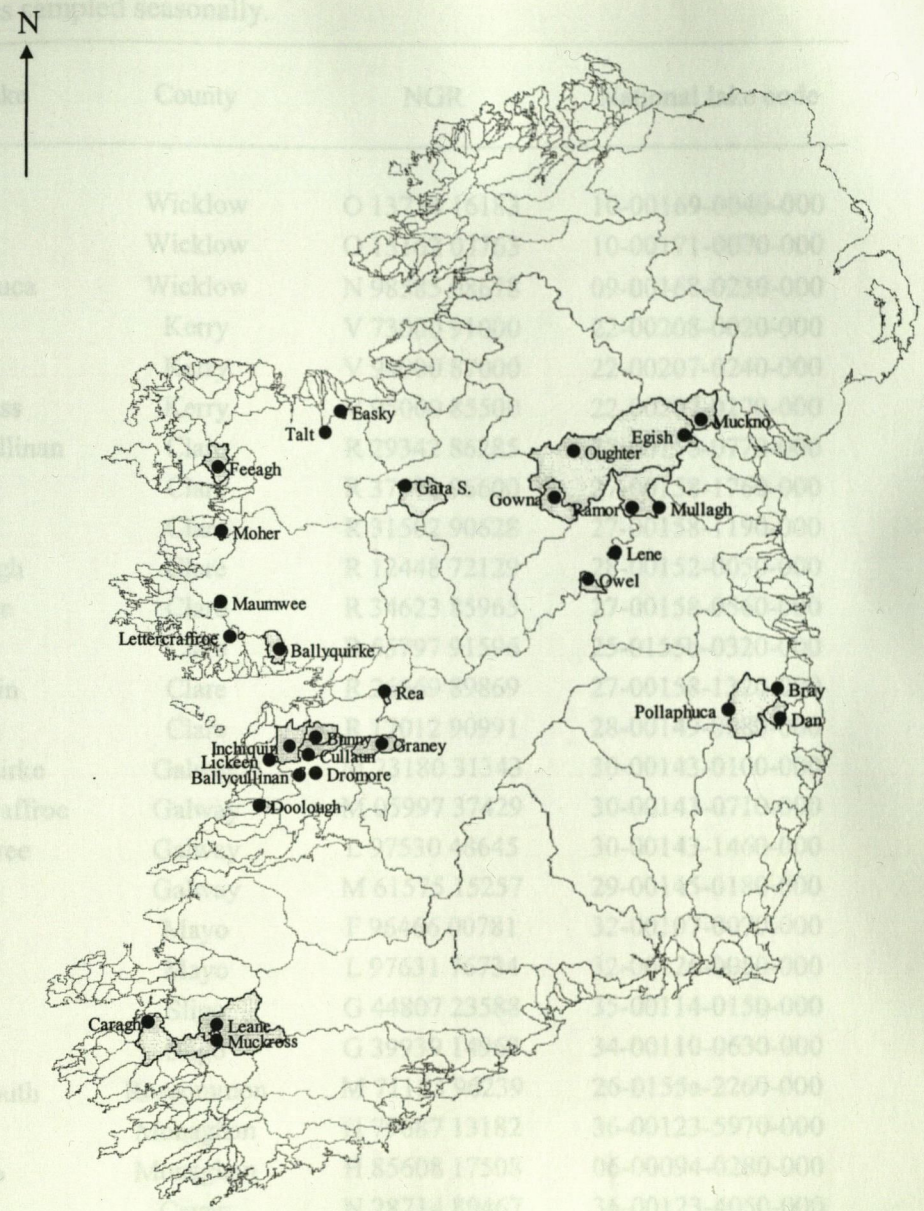


Figure 2.3 Location of lakes and catchments studied between March 1996 and December 1997 (n = 31).

Table 2.5 Lake name, county, national grid reference (NGR) and national lake code for the 31 lakes sampled seasonally.

Lake	County	NGR	National lake code
Bray	Wicklow	O 13724 16183	10-00169-0040-000
Dan	Wicklow	O 15162 03763	10-00171-0070-000
Pollaphuca	Wicklow	N 98585 08678	09-00168-0230-000
Caragh	Kerry	V 73000 91000	22-00208-0020-000
Leane	Kerry	V 94000 87000	22-00207-0240-000
Muckross	Kerry	V 95000 85500	22-00207-0270-000
Ballycullinan	Clare	R 29342 86285	27-00158-0770-000
Bunny	Clare	R 37376 96600	27-00158-1760-000
Cullaun	Clare	R 31502 90628	27-00158-1190-000
Doolough	Clare	R 12448 72129	28-00152-0050-000
Dromore	Clare	R 34623 85965	27-00158-0560-000
Graney	Clare	R 55797 91596	25-0155b-0320-000
Inchiquin	Clare	R 26669 89869	27-00158-1320-000
Lickeen	Clare	R 17012 90991	28-00149-0080-000
Ballyquirke	Galway	M 23180 31343	30-00143-0100-000
Lettercraffroe	Galway	M 05997 37429	30-00143-0710-000
Maumwee	Galway	L 97530 48645	30-00143-1460-000
Rea	Galway	M 61575 15257	29-00145-0180-000
Feeagh	Mayo	F 96466 00781	32-00107-0070-000
Moher	Mayo	L 97631 76734	32-00126-0050-000
Easky	Sligo	G 44807 23588	35-00114-0150-000
Talt	Sligo	G 39939 14963	34-00110-0630-000
Gara South	Roscommon	M 71153 96239	26-0155a-2260-000
Egish	Monaghan	H 79687 13182	36-00123-5970-000
Muckno	Monaghan	H 85608 17508	06-00094-0280-000
Gowna	Cavan	N 28714 89467	36-00123-4050-000
Mullagh	Cavan	N 67797 85427	07-00159-0220-000
Oughter	Cavan	H 34195 07527	36-00123-3230-000
Ramor	Cavan	N 62138 85791	07-00159-0600-000
Lene	Westmeath	N 52015 68235	07-00159-1150-000
Owel	Westmeath	N 40176 58745	26-00157-0260-000

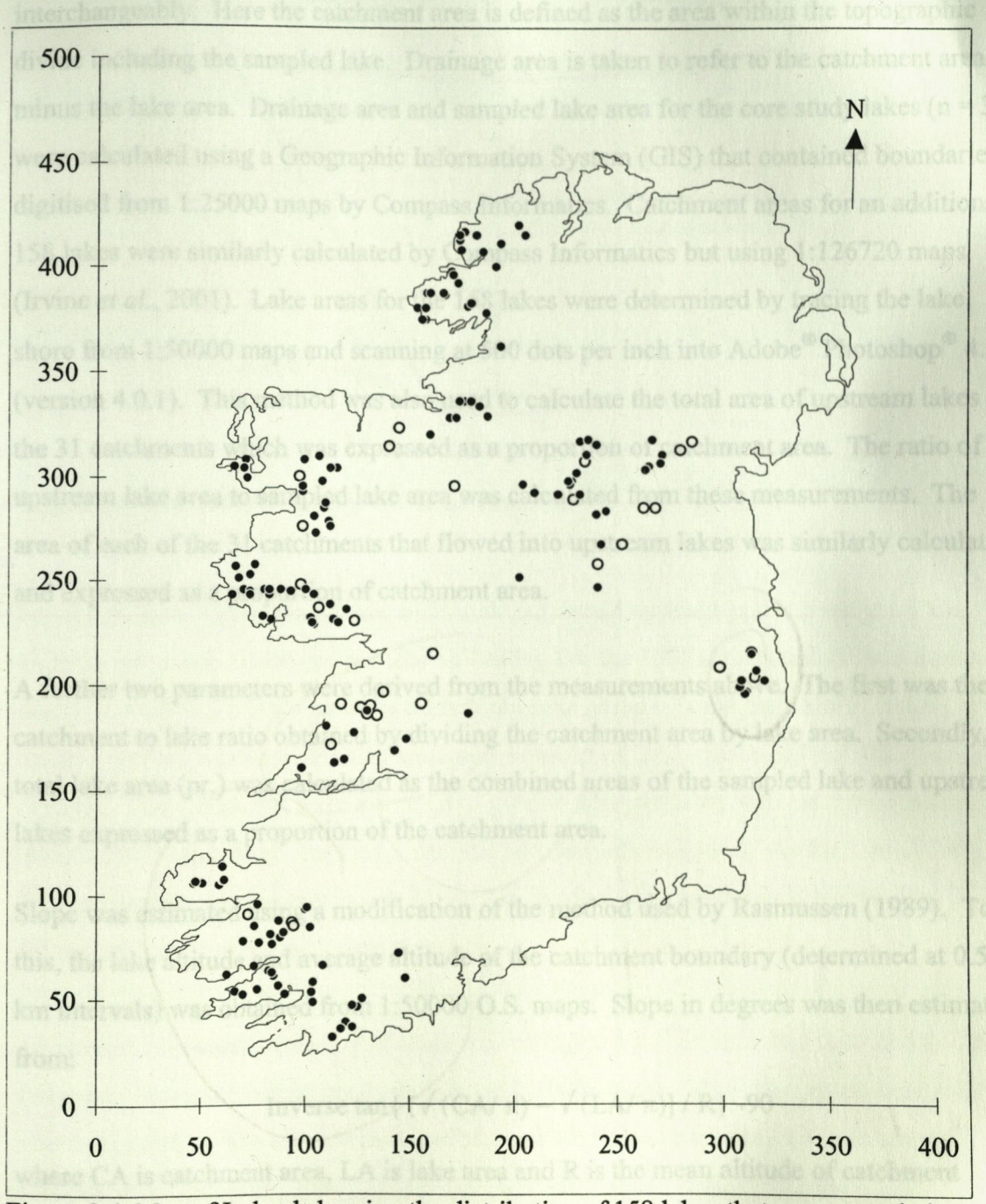


Figure 2.4 Map of Ireland showing the distribution of 158 lakes that were sampled once in summer or early autumn (●) together with the 31 sampled seasonally (O). Scale corresponds to part of the national grid in km.

2.2.1 Geophysical parameters

In the literature the terms catchment, drainage area and watershed are often used interchangeably. Here the catchment area is defined as the area within the topographic divide including the sampled lake. Drainage area is taken to refer to the catchment area minus the lake area. Drainage area and sampled lake area for the core study lakes (n = 31) were calculated using a Geographic Information System (GIS) that contained boundaries digitised from 1:25000 maps by Compass Informatics. Catchment areas for an additional 158 lakes were similarly calculated by Compass Informatics but using 1:126720 maps (Irvine *et al.*, 2001). Lake areas for the 158 lakes were determined by tracing the lake shore from 1:50000 maps and scanning at 500 dots per inch into Adobe® Photoshop® 4.0 (version 4.0.1). This method was also used to calculate the total area of upstream lakes in the 31 catchments which was expressed as a proportion of catchment area. The ratio of upstream lake area to sampled lake area was calculated from these measurements. The area of each of the 31 catchments that flowed into upstream lakes was similarly calculated and expressed as a proportion of catchment area.

A further two parameters were derived from the measurements above. The first was the catchment to lake ratio obtained by dividing the catchment area by lake area. Secondly, total lake area (pr.) was calculated as the combined areas of the sampled lake and upstream lakes expressed as a proportion of the catchment area.

Slope was estimated using a modification of the method used by Rasmussen (1989). To do this, the lake altitude and average altitude of the catchment boundary (determined at 0.5 km intervals) was obtained from 1:50000 O.S. maps. Slope in degrees was then estimated from:

$$\text{Inverse tan}\{ [\sqrt{(CA/\pi)} - \sqrt{(LA/\pi)}] / R\} - 90$$

where CA is catchment area, LA is lake area and R is the mean altitude of catchment boundary minus lake altitude in meters. Thus, the equation subtracts the radius of a circle that is equivalent to the lake area from the radius of the catchment area; this length now equals the opposite side of a right-angled triangle (Figure 2.5). The mean altitude of catchment boundary minus lake altitude (R) is the adjacent. Tan equals opposite divided by adjacent which was used to obtain the angle using mathematical tables. Subtracting this angle from 90° gives an estimate of the slope of the catchment.

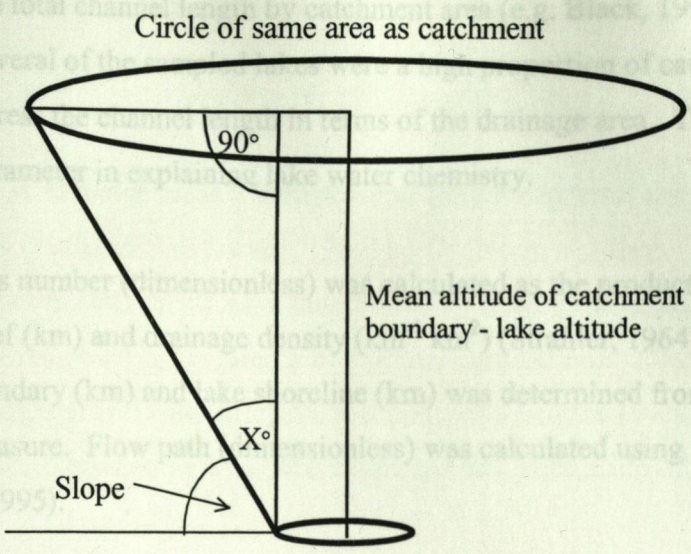


Figure 2.5 Calculation of slope of the catchments.

For the 31 lakes the mean catchment altitude (m) was estimated as the average of lake altitude and mean catchment boundary altitude. For the 158 lakes sampled once it was determined from 1:50000 maps by determining the altitude in the centre of each km^2 grid located predominantly within the catchment boundary (Grid square method after Strahler (1964)). These altitudes were averaged to give an approximate mean catchment altitude. Where catchments were less than 1 km^2 the lake altitude was used. As the Lough Derg and Ree catchments were exceptionally large, 256 random measurements (generated by Microsoft Excel) of altitude were made.

Maximum catchment boundary altitude was obtained from altitude data recorded at 0.5 km frequency along the catchment boundary on 1:50000 maps. Maximum catchment relief was calculated as lake altitude minus maximum catchment boundary altitude using 1:50000 maps (Strahler, 1964). A similar parameter, mean catchment relief, was calculated by subtracting lake altitude from mean catchment boundary altitude (Strahler, 1964). In an attempt to emulate a relief ratio (Strahler, 1964) catchment area (m^2) was divided by mean catchment relief (m).

Total channel length (km) was determined by measuring the length of all catchment rivers visible on 1:50000 maps with a map measure. Drainage density was calculated by dividing

total channel length (km) by drainage area (km^2). Ordinarily drainage density is calculated by dividing the total channel length by catchment area (e.g. Black, 1996; Strahler, 1964) but because several of the sampled lakes were a high proportion of catchment area it was decided to express the channel length in terms of the drainage area. This should be a more meaningful parameter in explaining lake water chemistry.

The ruggedness number (dimensionless) was calculated as the product of maximum catchment relief (km) and drainage density (km^{-1} km^2) (Strahler, 1964). The length of the catchment boundary (km) and lake shoreline (km) was determined from 1:50000 maps with a map measure. Flow path (dimensionless) was calculated using the equation below (Houle *et al.*, 1995).

Log_e[(drainage area in km^2/lake shoreline in km)/ slope in degrees)]

The compactness coefficient of the catchments was determined by multiplying 0.28 by the length of the catchment boundary (km) and dividing by the square root of the catchment area (km^2) (Gravelius cited in Wisler and Brater, 1959). The crenulation of catchment perimeter was calculated by dividing the length of the catchment boundary (km) by the catchment area (km^2) (Miller, 1953, cited in Mitchell and McDonald, 1995).

Results were expressed as either a proportion of the drainage area or as a proportion of the catchment area, depending on the catchment characteristic being determined. For example, both geology and soils are expressed as a proportion of the drainage area because lakes were not considered to be a soil or geological formation. In contrast, lake area was considered to be a land cover and all CORINE data is expressed as a proportion of catchment area. The difference in calculation will only be important for catchments where the lake sampled is a large proportion of the catchment. This was the case for twelve of the 31 lakes where the total lake area exceeded 10% of catchment area, namely Lough Bray, Dromore, Easky, Egish, Lene, Lettercraffroe, Lickeen, Muckross, Mullagh, Owel, Rea and Talt.

2.2.2 Geology

The rock type of the 31 drainage areas was determined from a digitised summary geological map of Ireland (scale 1:750000) (Geological Survey, 1985) using a GIS

operated by Compass Informatics. The geological composition is expressed as a proportion of the drainage area.

2.2.3 Soils

The soils of the 31 drainage areas were estimated from the general soil map of Ireland (scale 1:575000) (National Soil Survey, 1980) by Dr. Norman Allott. The areas of different soil types in catchments were determined by tracing the areas followed by cutting and weighing. Areas were aggregated into four soil associations. The four soil associations thought useful were peat, podzols and gleys, rendzinas and brown earths and rock and lithosols. These areas were then expressed as a proportion of the drainage area.

2.2.4 Land cover

The CORINE land cover GIS database was used by Compass Informatics to provide information on land cover for all catchments. The CORINE database was based on satellite images recorded by the Landsat Thematic Mapper satellite in 1989 and 1990. The CORINE project separated the satellite images into 44 hierarchical categories by computer-assisted photo-interpretation. The minimum size of land class resolved was 25 ha. Two of the standard categories were sub-divided for Ireland - pasture areas and peat bogs (O'Sullivan, 1992). For this study, three aggregations of CORINE land cover were also used. The first was termed total agriculture and consisted of the proportional sum of the CORINE land covers relating to agriculture: pasture high productivity, pasture low productivity, mixed pasture, principally agriculture, arable and complex cultivation. The second was termed total pasture and consisted of the proportional sum of pasture high productivity, pasture low productivity and mixed pasture. Thirdly, all peatland land covers (peat bogs, peat bogs unexploited, peat bogs exploited and moors and heathland) were summed and termed total peatlands.

In addition, information on farmland usage for all catchments was obtained from the 1990 census of agriculture by Compass Informatics. The principal farmland usage was grassland and this was recorded as four divisions by the survey: silage, permanent meadow, rough grazing and sum of rotation under five years. The amount of farmland used for arable agriculture was expressed as the category total crops. The total area farmed was calculated as the sum of the preceding categories. This data was provided by the

central statistics office in digital format for each district electoral division. As district electoral divisions did not correspond exactly to the location of catchments the data was partitioned according to the proportion of the district electoral division located within the catchment. Areas were expressed as a proportion of the drainage area.

2.2.5 Animal densities

The 1990 census of agriculture also included data on animal numbers for each District Electoral Division (DED). This provided estimates of cattle and sheep numbers for the catchments. Data was also available on human population numbers but not on pigs or poultry. Animal numbers were expressed per hectare of drainage area.

2.2.6 Climatic data

Three sets of data on precipitation were obtained. The first was a 30 year (1960-1990) average of net precipitation. This was generated by first calculating an estimate of evapotranspiration. This was calculated by using monthly evapotranspiration from 14 stations in Ireland to generate an interpolation surface (based on a triangular irregular network). This was used to calculate average monthly net precipitation for over 700 stations throughout Ireland. The data on net precipitation for these stations was then used to produce maps of net precipitation through a spatial interpolation process. Sections of this map were extracted and summarised by a GIS overlay technique to provide net precipitation for the catchments. In addition, monthly and annual net precipitation was calculated for the 31 catchments from January 1996 to December 1997. These data were generated from MetEireann data by Compass Informatics as above although spatial interpolation was performed using a grid cell or raster model rather than by a triangular irregular network (Irvine *et al.*, 2001).

Finally, an estimate of average monthly precipitation (1951 to 1980) was generated for the 189 lakes using the polynomial regression model of Gooddale *et al.* (1998). This model used catchment position and altitude to generate average monthly precipitation data. The predicted monthly precipitation data was summed to estimate annual precipitation. An estimate of net precipitation was calculated by averaging evapotranspiration for the 14 stations where it was measured and subtracting it from the predicted annual precipitation

(Rohan, 1986). Average evapotranspiration was 506 mm and varied little between stations (95% C.I. = 28 mm).

The model developed by Gooddale *et al.* (1998) was also used to estimate mean (1951 to 1980) monthly sunshine hours, monthly maximum temperature and monthly minimum temperature for all the catchments. This monthly data were averaged to give mean annual sunshine hours, mean annual maximum temperature and mean annual minimum temperature. Goodale *et al.* (1998) analysed the success of their predictive climatic models. The polynomial regression model had 95% confidence intervals of prediction of 33 mm for precipitation, less than 1°C for minimum and maximum temperature and 20 minutes for sunshine hours.

2.3 Results

Over 28 parameters were calculated in order to achieve a comprehensive description of the catchments. In this section, all catchment characteristics are presented in tabular form, but only the most important are considered in the text.

2.3.1 Geophysical parameters

The 31 catchments in the study had a wide range of physical characteristics (Table 2.6 to Table 2.10). Lake area ranged from 5 ha (Lough Ballycullinan) up to 1989 ha (Lough Leane). Catchment area ranged from 1.1 km^2 (Lough Mullagh) to 1478.7 km^2 (Lough Oughter) (Table 2.6). The catchment to lake area ratio for the 31 lakes ranged from three (Lough Leane and Mullagh) up to 135 for Lough Cullaun (Table 2.6). Thirteen lakes had a catchment to lake area ratio less than ten, namely Lough Lene, Mullagh, Rea, Owel, Lettercraffroe, Talt, Bray, Dromore, Egish, Easky, Lickeen, Lene and Mullagh.

The ratio upstream lake / sampled lake area ranged from 0 to 4.43 (Table 2.7). Lough Muckross, Cullaun, Ballyquirke and Oughter all had a smaller surface area than the combined area of upstream lakes. Twelve of the lakes had greater than 20% of their catchments flowing into upstream lakes (Table 2.7).

Lake altitude ranged from 6 m in Lough Ballyquirke to 378 m in Lough Bray. The highest maximum catchment boundary altitude was 970 m in the Leane and Muckross catchments. Catchment slopes ranged from 0.3° in Lough Gara South and Oughter to 12.9° and 18.9° in Lough Lettercraffroe and Bray (Table 2.8). The drainage density ranged from 0 in Lough Ballycullinan, Dromore and Mullagh to 2.19 in Lough Maumwee (Table 2.9).

Table 2.6 Sampled lake area, catchment area and catchment area / lake area. All tables in this chapter are ordered by county clockwise from Dublin (Table 2.5, Figure 2.3).

Lake	Lake area (ha)	Catchment area (ha)	Catchment area / lake area
Bray	25	143	6
Dan	105	6313	60
Pollaphuca	1974	30265	15
Caragh	499	16108	32
Leane	1989	55264	28
Muckross	275	6116	22
Ballycullinan	5	143	30
Bunny	102	7624	75
Cullaun	63	8436	135
Doolough	127	2198	17
Dromore	53	318	6
Graney	382	11172	29
Inchiquin	116	14893	129
Lickeen	84	818	10
Ballyquirke	79	7319	92
Lettercraffroe	84	386	5
Maumwee	27	425	16
Rea	307	1353	4
Feeagh	406	10033	25
Moher	40	934	23
Easky	123	1161	9
Talt	95	483	5
Gara South	203	18500	91
Egish	122	784	6
Muckno	364	16072	44
Gowna	1119	12834	11
Mullagh	35	114	3
Oughter	1106	147874	134
Ramor	741	25150	34
Lene	424	1169	3
Owel	1029	4694	5

Table 2.7 Upstream lake area (ha), upstream lake area (pr.), upstream lake / sampled lake area, proportion of catchment flowing into upstream lakes and total lake area (pr.) of the 31 catchments studied. pr. = proportion.

Lake	Upstream lake area (ha)	Upstream lake area (pr.)	Upstream lake / sampled lake area	Pr. of catchment flowing into upstream lakes	Total lake area (pr.)
Bray	0	0.00	0.00	0.00	0.17
Dan	50	0.01	0.48	0.29	0.02
Pollaphuca	13	0.00	0.01	0.00	0.07
Caragh	235	0.01	0.47	0.21	0.05
Leane	992	0.02	0.50	0.37	0.05
Muckross	361	0.03	1.31	0.88	0.10
Ballycullinan	1	0.00	0.20	0.00	0.04
Bunny	42	0.01	0.41	0.33	0.02
Cullaun	279	0.03	4.43	0.31	0.04
Doolough	3	0.00	0.02	0.01	0.06
Dromore	11	0.03	0.21	0.22	0.20
Graney	92	0.01	0.24	0.24	0.04
Inchiquin	9	0.00	0.08	0.01	0.01
Lickeen	3	0.00	0.04	0.04	0.11
Ballyquirke	200	0.03	2.53	0.76	0.04
Lettercraffroe	1	0.00	0.01	0.01	0.22
Maumwee	0	0.00	0.00	0.00	0.06
Rea	2	0.00	0.01	0.05	0.23
Feeagh	53	0.01	0.13	0.03	0.05
Moher	2	0.00	0.05	0.08	0.05
Easky	8	0.01	0.07	0.12	0.11
Talt	1	0.00	0.01	0.00	0.20
Gara South	9	0.00	0.04	0.01	0.01
Egish	4	0.00	0.03	0.05	0.16
Muckno	157	0.01	0.43	0.47	0.03
Gowna	26	0.00	0.02	0.03	0.09
Mullagh	0	0.00	0.00	0.00	0.31
Oughter	3785	0.03	3.42	0.60	0.03
Ramor	259	0.01	0.35	0.26	0.04
Lene	0	0.00	0.00	0.00	0.36
Owel	10	0.00	0.01	0.03	0.22

Table 2.8 Lake altitude, mean catchment boundary altitude, slope, mean catchment altitude, maximum catchment boundary altitude, maximum catchment relief and mean catchment relief of the 31 catchments.

Lake	Lake altitude (m)	Mean catchment boundary altitude (m)	Slope (°)	Mean catchment altitude (m)	Max. catchment boundary altitude (m)	Maximum catchment relief (m)	Mean catchment relief (m)
Bray	378	513	18.9	446	625	247	135
Dan	200	538	5.0	369	760	560	338
Pollaphuca	180	492	2.4	336	828	648	312
Caragh	15	432	4.0	224	950	935	417
Leane	17	401	2.0	209	970	953	384
Muckross	17	467	4.7	242	970	953	450
Ballycullinan	20	34	1.4	27	42	22	14
Bunny	17	99	1.1	58	260	243	82
Cullaun	16	53	0.4	34	228	212	37
Doolough	83	162	2.3	123	215	132	79
Dromore	16	26	1.0	21	43	27	10
Graney	46	197	1.8	122	393	347	151
Inchiquin	19	158	1.3	88	300	281	139
Lickeen	70	107	2.0	89	160	90	37
Ballyquirke	6	78	1.0	42	206	200	72
Lettercraffroe	155	209	5.3	182	278	123	54
Maumwee	46	244	12.9	145	585	539	198
Rea	81	111	1.6	96	170	89	30
Feeagh	11	334	4.1	173	684	673	323
Moher	88	137	2.1	113	210	122	49
Easky	185	340	6.8	263	510	325	155
Talt	136	243	8.9	190	370	234	107
Gara South	66	104	0.3	85	170	104	38
Egish	70	188	7.1	129	230	160	118
Muckno	90	176	0.8	133	330	240	86
Gowna	61	123	0.8	92	229	168	62
Mullagh	120	143	4.9	132	203	83	23
Oughter	45	137	0.3	91	270	225	92
Ramor	83	170	0.7	127	300	217	87
Lene	93	129	2.7	111	170	77	36
Owel	97	119	0.6	108	147	50	22

Table 2.9 Catchment area / mean catchment relief · 10^4, catchment boundary length, total channel length, drainage density and ruggedness number of the 31 catchments.

Lake	Catchment area (m^2) / mean catchment relief (m) · 10^4	Catchment boundary length (km)	Total channel length (km)	Drainage density (km^{-1} km^2)	Ruggedness number
Bray	1.1	4.5	1.1	0.93	0.23
Dan	18.7	33.3	64.2	1.03	0.58
Pollaphuca	97.0	82.8	366.9	1.30	0.84
Caragh	38.6	30.8	254.2	1.63	1.52
Leane	143.8	141.6	623.2	1.17	1.11
Muckross	27.5	67.3	191.5	1.55	1.47
Ballycullinan	10.5	4.5	0.0	0.00	0.00
Bunny	93.2	32.5	2.0	0.03	0.01
Cullaun	230.3	48.2	32.0	0.38	0.08
Doolough	27.7	18.0	24.7	1.19	0.16
Dromore	32.1	8.6	0.0	0.00	0.00
Graney	73.9	48.9	116.4	1.08	0.37
Inchiquin	107.3	65.3	43.4	0.29	0.08
Lickeen	21.9	10.5	9.2	1.25	0.11
Ballyquirke	101.2	39.0	73.6	1.02	0.20
Lettercraffroe	7.1	7.5	1.8	0.60	0.07
Maumwee	2.1	8.2	8.7	2.19	1.18
Rea	45.0	13.8	1.8	0.17	0.02
Feeagh	31.0	42.2	123.3	1.28	0.86
Moher	18.9	11.0	4.5	0.50	0.06
Easky	7.5	14.0	16.7	1.61	0.52
Talt	4.5	9.0	3.8	0.98	0.23
Gara South	490.9	61.5	137.4	0.75	0.08
Egish	6.6	12.5	4.0	0.60	0.10
Muckno	187.7	67.0	167.0	1.06	0.26
Gowna	207.6	58.7	94.7	0.81	0.14
Mullagh	4.9	3.8	0.0	0.00	0.00
Oughter	1603.2	232.0	1353.5	0.92	0.21
Ramor	288.5	89.0	235.6	0.97	0.21
Lene	32.6	16.1	0.4	0.05	0.00
Owel	211.2	22.3	11.8	0.32	0.02

Table 2.10 Flow path, crenulation of catchment perimeter and compactness coefficient for the 31 catchments.

Lake	Flow path	Crenulation of catchment perimeter	Compactness coefficient of catchment
Bray	-1.53	14.2	1.1
Dan	0.30	17.6	1.2
Pollaphuca	0.30	22.6	1.3
Caragh	0.30	5.9	0.7
Leane	0.90	36.3	1.7
Muckross	0.46	36.5	1.7
Ballycullinan	-0.01	13.9	1.0
Bunny	0.99	13.9	1.0
Cullaun	1.61	27.5	1.5
Doolough	0.21	14.7	1.1
Dromore	-0.30	23.3	1.4
Graney	0.69	21.4	1.3
Inchiquin	1.31	28.6	1.5
Lickeen	-0.20	13.5	1.0
Ballyquirke	1.04	20.8	1.3
Lettercraffroe	-0.89	14.6	1.1
Maumwee	-0.85	15.6	1.1
Rea	-0.06	14.0	1.0
Feeagh	0.29	17.7	1.2
Moher	0.13	12.9	1.0
Easky	-0.59	16.9	1.2
Talt	-1.06	16.8	1.1
Gara South	1.82	20.4	1.3
Egish	-0.91	19.9	1.2
Muckno	0.98	27.9	1.5
Gowna	0.70	26.8	1.4
Mullagh	-1.19	12.4	1.0
Oughter	1.81	36.4	1.7
Ramor	1.23	31.5	1.6
Lene	-0.67	22.2	1.3
Owel	0.55	10.5	0.9

2.3.2 Geology

The geological composition of the 31 catchments was diverse (Table 2.11). The geology was separated into three groups to facilitate interpretation and highlight differences between less resistant rock-types such as limestone and those that are more resistant such as granite (Table 2.11) (Plummer & McGeary, 1991). The first group contained drainage areas that had greater than 78% limestone (n = 9) and mainly occurred in Co. Clare and in the midlands. The second group had drainage areas that had greater than 77% of Ordovician and Silurian strata (n = 7) and were located in Cavan and Monaghan, with the exception of Lough Moher in Co. Mayo. The stratigraphic sequences in this region are dominated by greywackes of turbidite origin (Morris, 1984). The third category was dominated by other rock types that were typically resistant to weathering of which granite, Old Red Sandstone and schist/gneiss were the most common (n = 15). This group had a wide distribution.

Several of the lakes were known to have catchments with significant karstic drainage (Drew, 1975; Drew, 1988). In such catchments the topographic divide may differ considerably from the phreatic (water) divide. Thus, the geographic position and size of the catchment may be incorrect and therefore lead to inaccuracy in many of the descriptive parameters. It is therefore important to determine which of the 31 catchments had substantial groundwater drainage. This was done by examining the relationship between total river length and drainage area since lakes with substantial groundwater drainage may be expected to have less surface drainage. Figure 2.6 shows that drainage areas located on limestone (Group 1 Table 2.11) tended to have a shorter total river length than would be expected from their drainage area; these were Lough Inchiquin, Cullaun, Bunny, Dromore, Ballycullinan, Rea, Lene and Owel. It may be concluded that a substantial proportion of these catchments are drained by groundwater rather than surface water networks. Lough Gara South differed from the other limestone catchments in that its channel length was as high as catchments on non-limestone geology (Figure 2.6).

Table 2.11 Geology of the 31 catchments as a proportion of the drainage area.

Lake	Group	Granite	Old Red Sandstone	Schist & Gneiss	Quartzite	Coal Measures	Millstone Grit & Flagstone	Upper Avonian Shales and Sandstones	Lower Avonian/Carboniferous	Ryolites	Diorite, Gabbro, Dolerite	Ordovician	Silurian	Upper Carboniferous Limestone	Middle Carboniferous Limestone	Lower Carboniferous Limestone
Bray	3	1.00														
Dan	3	0.79										0.21				
Pollaphuca	3	0.80									0.01	0.19				
Caragh	3		0.99											0.01		
Leane	3		0.58			0.23	0.05	0.01		0.03				0.09	0.00	
Muckross	3		0.97			0.00								0.03	0.00	
Ballycullinan	1															1.00
Bunny	1													0.00		1.00
Cullaun	1															1.00
Doolough	3					0.54	0.46									
Dromore	1														0.31	0.69
Graney	3		0.64						0.02				0.34			
Inchiquin	1						0.07	0.15								0.78
Lickeen	3						0.49	0.51								
Ballyquirke	3	0.61		0.10										0.28		
Lettercraffroe	3	1.00														
Maumwee	3	0.42			0.58											
Rea	1								0.01					0.99		
Feeagh	3		0.11	0.44	0.44				0.01							
Moher	2											0.47	0.53			
Easky	3	0.42		0.58												
Talt	3	0.33		0.67												
Gara S.	1								0.07					0.93		
Egish	2											0.02	0.98			
Muckno	2											0.02	0.98			
Gowna	2					0.02			0.02			0.23	0.62	0.11		
Mullagh	2												1.00			
Oughter	2	0.03		0.01	0.00						0.05	0.31	0.46	0.09	0.08	
Ramor	2											0.02	0.98	0.00		
Lene	1														1.00	
Owel	1														1.00	

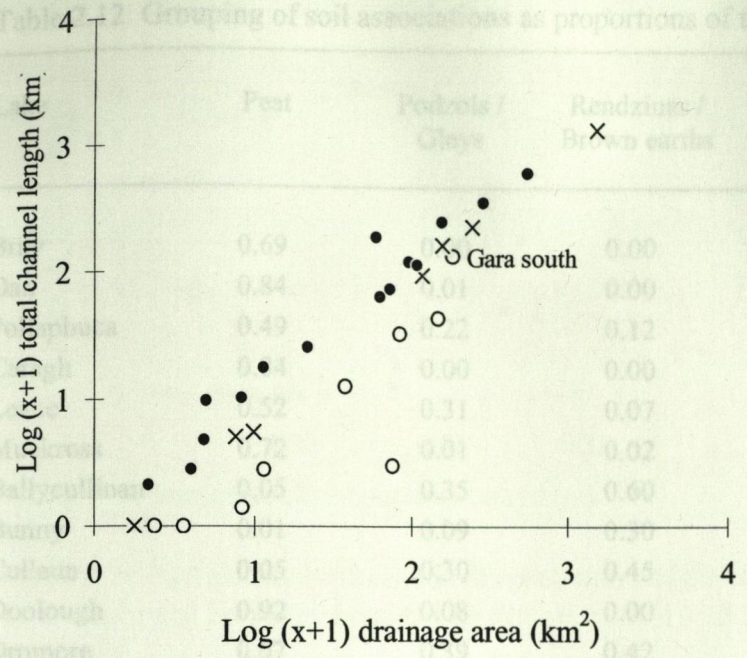


Figure 2.6 Relationship between log (x+1) total channel length (km) and log (x+1) drainage area (km^2). O = limestone ≥ 78%, X = Ordovician and Silurian rocks ≥ 77% and ● = other rock types.

2.3.3 Soils

Of the 44 soil associations differentiated on the general soil map of Ireland 28 were present in the 31 drainage areas that were examined. These associations were placed into four groups: peat soils, podzols/gleys, rendzinas/brown earths and rock/lithosols (Table 2.12). A regional and physiographic trend was present in the soil groups (Table 2.12). All drainage areas with a proportion of peat soils greater than 0.35 were located in the west of Ireland, or in the case of the Wicklow catchments (Bray, Dan and Pollaphuca) at high altitude (Table 2.5, Table 2.8 and Table 2.12). The podzols and gleys group occurred widely and was dominant in Lough Graney, Lickeen, Rea, Gara South, Lene and Owel. The rendzinas and brown earths group also occurred widely but was consistently a high proportion of the drainage areas in Cavan and Monaghan (Lough Egish, Muckno, Gowna, Mullagh, Oughter and Ramor) (Table 2.12). The rock and lithosols group had a tendency to comprise a higher proportion of soils in the limestone pavement areas of the Burren (Co. Clare) or in areas with a high mean catchment boundary altitude (> 400 m) (Figure 2.7).

Table 2.12 Grouping of soil associations as proportions of the 31 drainage areas.

Lake	Peat	Podzols / Gleys	Rendzinas / Brown earths	Rock / Lithosols
Bray	0.69	0.00	0.00	0.31
Dan	0.84	0.01	0.00	0.16
Pollaphuca	0.49	0.22	0.12	0.17
Caragh	0.84	0.00	0.00	0.16
Leane	0.52	0.31	0.07	0.09
Muckross	0.72	0.01	0.02	0.26
Ballycullinan	0.05	0.35	0.60	0.00
Bunny	0.01	0.09	0.30	0.60
Cullaun	0.05	0.30	0.45	0.20
Doolough	0.92	0.08	0.00	0.00
Dromore	0.07	0.39	0.42	0.12
Graney	0.43	0.57	0.00	0.00
Inchiquin	0.04	0.23	0.18	0.55
Lickeen	0.15	0.85	0.00	0.00
Ballyquirke	0.52	0.16	0.27	0.06
Lettercraffroe	1.00	0.00	0.00	0.00
Maumwee	0.42	0.00	0.00	0.58
Rea	0.16	0.70	0.14	0.00
Feeagh	0.81	0.16	0.01	0.02
Moher	0.90	0.00	0.00	0.10
Easky	0.94	0.00	0.00	0.06
Talt	1.00	0.00	0.00	0.00
Gara	0.35	0.64	0.01	0.01
Egish	0.25	0.00	0.75	0.00
Muckno	0.25	0.03	0.72	0.01
Gowna	0.15	0.42	0.43	0.00
Mullagh	0.15	0.10	0.75	0.00
Oughter	0.14	0.43	0.42	0.00
Ramor	0.18	0.40	0.42	0.00
Lene	0.04	0.91	0.05	0.00
Owel	0.16	0.80	0.04	0.00

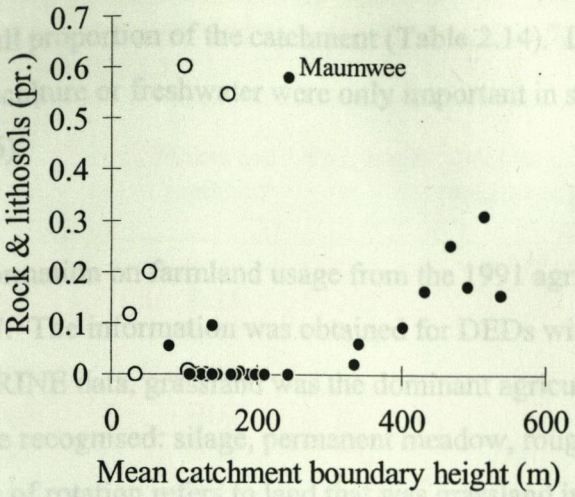


Figure 2.7 The relationship between the proportion of the rock and lithosols soil group and mean catchment boundary height. O = drainage areas with ≥ 78% limestone, ● = other rock types.

2.3.4 Land cover

The CORINE data distinguished 24 different types of land cover in the 31 catchments (Table 2.13 to Table 2.16). Peatland and agricultural land covers were the most important and together they accounted for an average proportion of 0.72 of catchment area. Freshwater was on average 0.10 of catchment area.

The total peatlands category consisted of four sub-divisions: moors and heathland, peat bogs, peat bogs (exploited) and peat bogs (unexploited). Peat bogs (unexploited) and moors and heathland were the most important categories (Table 2.13). The largest proportion of exploited peat bogs was 0.06 and was found in the Lough Gara South catchment. However, most peatlands are likely to have suffered some exploitation such as turf cutting or drainage. Sheehy Skeffington & O'Connell (1998) estimate that only 19% of Irish peatlands are intact.

Agricultural land was differentiated into six types: arable, complex cultivation, pasture (high productivity), pasture (low productivity), pasture (mixed) and principally agriculture. These categories were summed to give the total proportion of the catchment used for agriculture which ranged from 0.00 to 0.93. The pasture categories were also summed to give the total proportion of the catchment used for pasture. Pasture was the dominant

agricultural activity and where arable and complex cultivation were present they were a small proportion of the catchment (Table 2.14). Land cover types other than peatland, agriculture or freshwater were only important in some catchments (Table 2.15 and Table 2.16).

Information on farmland usage from the 1991 agricultural census is presented in Table 2.17. The information was obtained for DEDs within the catchments. As with the CORINE data, grassland was the dominant agricultural land use. Four grassland categories were recognised: silage, permanent meadow, rough grazing and the sum of rotation. The sum of rotation refers to land that was grassland in 1991 but may have been in alternative use in the previous five years. Silage and rotation tended to occupy a higher proportion of the drainage areas in Cavan, Monaghan and Westmeath than in Western Ireland. However, County Clare also tended to have high proportions of rotation. Rough grazing was a higher proportion in western drainage areas. The proportion of the drainage area used for crops (total crops) was small and reached a maximum of 0.04 in Lough Owel.

There were large discrepancies between the satellite derived CORINE land cover and that derived from the agricultural census (Table 2.14 and Table 2.17). This was most apparent in upland peat catchments such as Lough Bray, Dan, Pollaphuca, Caragh, Leane and Muckross where the census estimate of the proportion of agriculture was larger than the CORINE by 10 - 58%. The census data yielded overestimations, as it was only available for district electoral divisions, which did not coincide with catchment boundaries. This meant that upland areas may have had agricultural land use inferred from outside their catchment.

Table 2.13 CORINE data on moors and heathland, peat bogs, peat bogs (exploited), peat bogs (unexploited) and the sum of all four peatland categories. Data are proportions of catchment area.

Lake	Moors and heathland	Peat bogs	Peat bogs (exploited)	Peat bogs (unexploited)	**Total (peatlands)**
Bray	0.18			0.57	**0.75**
Dan	0.15	0.02		0.33	**0.50**
Pollaphuca	0.12			0.28	**0.39**
Caragh	0.45			0.20	**0.64**
Leane	0.21		0.00	0.28	**0.50**
Muckross	0.30			0.40	**0.71**
Ballycullinan					
Bunny					
Cullaun	0.03		0.01	0.04	**0.07**
Doolough	0.13			0.45	**0.58**
Dromore	0.03				**0.03**
Graney	0.21		0.01	0.17	**0.39**
Inchiquin	0.00			0.02	**0.03**
Lickeen				0.24	**0.24**
Ballyquirke	0.05		0.01	0.45	**0.51**
Lettercraffroe				0.39	**0.39**
Maumwee				0.93	**0.93**
Rea					
Feeagh				0.60	**0.60**
Moher				0.56	**0.56**
Easky				0.90	**0.90**
Talt				0.54	**0.54**
Gara			0.06	0.06	**0.12**
Egish					
Muckno				0.03	**0.03**
Gowna			0.00	0.03	**0.03**
Mullagh					
Oughter		0.00	0.00	0.01	**0.01**
Ramor				0.00	**0.00**
Lene					
Owel			0.00	0.01	**0.01**

Table 2.14 CORINE data on arable, complex cultivation, pasture (high productivity), pasture (low productivity), pasture (mixed), principally agriculture, sum of all agriculture classes and the sum of all pasture. Data are proportions of catchment area.

Lake	Arable	Complex cultivation	Pasture (high prod.)	Pasture (low prod.)	Pasture (mixed)	Principally agriculture	**Total (agri.)**	**Total (pasture)**
Bray								
Dan			0.01				**0.01**	**0.01**
Pollaphuca	0.00	0.04	0.15	0.01	0.03		**0.23**	**0.19**
Caragh				0.02	0.04	0.06	**0.11**	**0.05**
Leane	0.00	0.00	0.09	0.11	0.05	0.02	**0.27**	**0.25**
Muckross			0.00	0.00	0.00	0.02	**0.02**	**0.01**
Ballycullinan					0.44	0.01	**0.45**	**0.44**
Bunny		0.00	0.31	0.02	0.01	0.07	**0.41**	**0.34**
Cullaun	0.00		0.35	0.06	0.11	0.05	**0.57**	**0.52**
Doolough			0.03	0.20		0.06	**0.29**	**0.23**
Dromore			0.00		0.41		**0.41**	**0.41**
Graney			0.07	0.04	0.18	0.03	**0.31**	**0.28**
Inchiquin			0.17	0.10	0.04	0.10	**0.41**	**0.31**
Lickeen				0.45	0.01	0.19	**0.64**	**0.45**
Ballyquirke			0.09	0.04	0.01	0.15	**0.29**	**0.14**
Lettercraffroe								
Maumwee								
Rea		0.01	0.46	0.05	0.19	0.04	**0.76**	**0.70**
Feeagh			0.00	0.00	0.00	0.03	**0.03**	**0.00**
Moher						0.32	**0.32**	
Easky								
Talt				0.04	0.21		**0.25**	**0.25**
Gara			0.32	0.15	0.25	0.01	**0.73**	**0.72**
Egish			0.18		0.54	0.11	**0.83**	**0.72**
Muckno			0.46	0.14	0.25	0.05	**0.90**	**0.85**
Gowna		0.00	0.61	0.11	0.14	0.00	**0.86**	**0.86**
Mullagh			0.01	0.46	0.29		**0.76**	**0.76**
Oughter		0.00	0.58	0.11	0.23	0.01	**0.93**	**0.92**
Ramor		0.00	0.67	0.09	0.15	0.01	**0.92**	**0.90**
Lene	0.01	0.06	0.32	0.10	0.07		**0.56**	**0.49**
Owel	0.02		0.28	0.11	0.21	0.08	**0.70**	**0.60**

Table 2.15 CORINE data for natural grasslands, mixed forest, sparsely vegetated areas, transitional woodland / scrub, uncoded in CORINE, urban green and fresh water. Data are proportions of catchment area.

Lake	Natural grasslands	Mixed Forest	Sparsely vegetated areas	Transitional woodland / scrub	Uncoded in CORINE	Urban green	Fresh water
Bray	0.09						0.16
Dan	0.37			0.00			0.03
Pollaphuca	0.17			0.00			0.06
Caragh	0.07	0.02	0.08				0.05
Leane	0.07		0.01	0.00		0.01	0.06
Muckross	0.06		0.02				0.07
Ballycullinan				0.51			0.05
Bunny	0.00		0.05	0.05			0.04
Cullaun	0.01		0.07	0.09			0.03
Doolough							0.08
Dromore		0.14		0.09			0.21
Graney	0.01			0.02			0.01
Inchiquin	0.28		0.13	0.08			0.01
Lickeen							0.12
Ballyquirke	0.08		0.00	0.02			0.03
Lettercraffroe				0.00			0.22
Maumwee							0.07
Rea							0.22
Feeagh	0.09	0.00		0.04			0.06
Moher							0.04
Easky							0.10
Talt							0.21
Gara	0.13			0.01	0.00		0.01
Egish							0.17
Muckno		0.01				0.00	0.03
Gowna							0.09
Mullagh							0.24
Oughter	0.00	0.00		0.00			0.03
Ramor		0.01		0.02			0.04
Lene				0.07			0.37
Owel	0.01	0.01		0.01			0.22

Table 2.16 CORINE data on artificial surface, bare rocks, beach dunes sands, broadleaf forest, coniferous forest, inland marshes and data for which a classification was not available (N/A). Data are proportions of catchment area.

Lake	Artificial surface	Bare rocks	Beach dunes sands	Broadleaf forest	Coniferous forest	Inland marshes	N/A
Bray							
Dan					0.09		
Pollaphuca	0.01			0.00	0.13	0.00	
Caragh			0.00	0.01	0.01		
Leane	0.01			0.04	0.03	0.00	
Muckross				0.13	0.00		
Ballycullinan							
Bunny		0.41		0.01		0.02	
Cullaun		0.15		0.00		0.02	
Doolough					0.06		
Dromore				0.13			
Graney					0.25		
Inchiquin		0.06		0.01	0.00		
Lickeen							
Ballyquirke	0.00				0.05	0.01	
Lettercraffroe					0.39		
Maumwee							
Rea	0.02				0.00		
Feeagh					0.18		0.00
Moher					0.07		
Easky							
Talt					0.00		
Gara	0.00				0.00		
Egish							
Muckno	0.01			0.01	0.01		
Gowna	0.00			0.01	0.00	0.00	
Mullagh							
Oughter	0.00			0.00	0.01	0.01	
Ramor	0.00			0.00	0.01		
Lene							
Owel	0.00			0.01	0.01	0.01	

Table 2.17 Agricultural census data on silage, permanent meadow, rough grazing, sum of rotation under 5 years and total crops. Also presented are the sum of all pasture and the total proportion farmed. Data are proportions of drainage area.

Lake	Sum of rotation under 5 years	Silage	Permanent meadow	Rough grazing	Total crops	**Total area farmed**
Bray	0.12	0.02	0.02	0.03	0.01	**0.20**
Dan	0.09	0.02	0.02	0.09	0.00	**0.22**
Pollaphuca	0.15	0.03	0.02	0.13	0.00	**0.33**
Caragh	0.05	0.02	0.01	0.43	0.00	**0.51**
Leane	0.16	0.07	0.03	0.28	0.00	**0.54**
Muckross	0.09	0.03	0.01	0.47	0.00	**0.60**
Ballycullinan	0.24	0.06	0.07	0.20		**0.57**
Bunny	0.20	0.05	0.06	0.13	0.01	**0.45**
Cullaun	0.28	0.07	0.07	0.22	0.00	**0.64**
Doolough	0.25	0.05	0.09	0.20	0.00	**0.59**
Dromore	0.34	0.09	0.09	0.25		**0.77**
Graney	0.16	0.04	0.06	0.15	0.00	**0.41**
Inchiquin	0.22	0.04	0.05	0.26	0.00	**0.57**
Lickeen	0.55	0.07	0.14	0.06		**0.82**
Ballyquirke	0.14	0.01	0.02	0.16		**0.33**
Lettercraffroe	0.07	0.00	0.01	0.09	0.00	**0.17**
Maumwee	0.06		0.01	0.12		**0.19**
Rea	0.33	0.08	0.06	0.11	0.00	**0.58**
Feeagh	0.04	0.01	0.01	0.15		**0.21**
Moher	0.06	0.03	0.00	0.38		**0.47**
Easky	0.19	0.03	0.03	0.19		**0.44**
Talt	0.17	0.04	0.02	0.18		**0.41**
Gara South	0.36	0.06	0.09	0.06	0.00	**0.57**
Egish	0.50	0.16	0.06	0.07		**0.79**
Muckno	0.25	0.11	0.05	0.06	0.00	**0.47**
Gowna	0.48	0.20	0.08	0.05	0.00	**0.81**
Mullagh	0.72	0.25	0.14	0.05		**1.16**
Oughter	0.41	0.18	0.07	0.04	0.00	**0.70**
Ramor	0.47	0.18	0.08	0.02	0.00	**0.75**
Lene	0.71	0.13	0.13	0.04	0.02	**1.03**
Owel	0.51	0.10	0.09	0.03	0.04	**0.77**

2.3.5 Animal densities

The agricultural census also provided information on stocking density of cattle and sheep. Information was also available on human population numbers estimated by census. The data are expressed per hectare of drainage area (Table 2.18). Cattle density was highest in the north midlands (0.99 to 2.84 cattle ha^{-1}), intermediate in County Clare (0.52 to 1.09 cattle ha^{-1}) and lowest in Western Ireland and in County Wicklow (0.11 to 0.80 cattle ha^{-1}). The Lough Mullagh catchment had an exceptionally high density of cattle (2.84 cattle ha^{-1}).

There was no consistent pattern of sheep density with catchment types but density exceeded two sheep ha^{-1} in several peatland catchments (Bray, Pollaphuca, Moher, Easky) (Table 2.18). Human population density ranged from 0.03 ha^{-1} in Lough Maumwee to 1.08 ha^{-1} in Lough Owel (Table 2.18). Human density was higher in drainage areas with a high proportion of total area farmed (Table 2.17 and Table 2.18).

Table 2.18 Agricultural census data on cattle and sheep and population census data on human density. Data are expressed per hectare of drainage area.

Lake	Cattle (ha^{-1})	Sheep (ha^{-1})	Humans (ha^{-1})
Bray	0.14	2.42	0.20
Dan	0.17	1.97	0.08
Pollaphuca	0.32	2.35	0.20
Caragh	0.26	1.73	0.06
Leane	0.52	0.96	0.34
Muckross	0.24	1.26	0.11
Ballycullinan	0.78	0.70	0.19
Bunny	0.65	0.96	0.09
Cullaun	0.86	0.81	0.11
Doolough	0.59	0.02	0.12
Dromore	1.09	0.95	0.35
Graney	0.52	0.12	0.07
Inchiquin	0.67	0.35	0.08
Lickeen	1.07	0.22	0.16
Ballyquirke	0.38	0.30	0.24
Lettercraffroe	0.18	0.36	0.26
Maumwee	0.11	0.52	0.03
Rea	0.80	2.26	0.31
Feeagh	0.12	1.35	0.06
Moher	0.18	2.77	0.07
Easky	0.32	2.37	0.07
Talt	0.31	1.00	0.09
Gara South	0.80	0.54	0.13
Egish	1.68	0.24	0.47
Muckno	0.99	0.50	n/a
Gowna	1.55	0.70	0.28
Mullagh	2.84	0.82	0.93
Oughter	1.41	0.52	0.29
Ramor	1.56	0.64	0.29
Lene	1.63	2.31	0.96
Owel	1.12	1.22	1.08

2.3.6 Climatic data

Net precipitation ranged from 345 mm in Lough Lickeen (1996) to 1944 mm in Lough Caragh (1996) (Table 2.19). Net precipitation was generally higher in catchments located in the west or at high altitude (Table 2.8, Table 2.19 and Figure 2.3). Overall there were only minor differences between the thirty-year (1960 - 1990) average and that recorded in 1996 and 1997 (Table 2.19). Two notable differences were the Leane catchment which had 57 - 58% higher net precipitation in 1996 and 1997 and the Lickeen catchment which had 59% lower net precipitation in 1996 (Table 2.19). It is also noteworthy that catchments in County Clare had lower than average precipitation in 1996.

The model of Gooddale *et al.* (1998) was used to predict monthly precipitation, minimum and maximum temperature and sunshine hours. These monthly predictions were averaged to provide a mean yearly estimate (Table 2.19). Predicted mean annual maximum daily air temperature ranged from 10°C in the Lough Bray catchment (Co. Wicklow) to 13.5°C in Lough Dromore in Co. Clare. Predicted mean annual minimum daily temperature ranged from 2.6°C in Lough Bray to 6.0°C in Lough Ballycullinan and Dromore (Table 2.19). Predicted mean annual sunshine hours ranged from 3.3 hours in the north (Easky, Talt, Gara South, Gowna and Oughter) to 3.9 hours in the south and east (Bray, Dan and Caragh). This represented an increase of 18% in sunshine hours from north to south.

2.3.7 Inter-relationships between catchment characteristics

Many of the catchment characteristics were significantly correlated with each other (Spearman rank correlation coefficient (r_S) $\geq \pm 0.355$, $p \leq 0.05$, $n = 31$) (Table 2.20). In the matrix of 24 selected catchment characteristics 19 were significantly correlated with ten or more other catchment characteristics (Table 2.20).

Table 2.19 Estimates of precipitation, temperature and sunshine hours in the 31 catchments. Predicted values were based on the period 1951-1980 from the model of Gooddale *et al.* (1998).

Lake	Net rain (mm) 1996	Net rain (mm) 1997	Mean net rain (mm) 1960-1990	Predicted mean annual rain (mm)	Predicted mean annual max. daily air temperature °C	Predicted mean annual min. daily air temperature °C	Predicted mean annual sunshine hours day^{-1}
Bray	1027	986	881	1639	10.0	2.6	3.9
Dan	1463	1361	1107	1497	10.6	3.4	3.9
Pollaphuca	970	901	800	1399	10.9	3.4	3.8
Caragh	1944	1831	1679	1910	12.0	5.5	3.9
Leane	1352	1340	853	1765	12.2	5.4	3.8
Muckross	1703	1634	1734	1831	11.9	5.2	3.8
Ballycullinan	491	746	727	1095	13.5	6.0	3.5
Bunny	548	768	710	1119	13.2	5.6	3.4
Cullaun	519	743	730	1098	13.4	5.9	3.5
Doolough	704	938	796	1382	12.7	5.4	3.5
Dromore	471	684	635	1057	13.5	6.0	3.5
Graney	575	716	662	1170	12.8	5.0	3.4
Inchiquin	619	905	890	1232	13.0	5.5	3.5
Lickeen	345	699	839	1285	13.0	5.6	3.5
Ballyquirke	701	855	880	1176	13.2	5.8	3.4
Lettercraffroe	825	952	1264	1569	12.0	4.8	3.5
Maumwee	1559	1813	1241	1563	12.2	5.2	3.5
Rea	573	675	670	1095	12.9	5.1	3.4
Feeagh	1008	1060	1256	1740	11.7	5.1	3.5
Moher	767	940	1206	1550	12.3	5.5	3.5
Easky	924	1039	824	1689	11.1	3.9	3.3
Talt	778	859	925	1542	11.7	4.5	3.3
Gara South	604	740	675	1130	12.7	5.1	3.3
Egish	516	482	507	1005	12.2	4.7	3.5
Muckno	511	484	512	1019	12.2	4.7	3.5
Gowna	487	593	563	952	12.7	4.9	3.3
Mullagh	518	479	510	978	12.4	4.6	3.5
Oughter	510	534	530	969	12.6	4.9	3.3
Ramor	548	528	533	972	12.4	4.6	3.4
Lene	414	518	497	931	12.6	4.8	3.4
Owel	405	505	478	932	12.7	4.8	3.4

Table 2.20 Spearman rank correlation matrix of catchment characteristics. Significant correlations are in bold face ($p \leq 0.05$).

	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11	X12	X13	X14	X15	X16	X17	X18	X19	X20	X21	X22	X23	X24
X1 Mean net rain (mm) 1960-1990	**1.00**																							
X2 Predicted mean annual rain (mm)	**0.91**	**1.00**																						
X3 Lake altitude (m)	-0.15	-0.06	**1.00**																					
X4 Mean catchment boundary altitude (m)	**0.50**	**0.65**	**0.37**	**1.00**																				
X5 Slope°	**0.50**	**0.59**	**0.41**	**0.69**	**1.00**																			
X6 Mean catchment altitude (m)	**0.43**	**0.60**	**0.51**	**0.96**	**0.73**	**1.00**																		
X7 Drainage density (km^{-1} km^2)	**0.52**	**0.65**	-0.01	**0.68**	**0.36**	**0.63**	**1.00**																	
X8 Ruggedness number	**0.53**	**0.65**	-0.07	**0.79**	0.35	**0.70**	**0.93**	**1.00**																
X9 Compactness coefficient of catchment	-0.13	-0.12	-0.26	0.09	-0.35	-0.04	0.14	0.29	**1.00**															
X10 Peat	**0.62**	**0.73**	0.32	**0.68**	**0.58**	**0.72**	**0.63**	**0.59**	-0.16	**1.00**														
X11 Podzols & Gleys	**-0.58**	**-0.62**	-0.21	**-0.58**	**-0.70**	**-0.60**	-0.34	**-0.40**	0.22	**-0.65**	**1.00**													
X12 Rendzinas & Brown earths	**-0.64**	**-0.69**	-0.29	**-0.49**	**-0.51**	**-0.48**	**-0.55**	**-0.42**	0.35	**-0.69**	0.31	**1.00**												
X13 Rock & Lithosols	**0.54**	**0.52**	-0.26	0.27	0.15	0.18	0.23	0.35	0.14	0.04	**-0.41**	-0.15	**1.00**											
X14 Sum (peatlands)	**0.79**	**0.86**	0.01	**0.61**	**0.52**	**0.57**	**0.77**	**0.72**	-0.04	**0.78**	**-0.58**	**-0.75**	**0.46**	**1.00**										
X15 Sum (agri.)	**-0.81**	**-0.86**	-0.10	**-0.62**	**-0.70**	**-0.60**	**-0.51**	**-0.51**	0.18	**-0.67**	**0.61**	**0.72**	**-0.52**	**-0.82**	**1.00**									
X16 Sum (pasture)	**-0.84**	**-0.87**	-0.07	**-0.55**	**-0.66**	**-0.52**	**-0.48**	**-0.44**	0.25	**-0.69**	**0.63**	**0.73**	**-0.52**	**-0.83**	**0.96**	**1.00**								
X17 Fresh water	-0.16	-0.10	**0.40**	0.03	**0.47**	0.21	-0.20	-0.30	**-0.41**	0.06	-0.04	-0.06	**-0.37**	-0.10	-0.07	-0.03	**1.00**							
X18 Total area farmed	**-0.66**	**-0.67**	-0.11	**-0.51**	**-0.41**	**-0.47**	**-0.44**	**-0.50**	0.12	**-0.61**	**0.56**	**0.53**	**-0.45**	**-0.63**	**0.75**	**0.75**	0.29	**1.00**						
X19 Cattle (ha^{-1})	**-0.89**	**-0.88**	-0.03	**-0.60**	**-0.55**	**-0.55**	**-0.55**	**-0.58**	0.19	**-0.71**	**0.62**	**0.72**	**-0.55**	**-0.84**	**0.90**	**0.92**	0.18	**0.88**	**1.00**					
X20 Sheep (ha^{-1})	0.21	0.27	0.30	0.32	0.30	**0.43**	-0.01	0.09	-0.21	0.21	-0.18	-0.22	0.34	0.21	-0.34	-0.35	0.27	-0.17	-0.32	**1.00**				
X21 Humans (ha^{-1})	**-0.71**	**-0.66**	0.18	-0.34	-0.28	-0.23	**-0.54**	**-0.52**	0.14	**-0.40**	**0.47**	**0.58**	**-0.50**	**-0.66**	**0.58**	**0.63**	**0.52**	**0.61**	**0.72**	-0.07	**1.00**			
X22 Predicted mean annual max. daily air temperature °C	**-0.42**	**-0.55**	**-0.52**	**-0.92**	**-0.70**	**-0.96**	**-0.58**	**-0.66**	0.00	**-0.71**	**0.62**	**0.44**	-0.18	**-0.55**	**0.54**	**0.49**	-0.18	**0.48**	**0.54**	**-0.47**	0.23	**1.00**		
X23 Predicted mean annual min. daily air temperature °C	0.18	0.05	**-0.81**	**-0.61**	**-0.41**	**-0.69**	-0.19	-0.27	-0.05	-0.35	0.23	0.13	0.22	-0.04	0.08	-0.02	-0.28	0.17	0.02	-0.30	-0.18	**0.74**	**1.00**	
X24 Predicted mean annual sunshine hours day^{-1}	**0.48**	**0.52**	-0.02	**0.50**	**0.42**	**0.46**	0.26	0.33	-0.08	0.23	**-0.41**	-0.15	**0.50**	0.34	**-0.46**	**-0.46**	-0.01	-0.24	**-0.42**	0.20	-0.16	**-0.36**	0.06	**1.00**

2.3.8 Catchment characteristics for the 189 lakes

Table 2.21 presents summary statistics for a limited suite of catchment characteristics for 189 lakes. This data is fully tabulated in Appendix 4. The 189 lakes included data collected in June 1997 from the 31 principal lakes in the study. June 1997 was used, as it was the most contemporary with the other samples. This data set was used to test and explore relationships where the larger sample size was of benefit and where the reduced sampling strategy (one summer sample) was not a limitation.

As would be expected from the large sample size the catchment characteristics had a wide range of values (Table 2.21). Similar features were common with the 31 catchments such as the dominance of agricultural and peatland coverage (Table 2.21). One point worthy of note from the CORINE data set is that the land cover 'moors and heathland' tended to be a higher proportion when precipitation was greater than 1900 mm (Figure 2.8) (precipitation was predicted using the model of Goodale *et al.* (1998)).

In some cases it is beneficial to examine relationships on a regional level. To do this the 189 lakes were separated into six geographic groups (Figure 2.9).

Table 2.21 Summary statistics of catchment characteristics (n = 189).

Lake	Mean	Median	75th percentile	25th percentile	Minimum	Maximum
Catchment area (km^2)	115.12	3.75	20.33	1.29	0.06	10608.00
Area of lake (km^2)	2.39	0.24	0.82	0.08	0.01	117.50
Catchment area / lake area	43	17	34	8	3	945
Mean catchment elevation (m)	154	111	190	72	7	690
Total agriculture (CORINE)	0.34	0.21	0.70	0.00	0.00	1.00
Total peatlands (CORINE)	0.45	0.48	0.77	0.03	0.00	1.00
Total area farmed (Census)	0.48	0.48	0.70	0.20	0.00	1.00
Cattle (ha^{-1})	0.6	0.4	1.0	0.1	0.0	3.7
Sheep (ha^{-1})	1.0	0.8	1.4	0.4	0.0	4.7
Annual precipitation (mm)	1495	1498	1689	1232	868	2619
Annual net precipitation (mm)	989	992	1182	726	362	2113
Mean annual maximum daily temperature (°C)	12.1	12.4	12.8	11.6	8.3	13.5
Mean annual minimum daily temperature (°C)	5.2	5.2	5.9	4.8	0.6	7.4
Mean annual daily temperature (°C)	8.7	8.8	9.3	8.3	4.4	10.5
Mean annual sunshine hours day^{-1}	3.6	3.5	3.8	3.3	3.3	4.0

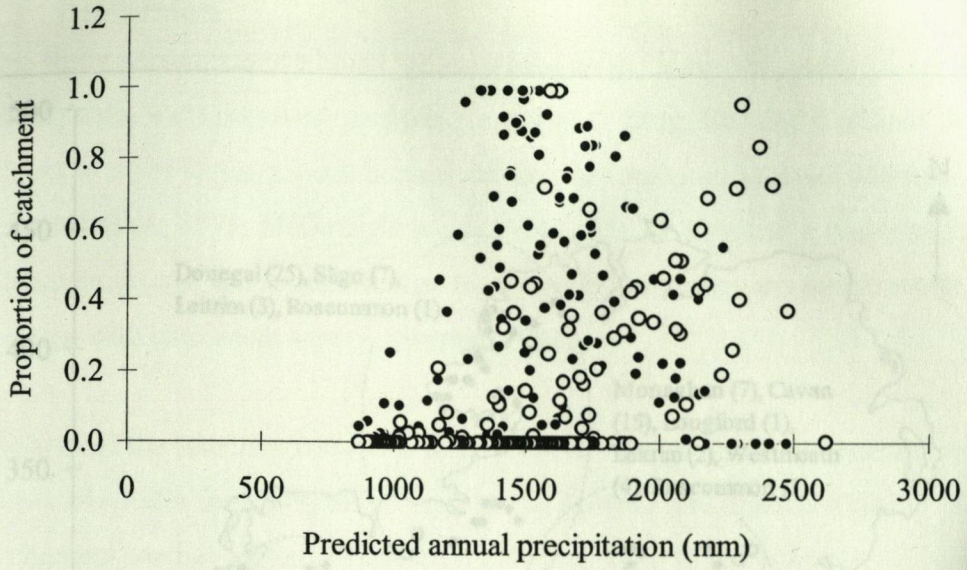


Figure 2.8 Proportion of total bogs (●) and moors and heathland (O) in relation to predicted annual precipitation (mm) in 189 catchments. Total bogs is the sum of peat bogs, peat bogs (exploited) and peat bogs (unexploited) extracted from the CORINE database. Precipitation was predicted using the model of Goodale *et al.* (1998).

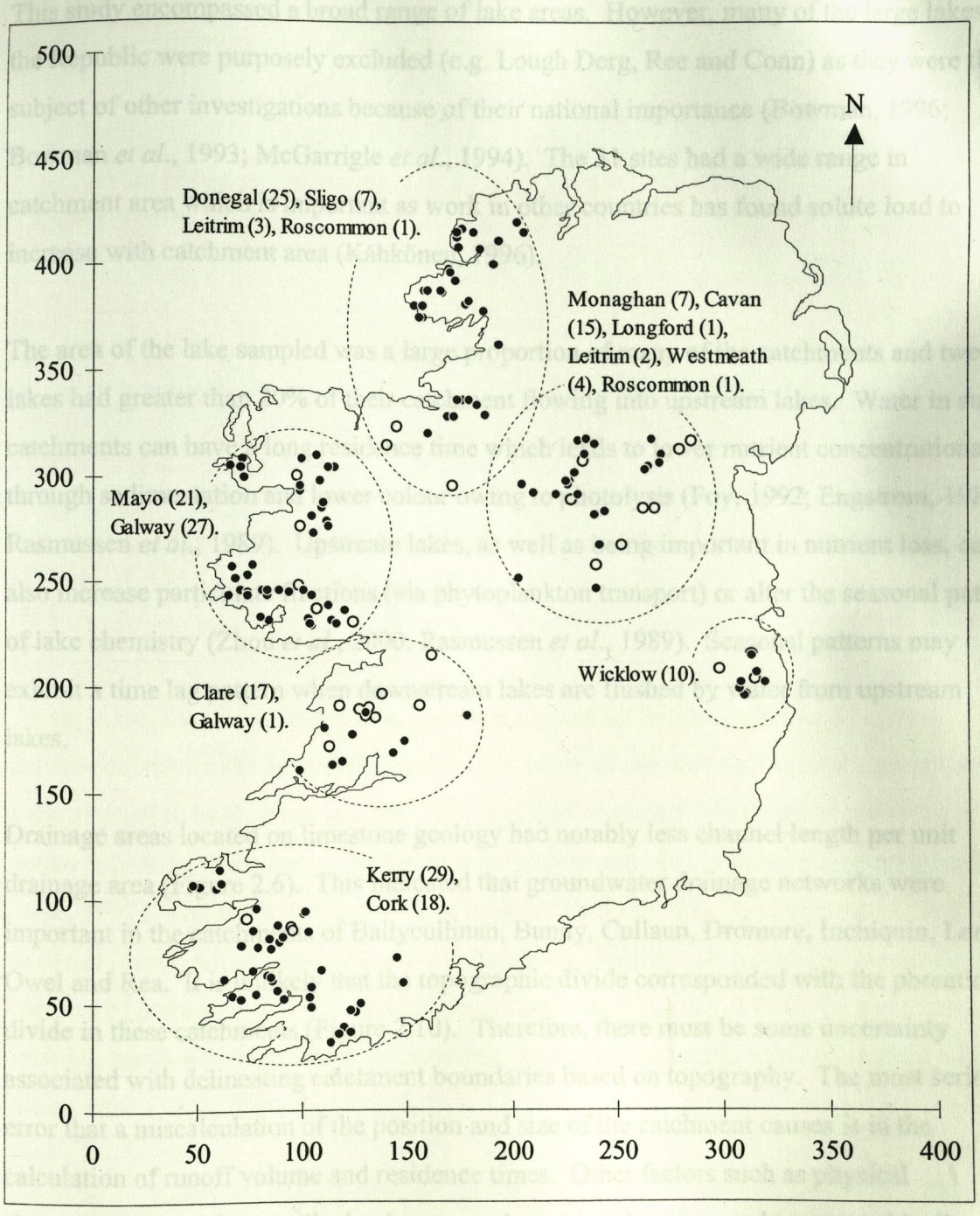


Figure 2.9 Map showing division of 189 lakes sampled into geographic groups. The 189 catchments include data from June 1997 for the 31 lakes sampled seasonally (O) as well as lakes sample once (●). Scale corresponds to part of the national grid in km.

2.4 Discussion

This study encompassed a broad range of lake areas. However, many of the large lakes in the Republic were purposely excluded (e.g. Lough Derg, Ree and Conn) as they were the subject of other investigations because of their national importance (Bowman, 1996; Bowman *et al.*, 1993; McGarrigle *et al.*, 1994). The 31 sites had a wide range in catchment area which is important as work in other countries has found solute load to increase with catchment area (Kähkönen, 1996).

The area of the lake sampled was a large proportion of many of the catchments and twelve lakes had greater than 20% of their catchment flowing into upstream lakes. Water in such catchments can have a long residence time which leads to lower nutrient concentrations through sedimentation and lower colour owing to photolysis (Foy, 1992; Engstrom, 1987; Rasmussen *et al.*, 1989). Upstream lakes, as well as being important in nutrient loss, can also increase particulate fractions (via phytoplankton transport) or alter the seasonal pattern of lake chemistry (Zhou *et al.*, 2000; Rasmussen *et al.*, 1989). Seasonal patterns may exhibit a time lag pattern when downstream lakes are flushed by water from upstream lakes.

Drainage areas located on limestone geology had notably less channel length per unit drainage area (Figure 2.6). This indicated that groundwater drainage networks were important in the catchments of Ballycullinan, Bunny, Cullaun, Dromore, Inchiquin, Lene, Owel and Rea. It is unlikely that the topographic divide corresponded with the phreatic divide in these catchments (Figure 2.10). Therefore, there must be some uncertainty associated with delineating catchment boundaries based on topography. The most serious error that a miscalculation of the position and size of the catchment causes is in the calculation of runoff volume and residence times. Other factors such as physical characteristics, geology, soils, land cover and stocking density may be geographically similar. Thus the error in calculating proportions of these variables will be not of paramount concern in the context of the very diverse catchments studied. It was also helpful to identify lakes that receive groundwater input, as the pathway of water from the drainage area to the lake is an important influence on some chemical parameters. For example, groundwaters may have lower phosphorus and colour because of adsorption

during percolation through mineral soils (Pierzynski *et al.*, 2000; Lucey *et al.*, 1999; McDowell & Likens, 1988).

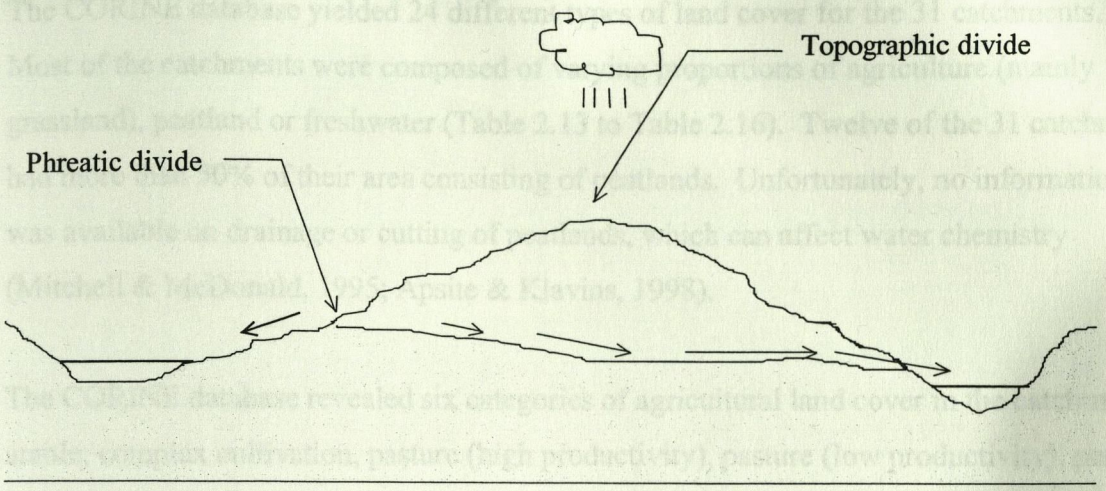


Figure 2.10 Illustration of phreatic and topographic divides. Modified after Gordon *et al.* (1992).

As expected, the proportion of peat soils was highest on the west coast or in upland catchments that received high precipitation. The rendzinas and brown earths group were a high proportion of the drainage areas in Cavan and Monaghan. Rendzinas and brown earths tend to be more freely drained relative to peat soils and podzols and gleys (Coulter *et al.*, 1998). The drainage properties of soils are likely to affect lake chemistry. For example, the poorly drained podzols and gley soils category may reduce nitrogen export because of increased denitrification in the drainage area (Jordan, 1989). In contrast, poor drainage and a high water table can increase overland flow which tends be high in phosphorus (Kurz, 2000; Kiely, 2000).

Although it is possible to form hypotheses about how the soil groups used in this study may affect lake chemistry, previous work has found barriers to making generalisations about soils. Diamond (1990) found that hydraulic conductivity among seven series of the gley group in east Waterford ranged across six orders of magnitude. From this it was concluded that it was not possible to treat gley soils as a single homogenous class for effluent disposal. However, not aggregating soil types makes it impossible to draw relationships with freshwater chemistry. For example, Neill (1989) cited the diversity of soil types in south-west Ireland (29 main soil types in five catchments) as a barrier to

inferring their influence on river nitrate – there were simply more independent parameters (soil types) than dependent variables (nitrate export from catchments).

The CORINE database yielded 24 different types of land cover for the 31 catchments. Most of the catchments were composed of varying proportions of agriculture (mainly grassland), peatland or freshwater (Table 2.13 to Table 2.16). Twelve of the 31 catchments had more than 50% of their area consisting of peatlands. Unfortunately, no information was available on drainage or cutting of peatlands, which can affect water chemistry (Mitchell & McDonald, 1995; Apsite & Klavins, 1998).

The CORINE database revealed six categories of agricultural land cover in the catchments: arable, complex cultivation, pasture (high productivity), pasture (low productivity), pasture (mixed) and principally agriculture (Table 2.14). Twelve of the 31 catchments had greater than 50% of their area consisting of agriculture. Pasture was dominant which is a feature of Irish agriculture because of the relatively wet climate that limits arable agriculture to the drier south-east.

Both the CORINE satellite imagery and the agricultural census provided information on the usage of land for farming. The agricultural census data provided information on actual land use (e.g. silage) whereas the CORINE data only provided information on land cover where the actual use is uncertain (e.g. pasture (high productivity)). That is, it is unclear from the CORINE data whether the pasture (high productivity) is used for silage, rotation or permanent meadow. It may only be assumed that pasture (high productivity) refers to grassland which was likely to be highly productive. However, the CORINE data may be more useful because it was geographically correct as the land covers were determined within the catchment boundary. In comparison, the census data was only available for district electoral divisions. This meant that some catchments had agricultural land use inferred from outside the catchment. In some cases this clearly led to an overestimation of the proportion of agriculture. This was apparent when visiting small western catchments such as Lough Maumwee, which confirmed that the CORINE estimation of zero agriculture was correct and that the census estimation of 19% total area farmed was in error (Figure 2.11). The census data on stocking density will also be similarly affected.



Figure 2.11 Lough Maumwee and part of its catchment in 1996.

Cattle density tended to be highest in the north midlands where pasture was a high proportion of catchment area. There was no consistent pattern of sheep density with catchment type but it is notable that density was high in some peatland catchments (Table 2.18).

The 31 catchments spanned a wide range of net precipitation (345 mm in the Lough Lickeen catchment to 1944 mm at Lough Caragh). Precipitation was generally greater in the west and at high altitudes.

Information on 189 catchments was obtained to validate relationships found with the 31 lakes and provide a more extensive data-set for some analyses. It was interesting to note that the CORINE land cover 'moors and heathland' tended to be more common and cover a larger proportion of catchments where precipitation was higher than 1900 mm (Figure 2.9). The 'moors and heathland' land cover may therefore be a useful division of the total peatland category. This category is found in areas with high precipitation which are likely to be at high altitude and have low temperatures. These factors may lower plant growth and consequently peat accumulation, which would result in a shallower depth of peat which may affect lake colour.

The 189 catchments were separated into six geographic groups (Figure 2.9). One of the benefits of sample stratification is the removal of some regional variation owing to geology, soils, geomorphology and climate or other parameters. This may aid in the identification of relationships between catchment characteristics and water chemistry (Rochelle *et al.*, 1989). In addition, sample stratification can provide validation of conclusions drawn from the full sample. Rasmussen *et al.* (1989) used this procedure to examine the similarity of multiple regression coefficients among regions. Kortelainen (1993) divided Finland into sub-regions based on latitude. This improved some relationships by removing variation due to climate, hydrology and anthropogenic activity. In contrast, Herlihy *et al.* (1998) found that subdivision resulted in some regions having virtually uniform catchments. The minor differences in land use within regions had a poor ability to describe chemistry.

Many catchment characteristics were significantly correlated with each other because of their morphogenic inter-relationships (Table 2.20). This is illustrated in Figure 2.12 where catchments with high precipitation tend to have a high proportion of peatland because high precipitation promotes peatland development. As peatland is a high proportion of the catchment it follows that there is a low proportion of pasture, low density of cattle and low human population. Also, areas with high precipitation tend to have a high mean catchment altitude. However, the r_S in this case is only 0.50, as the proximity to the Atlantic as well as altitude are important in increasing precipitation (Figure 2.12). Catchments with a high altitude tend to occur on resistant rock types (Table 2.8 and Table 2.11), have high slopes, low maximum temperatures and high drainage densities. These interrelationships are important because when relating a catchment characteristic to lake chemistry the catchment characteristic may partly or wholly act as a surrogate for other parameters. In addition, catchment characteristics that are strongly co-linear may not be used together as explanatory parameters in multiple regression models (Petruccelli *et al.*, 1999).

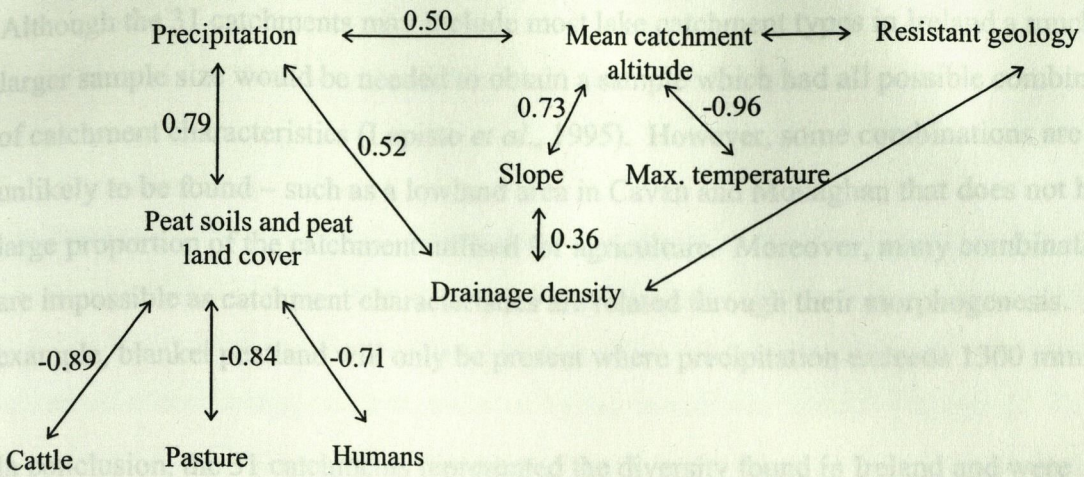


Figure 2.12 Example of interrelationships among catchment characteristics. Figures relate to Spearman rank correlation coefficients (r_S).

The catchment characteristics determined provided a comprehensive description of the 31 catchments. This comprehensive approach, although time consuming, was fruitful. For example, it enabled the identification of catchments with significant groundwater drainage through a comparison of drainage density and rock type. However, some potentially useful information was not readily available such as peatland depth and poultry and pig densities. An indication of peatland depth may be inferred from slope, altitude and temperature but poultry and pig densities could not be acquired because of data protection measures.

Overall, the 31 catchments had a diverse range of physical characteristics, rock type, soils, land cover, stocking density and climate. The 31 catchments are likely to be a good representation of the lake catchments typically encountered in Ireland. Twelve of the catchments were dominated (≥ 50% CORINE land cover) by peatlands and ten by agriculture. However, the inclusion of eight groundwater-fed lakes may be over-representative. One omission was that no catchments in the south-east were included. This was because this region has a very low density of natural lakes. The south-east generally has more arable agriculture than the rest of the country and has been found to have higher nitrate concentrations in rivers (Neill, 1989). Lakes in the south-east may therefore have different relationships with catchment characteristics owing to factors such as lower rainfall and a higher prevalence of arable agriculture.

Although the 31 catchments may include most lake catchment types in Ireland a much larger sample size would be needed to obtain a sample which had all possible combinations of catchment characteristics (Lepisto *et al.*, 1995). However, some combinations are unlikely to be found – such as a lowland area in Cavan and Monaghan that does not have a large proportion of the catchment utilised for agriculture. Moreover, many combinations are impossible as catchment characteristics are related through their morphogenesis. For example, blanket peatland will only be present where precipitation exceeds 1300 mm.

In conclusion, the 31 catchments represented the diversity found in Ireland and were comprehensively described. This will allow a thorough examination of the controls that catchment characteristics have on lake chemistry in Ireland.

3. GENERAL LIMNOLOGY OF THE 31 LAKES

3.1 Introduction

The purpose of this chapter is to describe some of the more important aspects of the limnology of the 31 lakes. Information is provided on stratification, acid status, trophic status and summer phytoplankton composition. Other information gathered concurrently as a result of the Ecological Assessment of Lakes project was listed in Chapter 1. The inclusion of this Chapter is recognition that internal processes as well as those in the drainage area influence lake chemistry. Previous studies of the lakes are listed in Table 3.1. The previous studies were based on infrequent sampling and considered relatively few limnological factors.

Table 3.1 Previous publications that contain chemical information on the lakes.

Lake	Previous publications
Ballycullinan	Allott (1986); Allott (1990)
Ballyquirke	
Bray	Caffrey *et al.* (1999); Webb (1947)
Bunny	
Caragh	Flanagan & Toner (1975); Caffrey *et al.* (1999); Webb (1947)
Cullaun	Allott (1986); Allott (1990)
Dan	Caffrey *et al.* (1999); O'Conner & Bracken (1978)
Doolough	Bowman (1991)
Dromore	Allott (1986); Allott (1990)
Easky	Flanagan & Toner (1975)
Egish	Flanagan & Toner (1975)
Feeagh	Flanagan & Toner (1975)
Gara	Flanagan & Toner (1975); Webb (1947)
Gowna	Flanagan & Toner (1975)
Graney	Flanagan & Toner (1975); Webb (1947)
Inchiquin	Flanagan & Toner (1975); Allott (1986); Allott (1990)
Leane	Flanagan & Toner (1975); Caffrey *et al.* (1999); Webb (1947); Bracken *et al.* (1977)
Lene	Flanagan & Toner (1975)
Lettercraffroe	Dalton (1999)
Lickeen	Bowman (1983)
Maumwee	Bowman (1991); Caffrey *et al.* (1999)
Moher	
Muckno	Flannagan & Toner (1975)
Muckross	Caffrey *et al.* (1999)
Mullagh	
Oughter	Flannagan & Toner (1975)
Owel	Flannagan & Toner (1975)
Pollaphuca	Caffrey *et al.* (1999)
Ramor	Flannagan & Toner (1975)
Rea	Flannagan & Toner (1975)
Talt	

3.2 Materials and methods

3.2.1 Sampling techniques

Thirty-one lakes were sampled between March 1996 and December 1997. The intensity of sampling was approximately monthly for 11 lakes, and quarterly for 20 lakes (Table 3.2). Sampling was usually divided into two stages. The first was of one-week duration and included lakes located in Counties Clare, Galway, Mayo, Sligo, Roscommon and Cavan. The second was of three days duration and included lakes in Counties Wicklow, Westmeath, Cavan and Monaghan.

The lakes were sampled using a 3.5 m Avon inflatable boat with a 5-horse power engine. Stations were generally located centrally in the lake at the point of maximum depth (station locations to ±100 m are listed in Chapter 2). Vertically-integrated samples for chemical, physical and phytoplankton analysis were taken using a tube of 2.5 cm internal diameter and 6 m in length. Two 6 m vertically-integrated samples provided 5 l of water. Where depth was insufficient, or the hypolimnion extended above 6 m, a dip sample was taken (~ 0.5 m). The sample bottles were polyethylene. Dedicated bottles were used for each lake and were replaced several times over the course of the project. Sample bottles were rinsed three times with surface water before use. Generally, two to four lakes were sampled per day.

In addition to the 31 lakes sampled seasonally, chemical data was obtained on a further 158 lakes that were sampled once during the summer of 1996 or 1997. This work was part of the EPA Ecological Assessment of Lakes project and samples were collected by C. Kennelly, S. Day, N. Allott, K. Irvine and G. Free (see Irvine *et al.* 2001 for more details). These lakes were sampled from the shoreline by throwing out a weighted bottle attached to a line. Only the 31 lakes that were the main focus of this study are considered in this chapter.

Table 3.2 Intensity of sampling, estimated time to initial processing and the method of sampling for 31 lakes sampled between March 1996 and December 1997.

Lake	Month Sampled 1996	Month Sampled 1997	Estimated time to initial processing	Method of sampling
Ballycullinan	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Ballyquirke	4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 12 hrs	Boat
Bray	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Bunny	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Caragh	4,6,7	1,6,7,8,9,12	< 24-48 hrs	Shoreline or Boat
Cullaun	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Dan	3,4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 12 hrs	Boat
Doolough	3,4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 12 hrs	Boat
Dromore	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Easky	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Egish	6,7,9	1,4,6,7,9,12	< 24-48 hrs	Boat
Feeagh	3,4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 12 hrs	Boat
Gara S.	7,9,10	1,4,6,7,9,12	< 12 hrs	Boat
Gowna	3,4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 12 hrs	Boat
Graney	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Inchiquin	4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 12 hrs	Boat
Leane	4,6,9	1,6,7,8,9,12	< 24-48 hrs	Shoreline or Boat
Lene	3,4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 24-48 hrs	Boat
Lettercraffroe	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Lickeen	3,4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 12 hrs	Boat
Maumwee	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Moher	3,4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 12 hrs	Boat
Muckno	4,6,7,9	1,4,6,7,9,12	< 24-48 hrs	Boat
Muckross	4,6,9	1,6,7,8,9,12	< 24-48 hrs	Shoreline or Boat
Mullagh	4,6,7,9	1,4,6,7,9,12	< 24-48 hrs	Boat
Oughter	3,4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Owel	3,4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 24-48 hrs	Boat
Pollaphuca	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Ramor	3,4,5,6,7,8,9,10	1,3,4,5,6,7,8,9,10,12	< 24-48 hrs	Boat
Rea	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat
Talt	4,6,7,9	1,4,6,7,9,12	< 12 hrs	Boat

3.2.2 Analytical techniques

Water samples were returned to the field station where initial processing took place. This involved filtration, measurement of some variables, sample preservation and pouring of samples into bottles for future laboratory analysis (Table 3.3). The delay to initial processing of samples varied from 2 to 48 hours and was usually more prompt during the first sampling stage that included western lakes (Table 3.2). The analytical techniques for results presented in this chapter are now detailed. The methods for other parameters are described in the following chapters.

Temperature and oxygen were measured at 1-2 m intervals using a WTW microprocessor Oximeter (OXI 196) with a WTW EOT 196 probe. Occasionally, temperature and oxygen was measured using a Windermere Profiler 2. All thermometers were checked regularly against a certified thermometer (type 305MM) obtained from S. Brannan & Sons Ltd., Cumbria.

pH was determined on 50-100 ml unstirred samples using a Jenway 3030 pH meter with a Reagecon combination pH electrode (GCFC11) which is suitable for low ionic strength water. The meter was fitted with a temperature probe and was calibrated prior to use using Reagecon buffers of pH 4 and 7. Following calibration, a quality control sample of 10^{-4} HCl (pH 4.00) was analysed and had an average pH of 4.03 and a standard deviation of 0.02 ($n = 93$). Quality assurance information is presented in Appendix 10 and measured pH was within the 95% confidence limits of the test solutions pH.

Chlorophyll *a* was determined using the methanol extraction method of the Standing Committee of Analysts (1980). Depending on sample turbidity, 0.1 to 2.5 l of sample was filtered through Whatman GF/C filter paper. Vacuum was maintained below 25 cm mercury. The filter paper was placed into a centrifuge tube containing 10 ml of methanol. The tubes were placed in darkness and stored at 4°C upon return to the laboratory. Samples were brought to boiling point (~75°C) for 60 seconds. After cooling, the filter papers were removed and the samples were centrifuged at 3500 rpm for 9 minutes. Absorbance was measured at 665 and 750 nm in a 4 cm cell. A Shimadzu UV-120-02 spectrophotometer was used in 1996 and a Shimadzu UV-1601 during 1997.

Phytoplankton were counted across a transect of a circular chamber (5-25 ml) using an inverted microscope (Leitz DM IL). Counting took place using a x20 objective on samples preserved with Lugol's Iodine. Results were expressed in cells or colonies ml^{-1}. Phytoplankton were identified to genera or, where possible, species using several floras: Bellinger (1992), Canter-Lund & Lund (1995), Lind & Brook (1980), Nygaard (1976), Prescott (1962), Prescott (1978) and West & Fritsch (1927).

Table 3.3 Initial processing (measurement, processing and pouring) and division of analysis between the field station and the Environmental Science's laboratory.

Performed at field station	Samples prepared in the field and returned to the lab. for analysis
Filtration through Whatman GF/C (0.1-2.5 l)	Filtrate for SiO_2-Si, NO_3^--N, Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, K^+, Ca^{2+} (100 ml)
Conductivity (100 ml)	Filtrate for MRP placed into test tubes with 100 µl 3.6 N H_2SO_4 (3 x 5 ml)
pH (100 ml)	Filter paper placed into centrifuge tube containing 10 ml methanol for chlorophyll *a*
Turbidity (3 x 25 ml)	Phytoplankton + 0.6 ml Lugol's iodine (250 ml)
Colour (3 x 25 ml)	TP (2 x 50 ml digestion flasks)
Alkalinity (50 or 100 ml)	TN/TSi (2 x 50 ml digestion flasks)
	Filtrate for TDN/TDSi (2 x 50 ml digestion flasks)

Mean depth, maximum depth and lake volume for each lake was estimated by Paul Mills of Compass Informatics (Irvine *et al.*, 2001). This was done by obtaining depth measurements for each lake either from digitising bathymetric charts or from field survey. The depth measurements were interpolated to produce a continuous estimate of depth across the lake. This allowed estimates to be made of mean depth, maximum depth and lake volume. These estimated were produced using raster-modelling software contained within Arc View Geographic Information System software. Depth at the sampling station was determined using a portable echo-sounder (Scubapro PDS-2). Residence time (t_w) in years was calculated by dividing lake volume (m^3) by the product of catchment area (m^2) and estimated annual runoff (m).

The maximum length (km) of the lake and orientation (degrees) were determined on 1:50000 maps. Shoreline length (L) was determined on 1:50000 maps using a map measure. Shoreline development (D_L) is the ratio of shoreline length to the circumference of a circle the same area as the lake:

$$D_L = L\ (km) / (2 \cdot \pi) \cdot (\sqrt{(lake\ area\ (km^2) / \pi)})$$

The ratio of mean depth (m) to the square root of the lake area (m^2) was calculated to give an index of lake basin shape (Nürnberg, 1995). A high value typically represents a deep lake with a small area whereas a low value represents a shallow lake with a large area.

3.3 Results and discussion

3.3.1 Physical characteristics

The 31 lakes had a wide range of physical characteristics (Table 3.4 and Table 3.5). Mean depth ranged from 1.0 m in Gara South to 31.3 m in Lough Muckross. Lough Muckross was the deepest lake having a maximum depth of 70 m. Residence time ranged from 0.015 years in Lough Gara South in 1996 to 5.25 years in Lough Lene in 1996. The high rainfall in Ireland meant that the lakes had relatively short residence times: in 1997 seven lakes were flushed more than ten times, eleven at least twice, six at least once and the remaining seven between 0.24 and 0.75 times. In lakes receiving substantial groundwater drainage (Chapter 2, Table 3.4) the estimate of residence time is likely to be only approximate. Lake areas were presented in Chapter 2 and ranged from 0.05 to 19.89 km^2. Shoreline development ranged from 1.19 in Lough Bray, Maumwee and Mullagh to 7.30 in Lough Oughter.

Table 3.4 Mean depth ($\bar{z}$), maximum depth (z_{max}), lake volume and water residence time (yr) (t_w) for 1996, 1997 and mean between 1960-1990. An asterisk highlights lakes where actual t_w was uncertain owing to substantial groundwater drainage.

Lake	$\bar{z}$ (m)	z_{max} (m)	Station depth (m)	Lake volume (m^3)	t_w (1996)	t_w (1997)	mean t_w (1960-1990)
Ballycullinan	3.4	10.0	8.0	170000	0.242*	0.159*	0.164*
Ballyquirke	2.5	12.2	11.0	1988125	0.039	0.032	0.031
Bray	19.8	45.7	38.0	4871250	3.321	3.461	3.871
Bunny	1.4	13.0	10.0	1388750	0.033*	0.024*	0.026*
Caragh	11.6	40.0	-	57958125	0.185	0.196	0.214
Cullaun	6.7	23.0	20.0	4215000	0.096*	0.067*	0.068*
Dan	13.0	37.9	32.0	13676910	0.148	0.159	0.196
Doolough	3.4	14.9	11.0	4270000	0.276	0.207	0.244
Dromore	5.9	19.0	19.0	3171875	2.119*	1.460*	1.571*
Easky	2.4	10.8	10.0	2913750	0.272	0.242	0.305
Egish	2.0	8.4	11.0	2488125	0.615	0.659	0.625
Feeagh	14.5	45.3	40.0	58890000	0.583	0.554	0.467
Gara South	1.0	-	2.0	2026604	0.018	0.015	0.016
Gowna	4.0	-	13.0	42170466	0.675	0.554	0.580
Graney	3.7	18.6	13.0	14249375	0.222	0.178	0.193
Inchiquin	10.2	29.0	27.0	11776875	0.128*	0.087*	0.089*
Leane	13.4	60.0	-	268671875	0.359	0.363	0.570
Lene	6.0	22.9	22.0	25409790	5.247*	4.197*	4.372*
Lettercraffroe	2.2	16.4	15.0	1886250	0.592	0.513	0.387
Lickeen	3.9	23.6	22.0	3275000	1.160	0.573	0.477
Maumwee	2.0	7.9	3.0	533750	0.081	0.069	0.101
Moher	2.9	13.4	15.0	1178125	0.164	0.134	0.105
Muckno	5.9	27.0	24.0	21376250	0.261	0.275	0.260
Muckross	31.3	70.0	-	86454375	0.830	0.865	0.815
Mullagh	2.3	8.1	8.0	780000	1.319	1.425	1.338
Oughter	3.0	14.0	11.0	24180625	0.032	0.031	0.030
Owel	7.2	22.8	17.0	73715625	3.881*	3.111*	3.285*
Pollaphuca	6.8	-	8.0	135000000	0.460	0.495	0.558
Ramor	3.0	5.5	3.0	22238125	0.161	0.167	0.166
Rea	4.0	20.9	20.0	12256250	1.582*	1.341*	1.352*
Talt	8.9	41.4	31.0	8458125	2.253	2.041	1.895

Table 3.5 Maximum length and orientation of lake axis, shoreline length (L), shoreline development (D_L) and $\bar{z} / \sqrt{}$ lake area. An asterisk indicates that results are estimates for the sampled lake basin; values in parenthesis are for the entire lake.

Lake	Max. length of lake axis (km)	Orientation of main lake axis (°)	L (km)	D_L	$\bar{z} / \sqrt{}$ lake area ($m\ km^{-1}$)
Ballycullinan	0.65	9	1.0	1.30	15.65
Ballyquirke	1.85	163	6.9	2.19	2.82
Bray	0.80	90	2.1	1.19	39.74
Bunny	1.95	35	7.2	2.01	1.36
Caragh	3.55	30	19.2	2.42	5.18
Cullaun	1.75	66	4.6	1.64	8.51
Dan	2.48	144	6.3	1.73	12.67
Doolough	2.50	83	5.7	1.43	2.99
Dromore	1.55	34	5.5	2.13	8.14
Easky	1.90	24	5.9	1.50	2.15
Egish	2.70	113	7.7	1.97	1.85
Feeagh	4.05	9	12.0	1.68	7.21
Gara South	3.85	88	8.9	1.76	0.70
Gowna	2.50*	97*	29.8*(55.2)	4.66	2.83*
Graney	4.15	167	12.5	1.80	1.90
Inchiquin	1.65	111	5.7	1.50	9.44
Leane	7.30	125	32.8	2.07	3.01
Lene	4.30	99	13.0	1.78	2.92
Lettercraffroe	1.55	163	4.5	1.38	2.44
Lickeen	2.55	89	6.0	1.85	4.26
Maumwee	0.85	141	2.2	1.19	3.78
Moher	1.13	178	3.2	1.42	4.58
Muckno	1.60*	159*	7.3* (20.2)	2.99	5.41*
Muckross	3.13	86	9.1	1.55	18.88
Mullagh	0.74	149	2.5	1.19	3.93
Oughter	2.05*	111*	7.2* (86.1)	7.30	2.86*
Owel	6.20	139	16.8	1.48	2.23
Pollaphuca	6.00	152	58.0	3.68	1.54
Ramor	4.82	143	21.5	2.23	1.10
Rea	2.71	124	7.6	1.22	2.28
Talt	2.10	127	5.0	1.44	9.08

3.3.2 Temperature

Surface temperature ranged from 2.1°C in Lough Rea on 12th January 1997 to 21.9°C in Lough Ramor on the 8th July 1997 (Figure 3.1). Profiles of temperature and oxygen are presented in Appendix 2.

To give an indication of the occurrence of stratification in the lakes, temperature-depth profiles were examined (Appendix 2). When the change in temperature per metre was greater than 1°C the lake was considered stratified (Table 3.6). This change is generally accepted to be indicative of a thermocline (Horne & Goldman, 1994). This is a simple approach to analysing thermal structure, but it does allow comparison among lakes. Stratification is known to be mainly dependent on wind speed, lake depth and temperature (Moss, 1992). This is reflected in Table 3.6 and Figure 3.2 which show that lakes that stratified most frequently tended to small and deep (i.e. a high $\dot{z} / \sqrt{}$ lake area) and located in the east of Ireland where wind speeds are lower (Rohan, 1986) (e.g. Bray, Dan and Muckno in Table 3.6). Three lakes had complex morphometry (Lough Gowna, Muckno and Oughter) and therefore $\dot{z} / \sqrt{}$ lake area was estimated for the lake basin sampled rather than the whole lake (Table 3.5). In lakes with several basins it is likely that only the morphometry of the basin examined will be relevant in influencing its stratification.

In many of the lakes stratification was a temporary phenomenon dependent on calm weather. Table 3.6 shows that during June 1997, 20 out of 28 lakes were stratified compared to only ten in June 1996. Therefore, most of the lakes are likely to be polymictic with some small deep eastern lakes being monomictic; of course, temperature profiles would need to be taken at a greater frequency to definitively classify their thermal structure. That many of the lakes are polymictic means that integrated water samples from the upper 6 m are more likely to be representative of the chemistry of the entire water column. This is important because mid-lake samples are used in Chapter 4 to calculate catchment export of major ions.

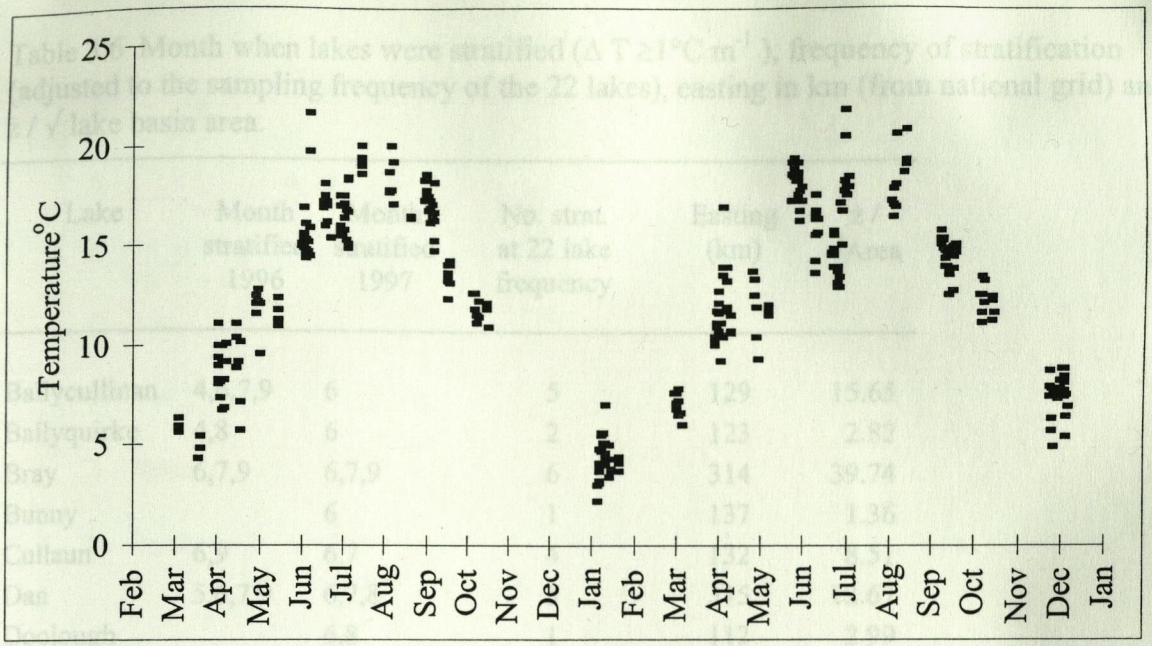


Figure 3.1 Surface temperature in 28 lakes between March 1996 and December 1997. Temperature was not measured in Lough Caragh, Leane and Muckross.

Table 3.6 Month when lakes were stratified ($\Delta T \geq 1°C\ m^{-1}$), frequency of stratification (adjusted to the sampling frequency of the 22 lakes), easting in km (from national grid) and $\dot{z} / \sqrt{}$ lake basin area.

Lake	Month stratified 1996	Month stratified 1997	No. strat. at 22 lake frequency	Easting (km)	$\dot{z} / \sqrt{}$Area
Ballycullinan	4,6,7,9	6	5	129	15.65
Ballyquirke	4,8	6	2	123	2.82
Bray	6,7,9	6,7,9	6	314	39.74
Bunny		6	1	137	1.36
Cullaun	6,9	6,7	4	132	8.51
Dan	5,6,7,9	6,7,8	5	315	12.67
Doolough		6,8	1	112	2.99
Dromore	9	6,7,9	4	135	8.14
Easky	6		1	145	2.15
Egish	7	6,7	3	280	1.85
Feeagh		5	1	96	7.21
Gara S	9		1	171	0.70
Gowna	5,6,8,	6,8	2	229	2.83
Graney		5	1	156	1.90
Inchiquin	7,8,9	5,6,7,8	4	127	9.44
Lene	7	6,8	2	252	2.92
Lettercraffroe		6	1	106	2.44
Lickeen		6	1	117	4.26
Maumwee			0	98	3.78
Moher		6,8	1	98	4.58
Muckno	6,7,9	6,7,9	6	286	5.41
Mullagh	6,7	6,7	4	268	3.93
Oughter	6	6,7	3	234	2.86
Owel	6,7	7,8	3	240	2.23
Pollaphuca		7	1	299	1.54
Ramor		7	1	262	1.10
Rea		6	1	162	2.28
Talt	7,9	6	3	140	9.08

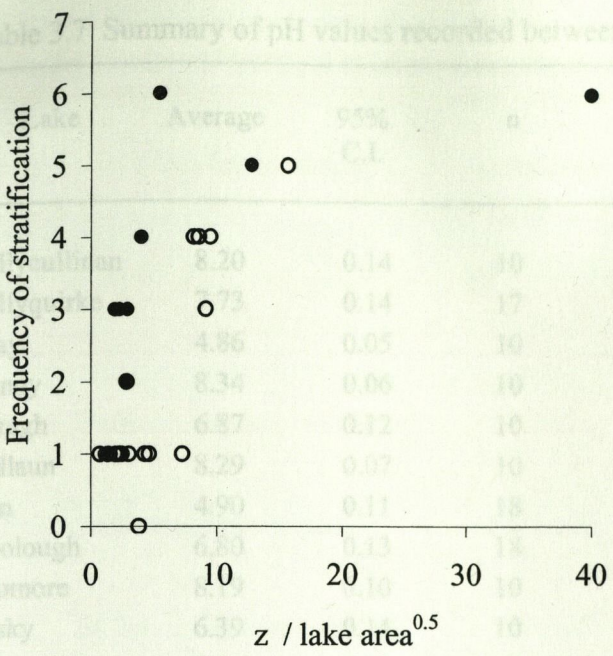


Figure 3.2 The frequency of stratification in relation to $\bar{z}$ / √ lake area for eastern (●) and western (O) lakes. Western lakes are between 96 – 171 km east on the national grid and eastern lakes are 229 - 315 km east.

3.3.3 Acid status of lakes

The average pH (calculated after conversion to arithmetic scale) of the lakes ranged from 4.86 in Lough Bray to 8.39 in Lough Rea (Table 3.7). The Economic Commission for Europe (ECE) have devised a classification system for ecological quality that includes five quality classes based on pH and alkalinity (Table 3.8) (Premazzi & Chiaudani, 1992). The system is based on toxicological impact of acidity on aquatic life as established in US-EPA practices. Three lakes (Lough Bray, Dan and Lettercraffroe) had a pH less than 6.00 where acidity could be harmful to fish and eleven had an alkalinity lower than 20 mg l^{-1} $CaCO_3$ where there is a risk that the pH may fluctuate to harmful values (Table 3.8). Results of alkalinity analysis are presented in Chapter 4.

Table 3.7 Summary of pH values recorded between March 1996 and December 1997.

Lake	Average	95% C.I.	n	Max.	Min.
Ballycullinan	8.20	0.14	10	8.55	7.95
Ballyquirke	7.73	0.14	17	8.17	7.37
Bray	4.86	0.05	10	5.00	4.74
Bunny	8.34	0.06	10	8.44	8.18
Caragh	6.87	0.12	10	7.06	6.58
Cullaun	8.29	0.07	10	8.45	8.15
Dan	4.90	0.11	18	5.24	4.60
Doolough	6.80	0.13	18	7.68	6.40
Dromore	8.19	0.10	10	8.55	8.02
Easky	6.39	0.14	10	6.72	6.13
Egish	8.11	0.20	9	9.17	7.91
Feeagh	6.83	0.12	18	7.14	6.46
Gara S.	8.09	0.33	9	8.80	7.64
Gowna	7.99	0.07	18	8.35	7.76
Graney	7.59	0.13	10	8.40	7.44
Inchiquin	8.22	0.09	17	8.56	8.01
Leane	7.52	0.14	9	7.96	7.33
Lene	8.30	0.04	18	8.45	8.17
Lettercraffroe	5.77	0.15	10	6.20	5.54
Lickeen	7.52	0.14	18	9.26	7.07
Maumwee	6.38	0.15	10	6.67	6.11
Moher	7.22	0.17	18	7.66	6.74
Muckno	7.84	0.08	10	8.02	7.66
Muckross	6.97	0.11	9	7.18	6.74
Mullagh	7.76	0.75	10	9.24	7.09
Oughter	7.89	0.12	10	8.19	7.63
Owel	8.32	0.06	18	8.57	8.14
Pollaphuca	7.47	0.29	10	7.80	6.99
Ramor	7.99	0.18	18	9.26	7.63
Rea	8.39	0.10	10	8.69	8.19
Talt	8.21	0.06	10	8.41	8.07

Table 3.8 ECE scheme for the classification of the ecological quality of lakes by acidity with the number of sampled lakes within each class.

Class	Class interpretation	Alkalinity of class mg l^{-1} $CaCO_3$	no. of lakes in class by alkalinity	pH of class	no. of lakes in class by pH
I	Buffering capacity very good	> 200	0	9.0 - 6.5	27
II	Buffering capacity good	200 - 100	8	6.5 - 6.3	2
III	Buffering capacity weak but keeps the acidity at levels suitable for most fish	100 - 20	13	6.3 - 6.0	0
IV	Buffering capacity is exceeded, leading to levels of acidity which affect the development of spawn.	20 - 10	2	6.0 - 5.3	1
V	Buffering capacity absent and the acidity is toxic for fish species	< 10	9	< 5.3	2

3.3.4 Trophic state

Trophic state for 1997 was assigned using maximum chlorophyll *a* and mean total phosphorus (TP) following OECD (1982) (Table 3.9, Table 3.10). Only a very broad correspondence between the trophic states assigned by the two variables was found (Table 3.10). Based on maximum chlorophyll *a*: two lakes were ultra-oligotrophic, ten were oligotrophic, twelve were mesotrophic, six were eutrophic and one was hypertrophic. The lakes therefore had a wide range in trophic status. This is in contrast with Northern Ireland where a survey of 604 lakes (87% of all the lakes between 1 and 100 ha) found only four to be oligotrophic based on TP concentration. A more limited survey in England (n = 128) found a similar situation whereas in Scotland a survey of all 170 lochs with a surface area greater than 100 ha found that 73% were oligotrophic (Gibson *et al.*, 1995a; Foy & Bailey-Watts, 1998).

Table 3.9 Trophic classification scheme according to chlorophyll *a* and TP as proposed by the O.E.C.D. (1982).

Trophic category	Chlorophyll *a* μg l^{-1}		TP μg l^{-1}
	Mean	Maximum	Mean
Ultra-oligotrophic	< 1.0	< 2.5	< 4
Oligotrophic	< 2.5	< 8.0	< 10
Mesotrophic	2.5 - 8	8 - 25	10 - 35
Eutrophic	8 - 25	25 - 75	35 - 100
Hypertrophic	> 25	> 75	> 100

Table 3.10 Trophic state in 1997 as assigned by maximum chlorophyll *a* and mean TP (OECD, 1982). Lakes are ranked by maximum chlorophyll *a*. Chlorophyll *a* for Lough Egish was suppressed by algaecide ($CuSO_4$).

Lake	n	Max. Chl. *a* $\mu g\ l^{-1}$ 1997	Mean TP $\mu g\ l^{-1}$ 1997	Trophic State Max. Chl *a*	Trophic State Mean TP
Bunny	6	2.1	<4	Ultra-oligotrophic	Ultra-oligotrophic
Maumwee	6	2.4	<4	Ultra-oligotrophic	Ultra-oligotrophic
Muckross	6	2.8	<4	Oligotrophic	Ultra-oligotrophic
Talt	6	2.9	<4	Oligotrophic	Ultra-oligotrophic
Cullaun	6	3.3	<4	Oligotrophic	Ultra-oligotrophic
Dan	10	3.9	14	Oligotrophic	Mesotrophic
Easky	6	3.9	<4	Oligotrophic	Ultra-oligotrophic
Caragh	6	4.0	<4	Oligotrophic	Ultra-oligotrophic
Rea	6	4.0	5	Oligotrophic	Oligotrophic
Feeagh	10	4.1	10	Oligotrophic	Mesotrophic
Inchiquin	10	6.9	26	Oligotrophic	Mesotrophic
Lene	10	7.9	13	Oligotrophic	Mesotrophic
Moher	10	9.3	13	Mesotrophic	Mesotrophic
Owel	10	10.4	11	Mesotrophic	Mesotrophic
Poulaphuca	6	11.2	9	Mesotrophic	Oligotrophic
Doolough	10	11.7	17	Mesotrophic	Mesotrophic
Gara S.	6	12.1	30	Mesotrophic	Mesotrophic
Ballyquirke	10	12.4	20	Mesotrophic	Mesotrophic
Graney	6	14.7	16	Mesotrophic	Mesotrophic
Dromore	6	15.1	16	Mesotrophic	Mesotrophic
Muckno	6	17.4	37	Mesotrophic	Eutrophic
Ballycullinan	6	20.6	26	Mesotrophic	Mesotrophic
Lettercraffroe	6	22.5	10	Mesotrophic	Mesotrophic
Oughter	6	24.1	80	Mesotrophic	Eutrophic
Gowna	10	32.9	47	Eutrophic	Eutrophic
Bray	6	44.7	10	Eutrophic	Mesotrophic
Lickeen	10	48.1	17	Eutrophic	Mesotrophic
Leane	6	54.6	11	Eutrophic	Mesotrophic
Egish	6	60.8	336	Eutrophic	Hypertrophic
Mullagh	6	68.5	56	Eutrophic	Eutrophic
Ramor	10	184.9	91	Hypertrophic	Eutrophic

3.3.5 Phytoplankton

Phytoplankton were not examined in all samples owing to time constraints. This chapter presents results from June or July 1996 for all 31 lakes in order to facilitate a comparison between them (Table 3.11 to Table 3.14). Information on eleven lakes that had phytoplankton enumerated at monthly frequency for 1996 may be found in Appendix 6.

Over 20 Cyanophyta (blue-green bacteria) taxa were found in the lakes (Table 3.11). The most numerous was a small species (< 1 μm), tentatively identified as belonging to the *Synechocystis* genus, found in Lough Bray. This species and the high number of *Botryococcus braunii* were responsible for Lough Bray's high chlorophyll *a* (39 – 45 μg l^{-1}) during June and July 1996 and 1997. This high abundance of phytoplankton was unusual for an upland dystrophic lake with low TP (4 – 16 μg l^{-1}). The most widespread Cyanophyta throughout the range of sampled lakes were *Anabaena flos-aquae, Aphanizomenon flos-aquae, Aphanothece sp., Gomphosphaeria sp.* and *Oscillatoria sp.* Cyanophyta that occurred in large numbers included *Anabaena flos-aquae* in Lough Egish (5726 colonies ml^{-1}) and *Aphanizomenon flos-aquae* in Lough Ballycullinan (6298 colonies ml^{-1}). Cyanophyta tended to be more dominant at low NO_3-N to MRP ratios than at high ratios (> 50) (Figure 3.3). This is a result of the ability of some Cyanophytes such as *Anabaena flos-aquae* and *Aphanizomenon flos-aquae* to fix N.

The phylum Chlorophyta (green algae) was represented by 53 taxa which was more than in any other phylum (Table 3.12). Several taxa occurred in more than 10 lakes; examples include *Scenedesmus sp., Monoraphidium contortum, Sphaerocystis schroeteri* and *Botryococcus braunii*. Eutrophic lakes in the north midlands had the most diverse assemblages of green algae. For example, 15 taxa were found in Lough Gowna, 12 in Lough Muckno and Oughter and 10 in Lough Mullagh. In contrast, only four taxa of green algae were found in Lough Ramor, which is hypertrophic. Green algae were poorly represented in lakes at the other end of the trophic scale such as Lough Dan, Feeagh and Bunny. The poor diversity of green algae in the oligotrophic lakes is likely to be an artefact of the sampling regime – only small volumes of quantitative samples were enumerated (a transect of a 5 - 25 ml chamber). A larger sample, such as that provided by a net, would reveal a greater diversity. For example, only seven Chlorophyta were found

in Lough Maumwee compared with 167 in both quantitative and net samples taken between 1987 and 1989 (Bowman, 1991).

Sixteen taxa of Bacillariophyta (diatoms) were found in the lakes (Table 3.13). The most frequently occurring were *Cyclotella sp.* (18 lakes), *Melosira sp.* (14 lakes), *Asterionella formosa* (13 lakes) and *Fragillaria crotonensis* (9 lakes). The taxa *Asterionella formosa* and *Melosira sp.* occurred in high numbers (> 500 cells ml^{-1}) in several of the more productive lakes such as Lough Ballyquirke, Gowna, Oughter and Ramor.

A small number of taxa from the Chrysophyta (chrysophytes), Pyrrhophyta (dinoflagellates) and Cryptophyta (cryptomonads) were present in the lakes (Table 3.14). The cryptomonads *Rhodomonas minuta* and *Cryptomonas sp.* (probably mainly *C. ovata*) were present in almost all samples, and were the most ubiquitous of the phytoplankton taxa encountered. The chrysophyte *Dinobryon sp.* was present in 14 lakes and was particularly numerous in some of the calcareous lakes such as Lough Owel, Dromore and Lene. The dinoflagellate *Ceratium hirundinella* occurred in 11 of the lakes.

Summer chlorophyll *a* concentrations were correlated with the numbers of cyanophytes ($r_S = 0.79$, $p \leq 0.0001$) and bacillariophytes ($r_S = 0.48$, $p = 0.005$) but not with the chlorophytes ($r_S = -0.03$, $p = 0.87$). This indicated that the former two groups accounted for most of the phytoplankton biomass in summer. In certain cases small (mainly < 5 μm) unicellular algae dominated phytoplankton biomass. Small unicells in Lough Lene had an almost identical seasonal pattern to that of chlorophyll *a* indicating that they accounted for most of the phytoplankton biomass (Figure 3.4). Moreover, the pattern of other phytoplankton was dissimilar to that of chlorophyll *a* (Figure 3.5).

Table 3.11 Cyanobacteria ml^{-1} in lakes sampled between 29/6/96 and 25/7/96 (Lough Muckross and Leane were sampled on 12/6/96). An asterisk indicates that the result is in colonies ml^{-1}. Lakes are ranked by sample chlorophyll *a*.

Lake	*Anabaena flos-aquae**	*Anabaena circinalis**	*Anabaena solitaria**	*Anabaena spiroides**	*Aphanizomenon**	*Aphanothece**	*Aphanocapsa delicatissima**	*Aphanocapsa sp.**	*Coelosphaerium**	*Gomphosphaeria**	*Merismopedia glauca*	*Merismopedia sp.*	*Microcystis aeruginosa**	*Microcystis flos-aquae**	*Microcystis sp.**	*Oscillatoria agardhii**	*Oscillatoria limnetica**	*Oscillatoria rubescens**	*Oscillatoria sp.**	*Synechocystis sp.*
Dan																				
Feeagh																				
Bunny	2					5			2	1		37								
Muckross										0										
Moher	0					54	0										0			
Gara N.						2														
Talt						45				1				0						
Caragh																				
Cullaun	8								2								15			
Gara S.																				
Lettercraffroe						1											1			
Inchiquin	7		2		8	1											0		0	
Maumwee																				
Rea	40					102			64		49									
Doolough					34															
Owel	1					44		5		90							10			
Muckno	6														1					
Leane					1														3	
Lene	22					39				2							45		22	
Graney			4		156					15									7	
Easky	43					86		1				81								
Mullagh	26		4	33		4			133	19			7	4						
Pollaphuca						39				10							3	8		
Lickeen	3				28	10				33										
Ballyquirke	193				119	219									2				3	
Gowna	31				16				8	31							235			
Bray																				744947
Oughter	327										1432									
Dromore					51												2			
Ramor	30	128	23	45	15															
Ballycullinan			4		6298												136	153		
Egish 1	5726																			

Table 3.12 Chlorophyta ml^{-1} in lakes sampled between 29/6/96 and 25/7/96 (Lough Muckross and Leane were sampled on 12/6/96). An asterisk indicates that the result is in colonies ml^{-1}. Lakes are ranked by sample chlorophyll *a*.

Lake	*Ankistrodesmus sp.*	*Ankistrodesmus spiralis*	*Ankistrodesmus spiralis**	*Ankyra judayi*	*Botryococcus braunii**	*Chlamydomonas sp.*	*Chlorella sp.*	*Chlorogonium sp.*	*Closterium acerosum*	*Closterium acutum var. variabile*	*Closterium parvulum*	*Closterium sp.*	*Coelastrum sp.*	*Cosmarium sp.*	*Crucigenia rectangularis*	*Crucigenia sp.*	*Dictyosphaerium sp.*	*Elakatothrix biplex var. conglutinata*	*Elakatothrix sp.*	*Eudorina elegans*
Dan																				
Feeagh	5																			
Bunny					0															
Muckross					0									1						
Moher		1			0			12				0			6			1		
Gara N.							2										6			1
Talt					0	5														
Caragh										3				3						
Cullaun	2																			
Gara S.	2																			
Lettercraffroe							27				0							0		
Inchiquin																		0		13
Maumwee	6			1						3				2						
Rea					2									2	24					
Doolough																				
Owel					2														7	
Muckno	58												18					5		
Leane	1									1										
Lene		11																6		
Graney												11					4			
Easky	2		9		1							2								
Mullagh					15												4	4		
Pollaphuca																				
Lickeen	1											6		6						
Ballyquirke					4	48	4					4					44			
Gowna				70		8							78			31	305	16		
Bray					72	1														
Oughter															859		205			
Dromore																				
Ramor																				
Ballycullinan																				
Egish				4																

Table 3.12 Continued.

Lake	*Eudorina sp.*	*Gonium sp.*	*Kirchneriella contorta*	*Kirchneriella obesa*	*Kirchneriella sp.*	*Koliella longiseta*	*Kirchneriella lunaris*	*Lagerheimia sp*	*Micractinium sp.*	*Monoraphidium arcuatum*	*Monoraphidium capricornutum*	*Monoraphidium contortum*	*Monoraphidium sp.*	*Mougeotia sp.*	*Oocystis lacustris*	*Oocystis solitaria*	*Oocystis sp.*	*Pediastrum sp.**	*pseudosphaerocystis sp.*	*Quadrigula sp.*
Dan																				
Feeagh												100	5							
Bunny																		2		1*
Muckross						1						6	1						29	
Moher												2	0				24			
Gara N.							2									2		1		
Talt						12														1
Caragh													3							
Cullaun																				
Gara S.										2										
Lettercraffroe					0									10		0				
Inchiquin															4	0	3			
Maumwee	1																			
Rea																				
Doolough	14												15							
Owel																				
Muckno	0											56			18	3	3	2		
Leane																				
Lene				22			9			2		6								
Graney												7								
Easky																				
Mullagh	7								11								11	4		
Pollaphuca												13					5			
Lickeen																				
Ballyquirke		152				48			63			59								
Gowna						39		8	407			587			204	47				
Bray																				
Oughter			82	20					1657		102	348						41		
Dromore	2																			
Ramor									8			30						8		
Ballycullinan																				
Egish																	4	2		

Table 3.12 Continued.

Lake	*Scenedesmus acuminatus*	*Scenedesmus sp.*	*Schroederia setigera*	*Sphaerocystis schroeteri**	*Spondylosium planum*	*Spirulina sp.**	*Spirogyra sp.* (condensata group)*	*Staurastrum sp.*	*Staurodesmus sp.*	*Tetraedron caudatum*	*Tetraedron sp.*	*Tetrastrum triangulare*	*Volvox sp.**
Dan													
Feeagh				2									
Bunny		44		8							1		
Muckross		6		0								24	
Moher		1		5					0				
Gara N.		53		0						2			
Talt		6		0					0				
Caragh		3	43	1									
Cullaun													
Gara S.		37				2							
Lettercraffroe							0	1					
Inchiquin				3				0					0
Maumwee		7		6									
Rea		12											
Doolough													
Owel				1									
Muckno		11		3				1					
Leane				1									
Lene		19											
Graney													
Easky				4									
Mullagh			11					4					11*
Pollaphuca					1								
Lickeen								3					
Ballyquirke		44											
Gowna	31	188								16			
Bray													
Oughter		818	82							20	20		
Dromore		34		2									
Ramor		23											
Ballycullinan													
Egish			4										

Table 3.13 Bacillariophyceae ml^{-1} in lakes sampled between 29/6/96 and 25/7/96 (Lough Muckross and Leane were sampled on 12/6/96). An asterisk indicates that the result is in colonies ml^{-1}. Lakes are ranked by sample chlorophyll *a*.

Lake	*Asterionella formosa*	*Cyclotella sp.*	*Fragilaria crotonensis* (cells)	*Fragilaria crotonensis* (colony)	*Melosira sp.*	*Navicula sp.*	*Nitzschia sp.*	*Rhizosolenia sp.*	*Stephanodiscus sp.*	*Synedra acus*	*Synedra sp.*	*Synedra ulna*	*Tabellaria cells*	*Tabellaria fenestrata var. asterionelloides*	*Tabellaria flocculosa*	*Diatom sp.*
Dan		2													3	
Feeagh	3				6						2			6	3	
Bunny		2														
Muckross		5	4											0		
Moher		9			1											
Gara N.																
Talt	0	3									5					
Caragh	1*				0*			3						2	9	
Cullaun	11	3	11	12												
Gara S.						3										
Lettercraffroe															2	
Inchiquin		1														
Maumwee																
Rea	11	84	2													
Doolough	7				3*									21	3	
Owel		14	59													
Muckno		2				2										
Leane	10	3			21*											
Lene			22		9		6			2						
Graney		19			7											
Easky											1			3	2	
Mullagh					63											
Pollaphuca	16	104	10		57			330	5			5				34
Lickeen	3*	3											42			
Ballyquirke	26	4			723	4	11									
Gowna	736	70	8		2569											
Bray																1
Oughter	1984	20			532		20			20						
Dromore	61*		664		4*					23						
Ramor		38			686						53					
Ballycullinan			51							51						
Egish																

Table 3.14 Chrysophyta, Pyrrhophyta, Euglenophyta and Cryptophyta ml^{-1} in lakes sampled between 29/6/96 and 25/7/96 (Lough Muckross and Leane were sampled on 12/6/96). An asterisk indicates that the result is in colonies ml^{-1}. Lakes are ranked by sample chlorophyll *a*.

Lake	*Bitrichia sp.*	*Ceratium hirundinella*	*Chromulina sp.*	*Colacium sp.*	*Dinobryon sp.*	*Dinobyron sp.* (out of case)	*Gymnodinium sp.*	*Cryptomonas sp.*	*Mallomonas sp.*	*Rhodomonas minuta*	*Trachelomonas sp.*
Dan								8		9	
Feeagh								3		70	
Bunny		2			10		3	3		11	
Muckross		0					1	5		71	
Moher		0		1				9		365	
Gara N.							3	73		219	
Talt		1	2		14		2	39		155	
Caragh					70			103	3	48	
Cullaun					5			39		36	
Gara S.								110		798	
Lettercraffroe			13				2	11	0	18	0
Inchiquin		0					0	44		431	
Maumwee					5		3	24		3	
Rea	9	8			20		2	26		66	
Doolough					5			3	29	16	
Owel					433			7		13	
Muckno		1								5	
Leane								42		82	
Lene		1			181	112	4	6		19	
Graney							4	33			
Easky					3			8		6	
Mullagh											
Pollaphuca		1			13			13		16	
Lickeen								24		4	
Ballyquirke		9			15		7	41		59	
Gowna							8	196		274	
Bray								2		8	
Oughter								614		368	
Dromore		4			1166		6	121		13	
Ramor								8			
Ballycullinan					25		21	119			
Egish								55		11	

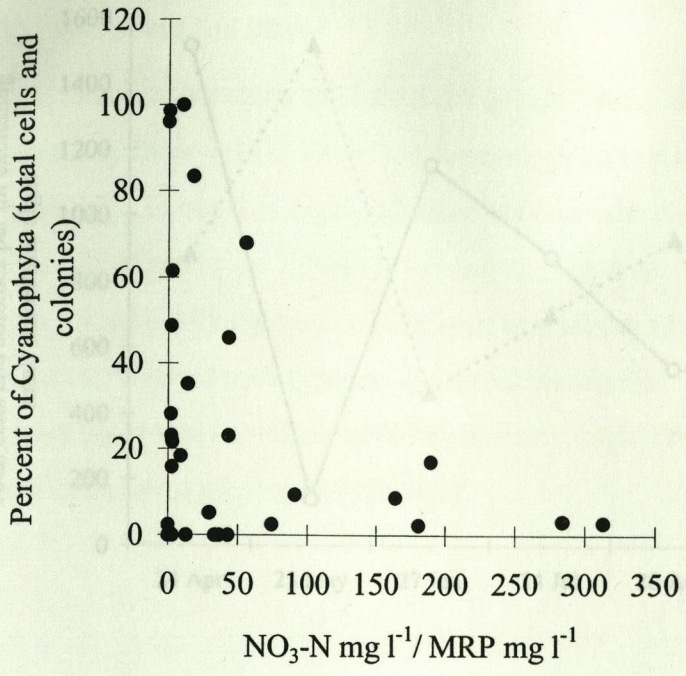


Figure 3.3 Percentage of Cyanophyta (cells and colonies) and the ratio NO_3-N mg l^{-1} / MRP mg l^{-1} in 32 lakes sampled in July 1996.

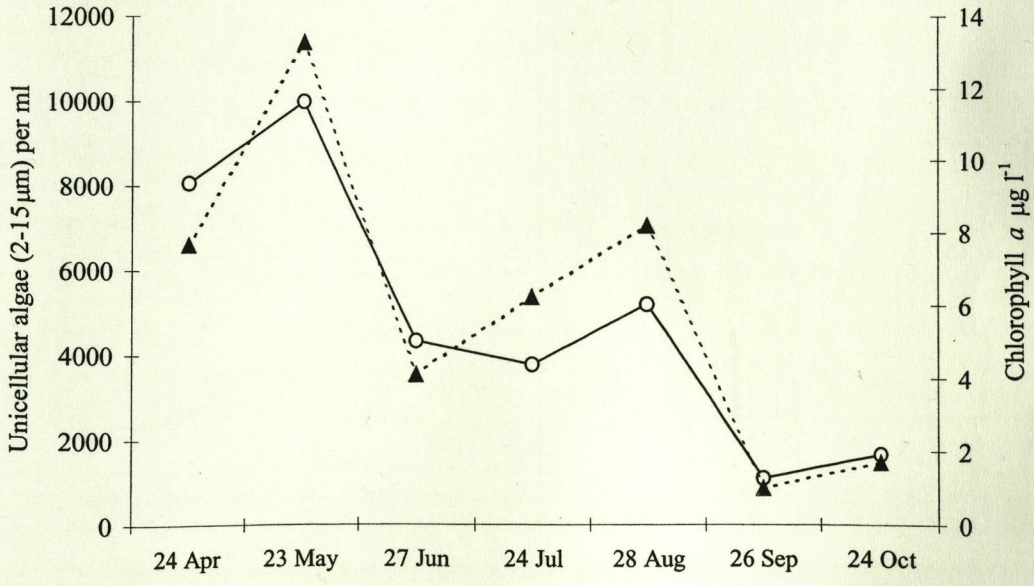


Figure 3.4 Unicellular algae per ml (2-15 µm) (—O—) and chlorophyll *a* (µg l^{-1}) (- - -▲- - -) in Lough Lene between April and October 1996.

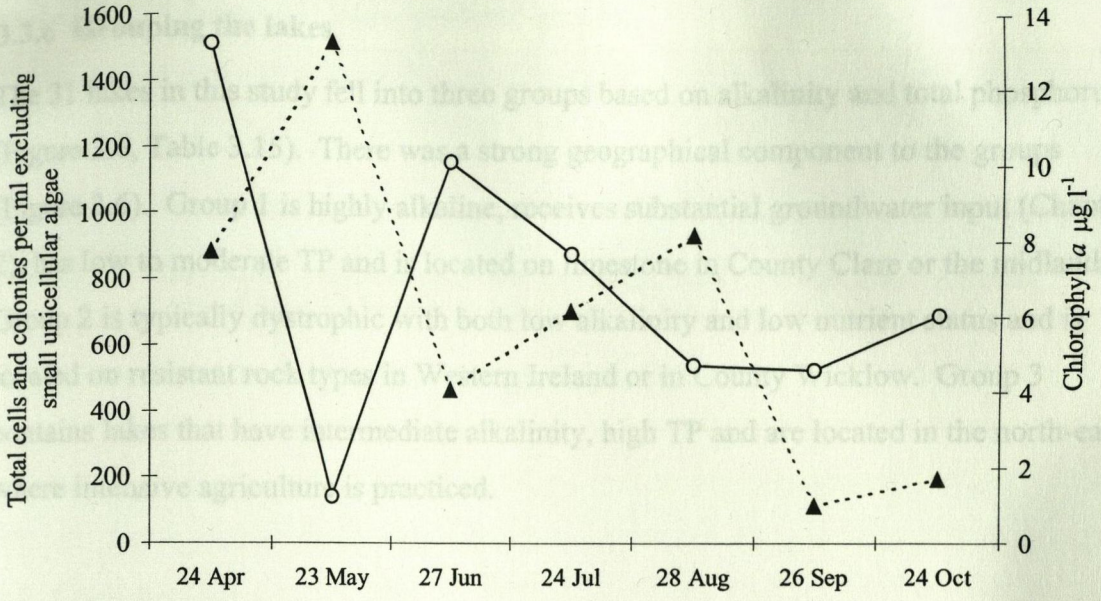


Figure 3.5 Total cells and colonies per ml excluding small (2-15 µm) unicellular algae (—○—) and chlorophyll *a* (µg l^{-1}) (· · ·▲· · ·) in Lough Lene between April and October 1996.

3.3.6 Grouping the lakes

The 31 lakes in this study fell into three groups based on alkalinity and total phosphorus (Figure 3.6, Table 3.15). There was a strong geographical component to the groups (Figure 3.6). Group 1 is highly alkaline, receives substantial groundwater input (Chapter 2), has low to moderate TP and is located on limestone in County Clare or the midlands. Group 2 is typically dystrophic with both low alkalinity and low nutrient status and is located on resistant rock types in Western Ireland or in County Wicklow. Group 3 contains lakes that have intermediate alkalinity, high TP and are located in the north-east where intensive agriculture is practiced.

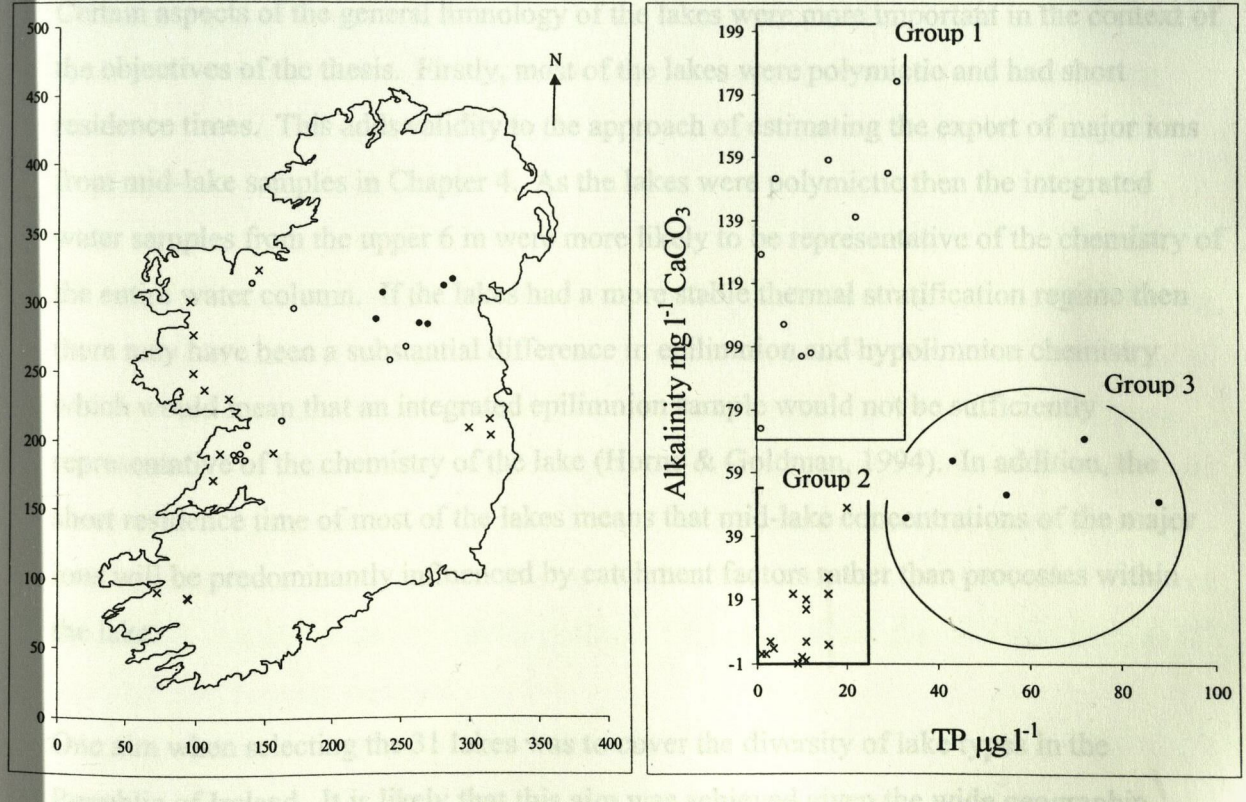


Figure 3.6 The separation of the 31 lakes into Group 1 (O), Group 2 (X) and Group 3 (●) based on total phosphorus and alkalinity. Scale on the map corresponds to part of the national grid in km. Lough Egish (Group 3) is omitted from the graph because of its high TP concentration (344 µg l^{-1}).

Table 3.15 Division of 31 lakes into three groups.

Group	Lakes
Group 1	Ballycullinan, Bunny, Cullaun, Dromore, Gara S, Inchiquin, Lene, Owel, Rea, Talt.
Group 2	Ballyquirke, Bray, Carragh, Dan, Doolough, Easky, Feeagh, Graney, Leane, Lettercraffroe, Lickeen, Maumwee, Moher, Muckross, Pollaphuca.
Group 3	Egish, Gowna, Muckno, Mullagh, Oughter, Ramor.

3.4 Conclusions

Certain aspects of the general limnology of the lakes were more important in the context of the objectives of the thesis. Firstly, most of the lakes were polymictic and had short residence times. This adds validity to the approach of estimating the export of major ions from mid-lake samples in Chapter 4. As the lakes were polymictic then the integrated water samples from the upper 6 m were more likely to be representative of the chemistry of the entire water column. If the lakes had a more stable thermal stratification regime then there may have been a substantial difference in epilimnion and hypolimnion chemistry which would mean that an integrated epilimnion sample would not be sufficiently representative of the chemistry of the lake (Horne & Goldman, 1994). In addition, the short residence time of most of the lakes means that mid-lake concentrations of the major ions will be predominantly influenced by catchment factors rather than processes within the lake.

One aim when selecting the 31 lakes was to cover the diversity of lake types in the Republic of Ireland. It is likely that this aim was achieved given the wide geographic distribution of the lakes and their diverse trophic and acid status. However, it is hard to verify this given the lack of information on the total population of over 5500 lakes in Ireland (Irvine *et al.*, 2001).

4. THE RELATIONSHIP BETWEEN MAJOR IONS AND CATCHMENT CHARACTERISTICS

4.1 Introduction

The principal aim of this chapter is to explain the variation in the concentration and export of major anions and cations in terms of catchment characteristics. The calculation of the loads exported will add to current knowledge of both terrestrial and limnetic systems in Ireland. Understanding how the catchment controls the flux of the major ions is important for a number of reasons. Some of the ions are important in agriculture such as SO_4^{2-} and K^+ whereas others such as Na^+ are important in ion exchange (Allott *et al.*, 1997). Considered together, the export of major base cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) yields information about chemical weathering which is important in soil formation and acid neutralisation (Johnson *et al.*, 1994). In addition, export calculations can be used to estimate total atmospheric deposition to catchments where no net accumulation or release of elements is assumed (Ross & Lindberg, 1994).

The main sources of elements in catchments are precipitation and soil and rock weathering; the relative importance of these can be used to classify waters (Gibbs, 1970). For many of the elements considered their dependence on catchment characteristics will be obvious. For example, the export of Ca^{2+} will be highly influenced by the presence of limestone and Cl^- and Na^+ by distance from the Atlantic Ocean. However, within these straightforward relationships some variation remains to be explained, such as the variation in Ca^{2+} between catchments that are located on similar geology. The controls on other elements such as K^+ and SO_4^{2-} may be more complex.

4.1.1 Sodium and chloride

The main source of sodium and chloride in surface waters is sea-salt. The atmospheric deposition of sea-salt is highest on the west coast and decreases eastwards (Table 4.1) (Jordan, 1997). To reveal other sources of elements, the proportion that is derived from sea-salt is often subtracted when reporting results. These results are reported as non-marine concentrations and may be derived from soil and rock weathering, anthropogenic sources or air-borne dust. Estimation of non-marine concentration is often achieved by assuming all Cl^- is derived from marine sources and using this concentration to subtract a proportion of each element relative to its ratio to Cl^- in seawater (Allott *et al.*, 1997; Hedin *et al.*, 1995).

Chloride is the most appropriate tracer of marine inputs in catchments because of its high mobility in soils (Hedin *et al.*, 1995; Meybeck *et al.*, 1996). However, its use as a tracer for marine inputs will not be valid if non-marine sources of Cl^- are important. This is not a concern in Ireland because substantial geological sources such as halite (NaCl) are absent (Brownlow, 1996; Geological Survey, 1985) and dissociation of HCl derived from coal burning power stations is not important (Jordan, 1997). Only one case of a geological source of Cl^- has been reported in Ireland. This was in the Vartry catchment in Wicklow where elevated concentrations were attributed to rock type of marine origin. Although, re-examination of the data reveals that differences in export between catchments, as opposed to concentration, may have been small (Table 4.2).

Non-marine Na^+ is largely derived from weathering of minerals. The amount of Na^+ weathered is a function of rock type and denudation rate. For example, granitoids and greywacke contain similar amounts of Na^+ (2.64% and 2.44%) but greywacke should release more Na^+ as it has a denudation rate of 0.25 mm yr^{-1} in comparison with just 0.02 mm yr^{-1} for granitoids (Giusti, 1999). Naturally, only a portion of the elements weathered are exported from catchments. Giusti (1999) estimated that of 31.6 kg ha^{-1} Na^+ weathered only 2.0-4.3 kg ha^{-1} was exported from a peatland catchment in Scotland, probably owing to the retention of Na^+ in clay minerals.

Previous studies in Ireland have noted a decrease in Na^+ and Cl^- concentration with distance eastwards from the Atlantic Ocean. Webb (1947) noted this and attributed higher Cl^- in the west to increased sea-spray because of the increased frequency and force of westerly winds. Webb (1947) also noted significant variation in Cl^- in lakes within localities which he attributed to differences in topography, weather and season. Some evidence of geologically derived Na^+ and its adsorption in soils was also found. Flanagan & Toner (1975) and Bowman (1991) also found higher Na^+ and Cl^- in western freshwaters.

Allott *et al.* (1997) noted that Na^+ and Cl^- in Irish streams increased in response to westerly gales and was higher in forested catchments because of increased interception of sea-salts. In addition, concentrations were also considered to be influenced by the proximity to the Atlantic, aspect, slope and altitude of the catchment. Evidence was also found for retention of Na^+ in the catchments after storms with an accompanying increase in stream H^+ concentration. This retention of Na^+ was followed by positive values of non-marine Na^+ for the next three seasons. Bowman (1991) also noted correspondence between H^+ ion increase and high sea-salt deposition in Lough Veagh in the North-West of Ireland. However, Bowman (1991) did not find a corresponding lower stream concentration of Na^+ which would indicate ion exchange between H^+ and Na^+. Instead, a net retention of Cl^- was noted. In Irish catchments it may be difficult to discern export of non-marine Na^+ weathered from rocks from that previously adsorbed in the catchment.

It is clear from previous studies that that Na^+ and Cl^- decrease from west to east. However, only poor relationships are generally found (e.g. Webb, 1947). One objective of this work is to investigate why this relationship is poor and provide a better explanation using catchment characteristics.

Table 4.1 Major ion concentration and deposition determined from bulk precipitation samples from Valentia (west coast) and Dublin airport (east coast) (Jordan, 1997). Data are mean values for the period 1992-4.

	Valentia mg l^{-1}	Valentia kg ha^{-1} yr^{-1}	Dublin airport mg l^{-1}	Dublin airport kg ha^{-1} yr^{-1}
Rainfall (mm)	1566		763	
Na^+	10.24	160	4.80	37
Cl^-	17.78	278	7.98	61
Mg^{2+}	1.17	18	0.61	5
Ca^{2+}	0.54	8	3.10	24
K^+	0.43	7	0.54	4
SO_4^{2-}	3.24	51	5.06	39

Table 4.2 Differences in Cl^- concentration, rainfall (Kelly-Quinn *et al.*, 1997) and approximate Cl^- export between a site with a proposed geological source of Cl^- (V1B) and one without (GLM). Net rainfall was estimated by subtraction of mean evapotranspiration of 506 mm (Rohan, 1986).

Site	Geology	Cl^- mg l^{-1}	rainfall (mm)	net rainfall (mm)	approximate export (kg ha^{-1} yr^{-1})
V1B	Palaeozoic sediments	12.4	979	473	59
GLM	Granite	6.1	1486	980	60

4.1.2 Sulphate

Previous work on SO_4^{2-} has focused mainly on the acidification potential of anthropogenic emissions resulting from the burning of fossil fuels. An example of how emissions of SO_2 can result in the deposition of sulphuric acid is presented below (O'Neill, 1993).

$$OH + SO_2 \longrightarrow HSO_3 \xrightarrow{O_2} HSO_5 \xrightarrow{NO} HSO_4 + NO_2 \xrightarrow{H_2O} H_2SO_4 + NHO_3$$

Estimates of anthropogenic S emissions into the Earth's atmosphere range from 70 to 100 million tonnes which is higher than natural emissions of approximately 60 million tonnes (Hultberg *et al.*, 1994). Sulphur deposition from anthropogenic sources can be derived locally or from long-range transport (O'Neill, 1993). In Ireland, the atmospheric deposition of SO_4^{2-} is derived from both anthropogenic and marine sources. Total sulphur deposition in Ireland is generally higher in the west (50.8 kg SO_4^{2-} ha^{-1} yr^{-1} at Valentia) than in the east (19.0 kg SO_4^{2-} ha^{-1} yr^{-1} at Birr) but local pollution can cause higher deposition (38.7 kg SO_4^{2-} ha^{-1} yr^{-1} at Dublin) (Jordan, 1997). The high deposition in the west is a result of both the high concentration of sea-salts and high precipitation. Non-marine sources can account for between 80% of total deposition in the north-east, to around 20% in the west (Jordan, 1997). The major source of non-marine SO_4^{2-} deposition is from air pollution carried by easterly winds as evidenced by the fact that maximum deposition of non-marine SO_4^{2-} coincides with periods of easterly winds (Bowman, 1991). The proportion of non-marine SO_4^{2-} in Ireland is generally lower than in northern Europe where 90% of atmospheric S is of anthropogenic origin (Hultberg *et al.*, 1994). This is probably because Ireland has a low population density and the wind direction is frequently westerly. Anthropogenic SO_4^{2-} in precipitation has been found to be in decline in Ireland since 1983 because of reduced SO_2 emissions. This has been accompanied by an increase in rainfall pH (Jordan, 1997).

Other inputs of S to catchments include the addition of fertilisers to agricultural land. However, direct losses of fertiliser S may not be the most important as over 90% of S in pasture soils can be in organic form and mineralisation from this pool can account for more than 75% of SO_4^{2-} leached (Sakadevan *et al.*, 1993). The amount of total S in a pasture increases over time with continued S fertiliser application (Freney & Williams, 1983).

Therefore, factors which are likely to be important in SO_4^{2-} leaching are an increased store of organic S owing to a history of fertiliser application and processes controlling mineralisation.

In Ireland, current S fertiliser use is lower than in the past because of a change in the type of fertilisers applied to pasture. Hanley (1969) states that the proportion of sulphur in fertiliser applied in Ireland was highest in 1951-52 because 65% of phosphorus was applied as superphosphate (12% S) and 83% of nitrogen as sulphate of ammonia (24% S). As fertiliser type shifted to combined fertilisers with no S then input declined from 37,000 tons in 1969 to a minimum of less than 8,000 tons in 1975. The latest figures for 1989 represent a small increase to 20,000 tons which reflects a successful campaign highlighting its beneficial effects on crop yield (Murphy, 1991).

The proportion of SO_4^{2-} in lakes that is derived from soil and rock weathering will be dependent on the rock composition, weathering rate and the proportion transported to the lake. Giusti (1999) found that granitoids, greywackes and mudstones contained 0.02% S, whereas shales had 0.1% S and therefore contributed most to the weathering of 7.5 kg SO_4^{2-} ha^{-1} yr^{-1} in a Scottish catchment. This was a large proportion in comparison to stream outputs which ranged from 9.3 to 37.7 kg SO_4^{2-} ha^{-1} yr^{-1} although the actual contribution from rock weathering would also be determined by sorption/desorption processes in the catchment (Giusti, 1999). Kähkönen (1996) related the high concentrations of SO_4^{2-} in parts of Finnish Lapland to sulphide minerals in soils and bedrock. In other areas atmospheric deposition was the main factor controlling concentration.

In Ireland, Bowman (1991) found a higher non-marine concentration of SO_4^{2-} in an eastern stream in comparison with streams in the west which may be explained by the higher non-marine deposition in the east. Allott *et al.* (1997) found that non-marine SO_4^{2-} contributed to the acidity of streams in western catchments. The source of the non-marine SO_4^{2-} was stated to be from precipitation and also natural processes in the catchment such as oxidation of sulphides and organic matter.

Gibson *et al.* (1995a) found SO_4^{2-} concentrations in 612 lakes in Northern Ireland generally ranged from 5 to 15 mg l^{-1}. They noted higher concentrations on greywacke geology

although a contour plot suggested lowland pasture as a source, but catchment land-use information was not available to confirm this. Figures for SO_4^{2-} export from catchments are sparse: rates from an upland peat catchment were 34.8-36.9 kg SO_4^{2-} ha^{-1} yr^{-1} (Gibson *et al.*, 1995b) and river export to Lough Neagh averaged 115 kg SO_4^{2-} ha^{-1} yr^{-1} between 1989 and 1999 (Lennox *et al.*, 2000). Other work that has related SO_4^{2-} to catchment characteristics includes that by Thornton & Dise (1998) who attributed higher SO_4^{2-} in streams in the English lake district to higher proportions of forestry which scavenged atmospheric sulphur. D'Arcy & Carignan (1997) found that SO_4^{2-} had a negative relationship with altitude in lakes in Québec ($r^2 = 0.67$, $n = 30$) which was attributed to lower concentrations of anthropogenic SO_4^{2-} in precipitation at higher altitudes and evaporative concentration of SO_4^{2-} at lower altitudes. Generally, few figures are available for forms of S other than SO_4^{2-} in freshwaters. Houle *et al.* (1995) found that on average 91% of total dissolved S was present as SO_4^{2-} and 9% (0.185 mg l^{-1}) as dissolved organic S in 59 south-western Québec lakes.

There are several gaps in knowledge about SO_4^{2-} in Ireland which will be addressed in this study. Firstly, export estimates are sparse and were identified by Murphy (1991) as an area of future research needed to allow correct estimates of fertiliser application. Secondly, the variation in SO_4^{2-} in Northern Ireland remains unexplained but agriculture has been implicated (Gibson *et al.*, 1995a). This study combines lake chemistry data with comprehensive descriptions of catchments and should therefore resolve the main factors controlling SO_4^{2-} in Irish freshwaters.

4.1.3 Potassium

Inputs of K^+ from atmospheric deposition in the Republic of Ireland range from 1.85 kg ha^{-1} yr^{-1} at Birr in the midlands to 6.79 kg ha^{-1} yr^{-1} at Valentia observatory in the west (excluding extreme coastal deposition of 12.37 kg ha^{-1} yr^{-1} at Belmullet). The non-marine component of deposition can range from 0.60 kg K^+ ha^{-1} yr^{-1} in the midlands to 2.83 kg K^+ ha^{-1} yr^{-1} at Dublin airport (Jordan, 1997).

Potassium can be derived from the weathering of minerals such as micas (muscovite and biotite) and orthoclase feldspars (K-feldspars) (Plummer & McGeary, 1991). One example

is the reaction for the hydration of potassium feldspar to kaolinite which indicates that weathering would release twice as much silica as potassium (Walling, 1980);

$$2KAlSi_3O_8 \text{ (K-feldspar)} + 2H_2CO_3 + 9H_2O \rightarrow$$
$$Al_2Si_2O_5(OH)_4 \text{ (kaolinite)} + 2K^+ + 4H_4SiO_4 + 2HCO_3^-$$

Such weathering of K-feldspar does not always result in K^+ which is available for leaching. Potassium may be strongly adsorbed to negatively charged clay and organic colloids or reincorporated into silicate mineral structures (O'Neill, 1993); while 50.9 kg K ha^{-1} yr^{-1} was weathered in a Scottish upland peat catchment the observed export was only 2.0 - 5.8% of this (1.0-2.9 kg ha^{-1} yr^{-1}) (Giusti, 1999). Biological uptake can also reduce the export of K^+ from catchments (Reynolds *et al.*, 1997).

Potassium inputs to agriculture are substantial. In 1995 the average K^+ applied to the total grassland category (i.e. hay, silage and grazing) was 34 kg ha^{-1} (higher amounts of 57 kg ha^{-1} were applied to silage alone). Potassium is predominantly applied as compound fertiliser with N and P (Murphy *et al.*, 1997). Outputs from cattle farming are mainly through milk rather than meat. Culleton *et al.* (1996) found that milk outputs amounted to 14.5 kg K ha^{-1} yr^{-1} (2.2 livestock units ha^{-1}) whereas most fertiliser applied to grass for silage and then fed to beef cattle was recovered in slurry. The impact of cattle farming on lake chemistry may therefore be expected to be different depending on whether it is dairy or meat based. As 79% of cattle are used for meat (June 1995, Department of Agriculture, Food and Forestry, 1997) there is little removal of K^+ in farm produce. Given that fertiliser use has remained fairly constant since 1970 (Figure 4.1, Murphy *et al.*, 1997) it may not be surprising that Culleton *et al.* (1996) have observed an increase in soil potassium from 20 mg kg^{-1} in 1950 to 108 mg kg^{-1} in 1994 in Ireland.

Gibson *et al.* (1995a) in a survey of 612 lakes in Northern Ireland found the majority of lakes had a K^+ concentration less than 0.5 mg l^{-1}. Thirty-six of the lakes had concentrations greater than 4.5 mg l^{-1} and these lakes were situated in the lowlands and tended to be enriched with P and Cl^-. This indicated that lowland agriculture was important in elevating K^+ concentration in these lakes.

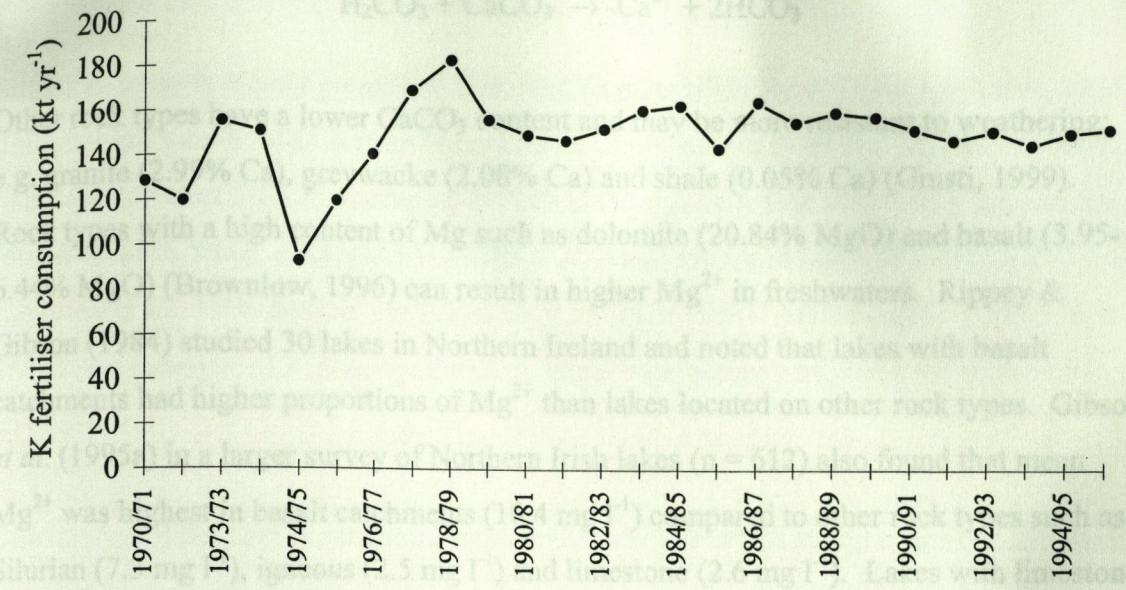


Figure 4.1 K^+ fertiliser use from 1970/1 to 1995/96 (kilo-tonnes yr^{-1}) (Minister for Agriculture Food and Forestry, 1999†; Murphy *et al.*, 1997).

4.1.4 Magnesium, calcium and alkalinity

Inputs of Mg^{2+} and Ca^{2+} from atmospheric deposition can be large (Table 4.1). Jordan (1997) found Ca^{2+} deposition decreased from 20 - 40 kg ha^{-1} yr^{-1} in the west to 0 - 5 kg ha^{-1} yr^{-1} in the east. Similarly, Mg^{2+} deposition ranged from 20 - 60 kg ha^{-1} yr^{-1} in the west to 0 - 5 kg ha^{-1} yr^{-1} in the east. On average, 77% of Ca^{2+} deposited was from non-marine sources whereas Mg^{2+} deposition was predominantly derived from marine sources (Jordan, 1997).

Calcium, alkalinity and Mg^{2+} in lakes are also dependent on the rock type and soils of a catchment. If limestone rocks are present they will naturally be a dominant source of Ca^{2+} and alkalinity. This is because limestone is over 96% $CaCO_3$ and is weathered rapidly (Brownlow, 1996; Plummer & McGeary, 1991). Dissolution of limestone takes place according to the equation below where carbonic acid in precipitation reacts with calcium carbonate to produce two molecules of bicarbonate (the major component of alkalinity in natural waters) and one calcium ion (Horne & Goldman, 1994).

† http://www.irlgov.ie/daff/tabmenu.htm

$$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

Other rock types have a lower $CaCO_3$ content and may be more resistant to weathering: e.g. granite (2.99% Ca), greywacke (2.08% Ca) and shale (0.05% Ca) (Giusti, 1999). Rock types with a high content of Mg such as dolomite (20.84% MgO) and basalt (3.95-6.44% MgO) (Brownlow, 1996) can result in higher Mg^{2+} in freshwaters. Rippey & Gibson (1984) studied 30 lakes in Northern Ireland and noted that lakes with basalt catchments had higher proportions of Mg^{2+} than lakes located on other rock types. Gibson *et al.* (1995a) in a larger survey of Northern Irish lakes (n = 612) also found that mean Mg^{2+} was highest in basalt catchments (10.4 mg l^{-1}) compared to other rock types such as Silurian (7.3 mg l^{-1}), igneous (2.5 mg l^{-1}) and limestone (2.6 mg l^{-1}). Lakes with limestone catchments had the highest mean Ca^{2+} concentration (55.4 mg l^{-1}) whereas lakes on Silurian rock types had a median concentration (25.8 mg l^{-1}) and lakes on igneous rock types had the lowest (8.5 mg l^{-1}).

Other inputs of Ca^{2+} and Mg^{2+} to catchments include the addition of lime to agricultural soils. Approximately 0.9 million tonnes of lime was applied in 1997 (Goulding & Annis, 1998). As 68.1% of the Republic of Ireland (70,282 km^2) is used for agriculture (Chapter 2) this equates to 128 kg $CaCO_3$ ha^{-1} yr^{-1}. This is only an approximation as considerable regional variation would be expected. In the English Lake District, Thornton & Dise (1998) found that where streams were located on similar geology those draining agricultural land had higher Ca^{2+} and alkalinity. Among catchments with differing geology a relationship between stream alkalinity and catchment soils was found. Thick soils and gleyed soils had higher alkalinity than thin soils or peat soils. Low alkalinity in rivers was attributed to low weathering of bedrock, short hydraulic residence time of thin soils and acid precipitation.

Johnson *et al.* (1997) found that most variation in alkalinity in Michigan was explained by the percentage of row-crop agriculture, shrubs and herbs, and forestry in stream waters sampled in summer. Catchment characteristics for the entire catchment explained more variation than riparian data (100 m on either side of the streams).

4.1.5 Silicon

Silicon in lakes is mainly present in dissolved form as silicic acid (H_4SiO_4) (Aston, 1983). The principal source of Si is from weathering of soils and rocks in the catchment. Most rocks contain over 50% Si; examples include ortho-quartzite (99.54% SiO_2), greywacke (60.86-69.88% SiO_2), shale (25.05-93.76% SiO_2) and granitoid (60.74-65.08% SiO_2). Limestones generally contain much less Si (0.29 - 1.15% SiO_2) (Brownlow, 1996; Giusti, 1999). An example of Si release from K-feldspar weathering was presented in the section on potassium.

One obvious difficulty in examining relationships between catchment characteristics and Si is that losses within lakes can be substantial and thereby obscure relationships with catchment characteristics. This is because Si is an important macronutrient for diatoms and can comprise 25 - 60% of their dry weight. Therefore, large amounts of Si can be incorporated into diatom frustules as hydrated silica ($SiO_2 \cdot nH_2O$) and lost from the water column by sedimentation (Horne & Goldman, 1994). Concentration in lakes is therefore highly dependent on the seasonal cycle of diatoms.

4.1.6 Chemical weathering and catchment characteristics

Weathering in the environment consists of both physical and chemical processes. Weathering by physical processes dominates as 88% of the total material discharged to the oceans is in particulate form (Wollast & Mackenzie, 1983). This study is concerned with dissolved material produced as a result of chemical weathering which is important in soil formation and acid neutralisation. Chemical weathering in a catchment is often indicated by the export of base cations (Johnson *et al.*, 1994). This is calculated by first subtracting the contribution of base cations from non-geological sources such as sea-salt deposition. The remaining base cations can be taken to be a result of weathering if it is assumed that biotic uptake is negligible, that changes in the soil pool are minimal (Bricker *et al.*, 1994) and that there is no input of base cations from fertiliser and lime addition. However, in practice, not all of the base cations weathered from minerals actually get exported. Base cations that are released by weathering may be subsequently incorporated into minerals

(Giusti, 1999); therefore, the export of base cations may be said to represent the weathering "release" of base cations.

The amount of base cations exported is likely to be a function of rock type and weathering rate. Johnson *et al.* (1994) reviewed the export of base cations from small catchments on felsic bedrock (Si rich igneous rock) in Europe and North America. They found that in 28 catchments the export ranged from 0.16 to 2.29 keq ha^{-1} yr^{-1} and average export was 0.97 keq ha^{-1} yr^{-1} (S.D. = 0.58). This was much lower than an estimate for a catchment containing limestone (6.59 keq ha^{-1} yr^{-1}). Similarly, in the English Lake District, Thornton & Dise (1998) attributed higher concentrations of major ions to higher weathering rates of Silurian shales compared with other rock types. In catchments with similar geology the factors that may affect base cation export include temperature, depth of soil (affects groundwater residence time and flowpath), rainfall, acid loading, cation exchange and secondary mineral formation (Johnson *et al.*, 1994).

Kähkönen (1996) attributed low alkalinity in Finnish lakes to geochemically resistant bedrock and thin coarse-grained till soils. In addition, they found alkalinity increased with the catchment to lake area ratio, probably because larger catchments increased contact time between runoff and soils which increased neutralisation and cation concentration. In contrast, lakes in catchments with well buffered soils tended to have higher alkalinity and the catchment to lake area ratio was not as important.

Johnson *et al.* (1994) attempted to explain the variation in base cation export in 28 felsic catchments by differences in H^+ inputs. No significant relationship was found indicating that acid inputs did not exert significant control over base cation export. Therefore acid inputs may have been incompletely neutralised which would result in the acidification of freshwater.

Müller *et al.* (1998) studied 68 lakes on calcareous geology which had a wide range in altitude (334 - 2339 m). They attributed higher ion concentration at lower altitudes to increased weathering owing to higher temperatures, increased contact time with water and increased surface area of thicker lowland soils. In addition the application of fertilisers at lower altitudes may have increased soil acidity and weathering (Müller *et al.*, 1998;

Goulding & Annis, 1998). Müller *et al.* (1998) also found that agriculture or urbanisation in the catchments had significant relationships with the concentrations of major ions.

D'arcy & Carignan (1997) found higher Ca^{2+}, Na^{+} and K^{+} concentrations at lower altitudes and this was attributed to concentration by evapotranspiration. Slope generally had a negative relationship with major cation concentrations and this was attributed to lower slopes increasing the residence time of the groundwater.

Close & Davies-Colley (1990) examined base-flow chemistry in 96 New Zealand rivers. Multiple regression models indicated that the major ions were generally negatively related to hydrologic variables and positively related to the amount of soft sedimentary rock in the catchment. The percentage of pasture was also significant in increasing ion concentration.

4.1.7 Specific aims

The main aims of this chapter are:

- To examine the seasonal variation in the concentration of major ions.
- To produce estimates of export of the major ions from the 31 lakes.
- To improve on previous attempts to explain the variation in Na^{+} and Cl^{-} and explain why previous work found only a poor relationship between Cl^{-} concentration and easting.
- Estimate the amount of non-marine SO_4^{2-} in the lakes and whether it is principally controlled by atmospheric deposition, rock weathering, agricultural practice or other factors.
- To identify the factors controlling K^{+} export and specifically, whether agriculture is an important influence and whether K^{+} concentrations have increased in lakes since the 1970s in response to the build up of soil K^{+} over this period.
- To examine the variation of Mg^{2+}, Ca^{2+} and Si in relation to catchment geology.
- To determine which factors control chemical weathering (as indicated by non-marine base cation export) in upland catchments located on resistant rock types.

4.2 Materials and methods

Methods for calculation of catchment characteristics and lake sampling were described in Chapter 2 and 3.

Nitrate, chloride and sulphate were measured on filtrate (Whattman GF/C) by chemically suppressed ion chromatography (Dionex system). Samples were initially analysed in duplicate but this was reduced to a single determination owing to consistency of results. Determinations of nitrate, chloride and sulphate followed calibration with five standards.

Sodium, potassium, magnesium and calcium were determined on filtrate by flame atomic absorption (Perkin Elmer 3100) following addition of lanthanum chloride to a concentration of 4%. Owing to the conservative nature of the cations only one determination per sample was performed. Samples were not analysed after June 1997. Calibration consisted of four standards, readjustment of calibration was based on one standard using a reslope factor.

No consistent quality control was performed for the ions, although standards were run with samples to ascertain if drift was taking place. A reference water was obtained for quality assurance purposes and results for SO_4^{2-} and Cl^- were within 95% confidence limits of the certified mean (Appendix 10). In addition, absolute value, mean ion-balance error for 285 determinations was 2.48% (median 1.23%).

Silicate, total silicon and total dissolved silicon were measured according to Koroleff (1983a, b). Total silicon and total dissolved silicon were digested by alkaline persulphate oxidation on 50 ml samples. Samples were digested in duplicate. The measurement of silicate involved reaction with ammonium molybdate which was stopped with oxalic acid. This yellow silicomolybdic acid was then reduced using ascorbic acid to a blue complex. Absorbance was determined at 810 nm using a PYE Unicam SP6-350 spectrophotometer with a 1 cm cell and auto-sipper. Silicate was measured in triplicate, total silicon and total dissolved silicon were measured in duplicate. All determinations of total silicon and total dissolved silicon followed calibration with six standards in duplicate. Calibration for silicate involved seven standards in triplicate. Quality control for total silicon and silicate

consisted of a standard of 2 g l^{-1} Si which was serially diluted to 1 mg l^{-1} and digested (for TSi only). Usually six quality control aliquots for silicate and four for total silicon were analysed after standards. Standards of 1 mg l^{-1} concentration were analysed throughout the analysis. A separate standard was used for routine construction of standards (Na_2SiF_6). Koroleff (1983a) states that the error of the method ranges from 2.5 - 6%. Quality control charts for silicate and total silica are presented in Figure 4.2 and Figure 4.3. Quality assurance information is provided in Appendix 10; the measured mean was within the 95% confidence limits of the certified mean.

High-level alkalinity (50 ml sample) was determined by titration with 0.01 molar sulphuric acid to pH 4.5 using a Metrohm burette (E 485). Low-level alkalinity was determined by Gran titration (100 ml sample) to four end points between pH 4.3 and 3.8 (Mackereth *et al.*, 1989).

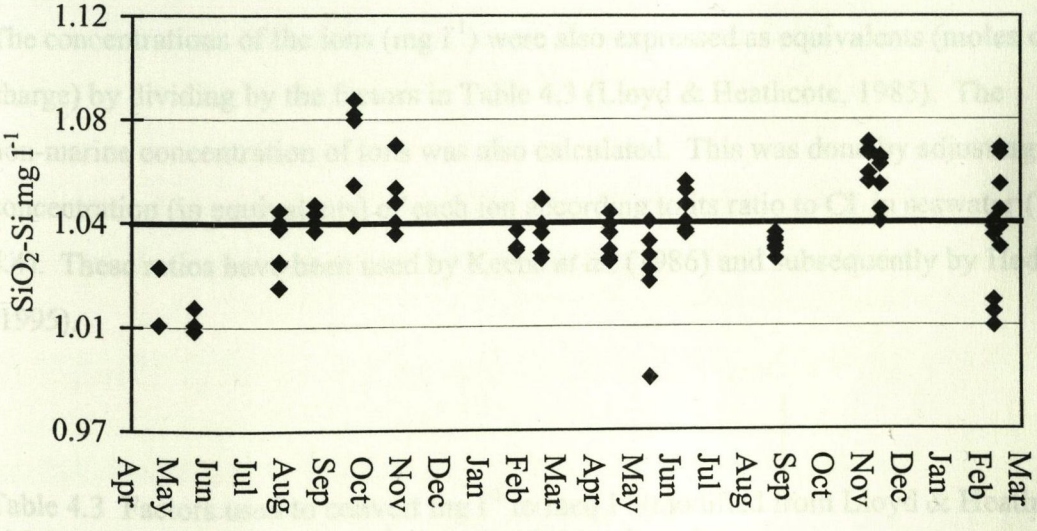


Figure 4.2 Quality control chart for silicate (mg l^{-1}). April 1996 to March 1998. Major gridline corresponds to average, minor gridlines represent 2 standard deviations.

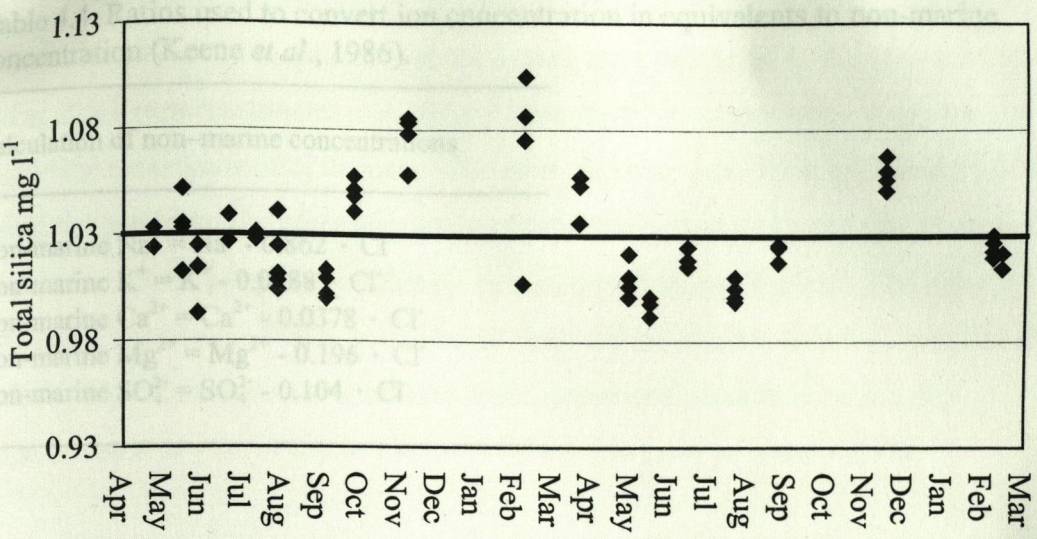


Figure 4.3 Quality control chart for total silica (mg l^{-1}) between April 1996 and March 1998. Major gridline corresponds to average, minor gridlines represent 2 standard deviations.

The concentrations of the ions (mg l^{-1}) were also expressed as equivalents (moles of charge) by dividing by the factors in Table 4.3 (Lloyd & Heathcote, 1985). The non-marine concentration of ions was also calculated. This was done by adjusting the concentration (in equivalents) of each ion according to its ratio to Cl^- in seawater (Table 4.4). These ratios have been used by Keene *et al.* (1986) and subsequently by Hedin *et al.* (1995).

Table 4.3 Factors used to convert mg l^{-1} to meq l^{-1} (modified from Lloyd & Heathcote, 1985). Concentrations in mg l^{-1} were divided by these factors.

Cations		Anions	
Na^+	22.99	HCO_3^-	50.00
K^+	39.10	SO_4^{2-}	48.03
Ca^{2+}	20.04	Cl^-	35.45
Mg^{2+}	12.16	NO_3-N	14.01

Table 4.4 Ratios used to convert ion concentration in equivalents to non-marine concentration (Keene *et al.*, 1986).

Calculation of non–marine concentrations
Non-marine $Na^+ = Na^+ - 0.862 \cdot Cl^-$
Non-marine $K^+ = K^+ - 0.0188 \cdot Cl^-$
Non-marine $Ca^{2+} = Ca^{2+} - 0.0378 \cdot Cl^-$
Non-marine $Mg^{2+} = Mg^{2+} - 0.196 \cdot Cl^-$
Non-marine $SO_4^{2-} = SO_4^{2-} - 0.104 \cdot Cl^-$

An estimate of the export of the ions from the lakes was calculated for the twelve-month period July 1996 to June 1997 inclusive. This period was chosen to maximise sample frequency and also because cations were not analysed for the second half of 1997. The calculation was based on the summation over a twelve-month period of the product of estimated monthly runoff and mid-lake concentration. The calculations used and a worked example for Lough Ballyquirke in January 1997 is presented below.

(1) Estimated average catchment runoff for month = [month's net rainfall (m) - accumulated soil moisture deficit from previous months (m) (if any)]

(2) Export Cl^- kg ha^{-1} yr^{-1} = Σ (months) [runoff m^3 ha^{-1} month $\cdot$ Cl^- (kg m^{-3})]

e.g. Ballyquirke Jan 97: 324.2 m^3 ha^{-1} $\cdot$ 0.02021 kg m^{-3} = 6.55 kg Cl^- ha^{-1}

Where ion concentrations were not available for some months they were estimated by linear interpolation. Export of ions for Lough Caragh, Muckross and Leane were estimated using mean (July 1996 to June 1997) ion concentration because sampling frequency was irregular and did not permit linear interpolation between months. The reliability of the figures produced will be partly dependent on the importance of loss processes which will vary depending on the element considered and residence time of each lake.

It was thought useful to estimate the amount of error contained in the estimates of export. Error in the export estimates may mainly arise from two sources: the water budget and the analytical measurement of the ions. The error that may arise from estimating outflow using net precipitation rather than measured discharge was estimated by Gibson *et al.* (1995b) as 3% in an upland catchment on basalt in Northern Ireland. The error in analytical measurement may be estimated from the median ion balance error which was 1.23%. Therefore the error contained in the export estimates may be roughly approximated as plus or minus the sum of these two error sources: 4.23%.

Potassium inputs to the catchments from agriculture were estimated using CORINE land class information and fertiliser application rates for each county (Murphy *et al.*, 1997). Specifically, the areas (ha) of the CORINE land classes: pasture (high productivity), pasture (low productivity), pasture (mixed) and principally agriculture were summed. This area was multiplied by each county's fertiliser application rate (kg ha^{-1} yr^{-1}) to grassland (total grassland category) (Murphy *et al.*, 1997). The input to crops was calculated by summing the CORINE land classes arable and complex cultivation and multiplying by the county fertiliser application to crops (mean of several crop types) (Murphy *et al.*, 1997). The input to forestry was calculated by summing the CORINE land classes; broad leaf forestry, coniferous forestry and mixed forest and multiplying by 22.22 kg ha yr^{-1} (200 kg over 9 years) (Clinch, 1999). Potassium inputs to the catchment by human excreta were derived by multiplication of the human population (from the 1991 census) by annual K^+ excretion (2.5 g K^+ day^{-1} as estimated by Smith (1976)).

The statistical procedures used are documented in Chapter 5.

4.3 Results

4.3.1 Sodium and chloride

The mean chloride concentration ranged from 7.5 mg l^{-1} in Lough Bray to 25.5 mg l^{-1} in Lough Lickeen (Table 4.5). Only minor seasonal variation in Cl^- was observed in 1996 (Figure 4.4). In contrast, the first half of 1997 had higher Cl^- concentrations in western lakes (e.g. Lough Inchiquin and Feeagh) but not in eastern lakes (e.g. Lough Gowna and Dan in Figure 4.4).

Chloride concentration was expected to be highest in the west because of higher atmospheric deposition of sea-salts derived from the Atlantic. Figure 4.5 shows that this was the case as chloride concentration significantly decreased from west to east ($r^2 = 0.32$, $p \leq 0.0009$, $n = 31$). However, Cl^- concentration was highly variable among western lakes. Interestingly, western catchments with high net precipitation ($\geq$ 1050 mm) tended to have lower concentrations (Figure 4.5). When included in multiple regression, net precipitation was a significant negative factor and explained an additional 45% of the variation in Cl^- (Table 4.6).

Export of Cl^- ranged from 45 kg ha^{-1} yr^{-1} in Lough Lene to 220 kg ha^{-1} yr^{-1} in Lough Caragh (Table 4.5). The export of Cl^- decreased logarithmically from west to east (Figure 4.6). Linear regression of the log transformed variables Cl^- export and easting was highly significant ($r^2 = 0.81$, $p \leq 0.0001$, $n = 31$). Mean catchment relief (lake height - mean catchment boundary height) was a positive factor in multiple regression ($p = 0.0007$) and explained an additional 7% of the variation in Cl^- export (Table 4.7).

Table 4.5 Mean chloride concentration and export for the period July 1996 to June 1997.

Lake	mean mg l^{-1}	95% C.I.	n	mean meq l^{-1}	Export kg ha^{-1} yr^{-1}
Ballycullinan	25.2	2.7	5	0.712	106.1
Ballyquirke	23.8	3.6	9	0.672	138.2
Bray	7.5	0.2	5	0.213	52.4
Bunny	20.8	3.1	5	0.587	93.5
Caragh	13.5	4.0	4	0.380	220.4
Cullaun	21.4	2.0	5	0.604	93.8
Dan	8.5	0.3	9	0.240	87.0
Doolough	20.7	1.8	9	0.585	137.1
Dromore	22.6	2.2	5	0.637	89.7
Easky	10.7	2.0	5	0.301	101.1
Egish	15.4	0.5	5	0.435	60.9
Feeagh	18.1	1.4	9	0.511	169.5
Gara South	15.1	0.9	6	0.425	94.8
Gowna	13.7	0.4	9	0.387	64.0
Graney	14.6	1.7	5	0.413	72.4
Inchiquin	23.1	3.4	9	0.650	124.1
Leane	13.6	2.2	3	0.383	164.5
Lene	11.7	0.2	9	0.330	45.1
Lettercraffroe	18.7	3.3	5	0.527	129.5
Lickeen	25.5	1.3	9	0.719	78.8
Maumwee	15.6	6.1	5	0.441	210.9
Moher	22.7	1.3	9	0.641	158.7
Muckno	15.9	0.5	5	0.449	62.8
Muckross	11.7	1.4	3	0.331	184.7
Mullagh	14.3	0.6	5	0.403	58.8
Oughter	16.3	1.4	5	0.459	69.4
Owel	13.8	0.6	9	0.389	55.3
Pollaphuca	8.5	0.3	5	0.239	58.0
Ramor	14.8	0.7	9	0.417	59.8
Rea	18.7	0.7	5	0.526	94.7
Talt	12.8	0.4	5	0.360	100.6

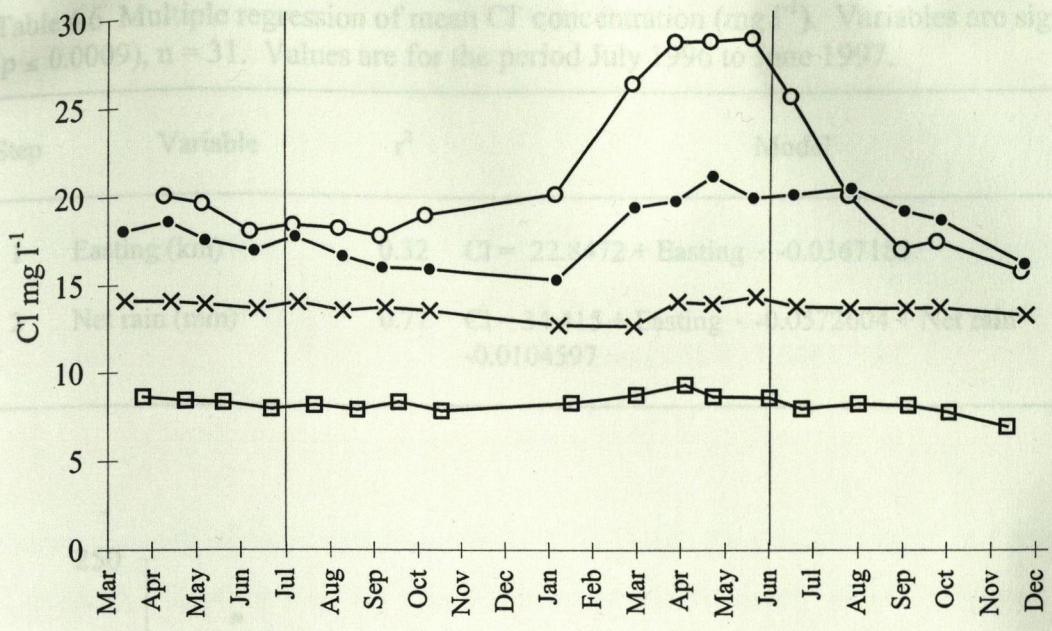


Figure 4.4 Seasonal variation in Cl^- between March 1996 and December 1997 in Lough Inchiquin (—O—), Feeagh (—●—), Gowna (—×—) and Dan (—⊟—). Vertical bars indicate period from which averages and exports were calculated.

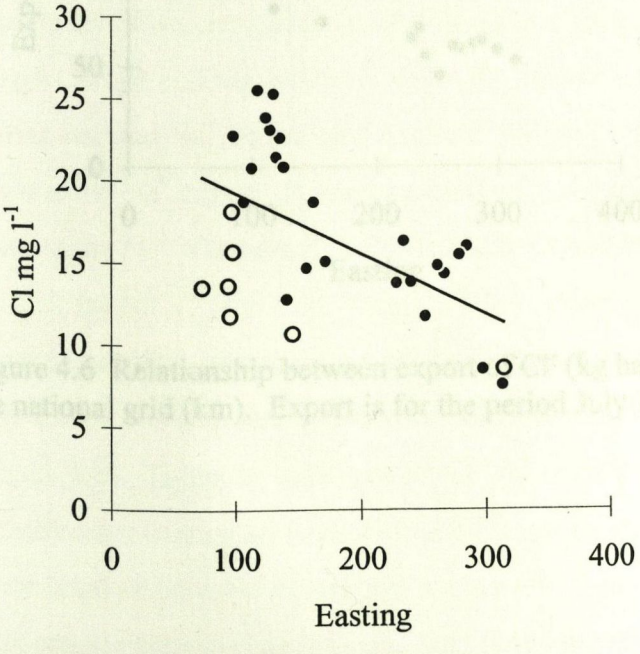


Figure 4.5 Relationship between Cl^- concentration and easting of lake position on the national grid (km). O = net precipitation (July 96 to June 97) ≥ 1050 mm, ● = ≤ 851 mm. Equation of line: $y = -0.0367x + 22.847$, $r^2 = 0.32$, $p \leq 0.0009$, $n = 31$.

Table 4.6 Multiple regression of mean Cl^- concentration (mg l^{-1}). Variables are significant ($p \leq 0.0009$), n = 31. Values are for the period July 1996 to June 1997.

Step	Variable	r^2	Model
1	Easting (km)	0.32	Cl = 22.8472 + Easting · -0.0367183
2	Net rain (mm)	0.77	Cl = 34.415 + Easting · -0.0572604 + Net rain · -0.0104597

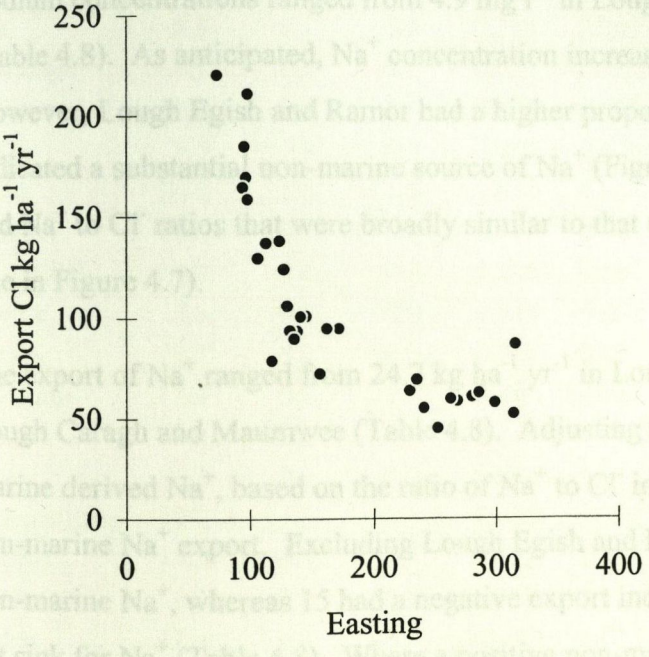


Figure 4.6 Relationship between export of Cl^- (kg ha^{-1} yr^{-1}) and easting of lake position on the national grid (km). Export is for the period July 1996 to June 1997.

Table 4.7 Multiple regression of log Cl^- export (kg ha^{-1} yr^{-1}). Variables are significant ($p \leq 0.0007$), n = 31. Export is for the period July 1996 to June 1997.

Step	Variable	r^2	Model
1	Log easting (km)	0.81	Log Cl export = 3.97168 + log easting · -0.905366
2	Mean catchment relief (m)	0.88	Log Cl export = 3.76483 + log easting · -0.835331 + mean catchment relief · 0.000393582

Sodium concentrations ranged from 4.9 mg l^{-1} in Lough Bray to 20.6 mg l^{-1} in Lough Egish (Table 4.8). As anticipated, Na^+ concentration increased linearly with Cl^- (Figure 4.7). However, Lough Egish and Ramor had a higher proportion of Na^+ relative to Cl^- which indicated a substantial non-marine source of Na^+ (Figure 4.7). The remainder of the lakes had Na^+ to Cl^- ratios that were broadly similar to that of seawater (0.862, represented by a line in Figure 4.7).

The export of Na^+ ranged from 24.7 kg ha^{-1} yr^{-1} in Lough Lene to 126.3 kg ha^{-1} yr^{-1} in Lough Caragh and Maumwee (Table 4.8). Adjusting these figures to subtract export of marine derived Na^+, based on the ratio of Na^+ to Cl^- in seawater, yielded estimates of non-marine Na^+ export. Excluding Lough Egish and Ramor, 14 lakes were found to export non-marine Na^+, whereas 15 had a negative export indicating that their catchments were a net sink for Na^+ (Table 4.8). Where a positive non-marine export was recorded it was generally small in comparison with total export (mean = 2.9 kg ha^{-1} yr^{-1}, S.D. = 1.8, n = 14). Lakes that exported non-marine Na^+ were located mainly in peatland catchments (Figure 4.8). This may indicate that the Na^+ estimated as being of non-marine origin may actually have originated from marine Na^+ and not catchment geology. This can occur when large amounts of marine Na^+ are adsorbed by peat soils during a storm owing to their high cation exchange capacity and then subsequently desorbed over a longer period (Allott *et al.*, 1997).

Table 4.8 Mean sodium concentration and export for the period July 1996 to June 1997. nm = non-marine.

Lake	mean mg l^{-1}	95% C.I.	mean nm mg l^{-1}	mean meq l^{-1}	mean nm meq l^{-1}	nm %	export kg ha^{-1} yr^{-1}	nm export kg ha^{-1} yr^{-1}
Ballycullinan	13.0	0.9	-1.1	0.565	-0.048	-9	53.5	-7.9
Ballyquirke	13.3	1.5	-0.1	0.577	-0.002	0	78.2	-1.8
Bray	4.9	0.0	0.7	0.215	0.032	15	34.7	4.4
Bunny	10.5	0.7	-1.2	0.455	-0.051	-11	49.4	-4.6
Caragh	7.7	1.5	0.2	0.336	0.008	2	126.3	-1.2
Cullaun	10.8	0.9	-1.2	0.469	-0.052	-11	46.8	-7.5
Dan	5.3	0.1	0.6	0.232	0.025	11	55.5	5.2
Doolough	12.1	0.7	0.5	0.528	0.024	4	80.8	1.5
Dromore	10.5	2.5	-2.1	0.456	-0.093	-20	45.9	-6.0
Easky	5.5	1.8	-0.5	0.239	-0.020	-8	61.0	2.5
Egish	20.6	1.6	11.9	0.894	0.520	58	83.0	47.7
Feeagh	10.6	0.7	0.5	0.462	0.022	5	101.0	3.0
Gara South	8.8	0.4	0.4	0.383	0.017	4	53.6	-1.2
Gowna	7.6	0.2	0.0	0.332	-0.002	-1	36.8	-0.2
Graney	8.7	0.2	0.5	0.377	0.021	6	45.8	4.0
Inchiquin	11.4	0.7	-1.5	0.495	-0.065	-13	63.2	-8.6
Leane	7.9	0.2	0.3	0.345	0.015	4	96.1	0.9
Lene	6.3	0.1	-0.2	0.274	-0.011	-4	24.7	-1.4
Lettercraffroe	10.7	1.3	0.3	0.465	0.011	2	75.1	0.2
Lickeen	14.7	0.5	0.4	0.639	0.020	3	44.5	-1.1
Maumwee	9.2	2.8	0.4	0.399	0.018	5	126.3	4.3
Moher	12.4	0.6	-0.3	0.540	-0.013	-2	88.4	-3.3
Muckno	9.2	0.4	0.3	0.400	0.013	3	37.0	0.7
Muckross	7.1	0.4	0.6	0.310	0.025	8	112.3	5.4
Mullagh	8.3	0.3	0.3	0.360	0.013	4	34.8	0.8
Oughter	9.4	1.0	0.3	0.408	0.012	3	39.6	-0.6
Owel	6.9	0.2	-0.8	0.302	-0.033	-11	27.7	-4.3
Pollaphuca	5.5	0.2	0.8	0.238	0.033	14	38.0	4.4
Ramor	10.9	0.8	2.6	0.472	0.113	24	46.2	11.6
Rea	9.7	0.2	-0.8	0.420	-0.033	-8	50.1	-4.7
Talt	7.7	0.1	0.5	0.333	0.023	7	61.4	3.2

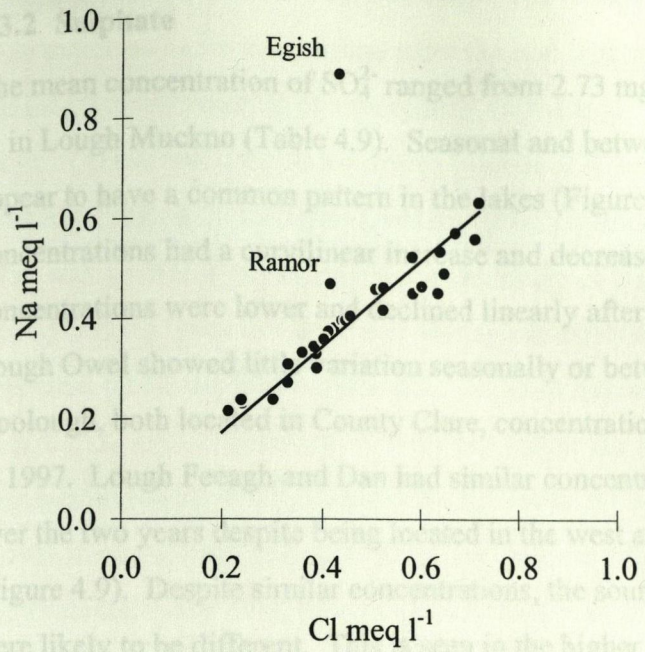


Figure 4.7 Relationship between the mean concentration of Na^+ and Cl^- (meq l^{-1}). Line represents the theoretical ratio of Na^+ to Cl^- in seawater (0.862) (Keene *et al.*, 1986).

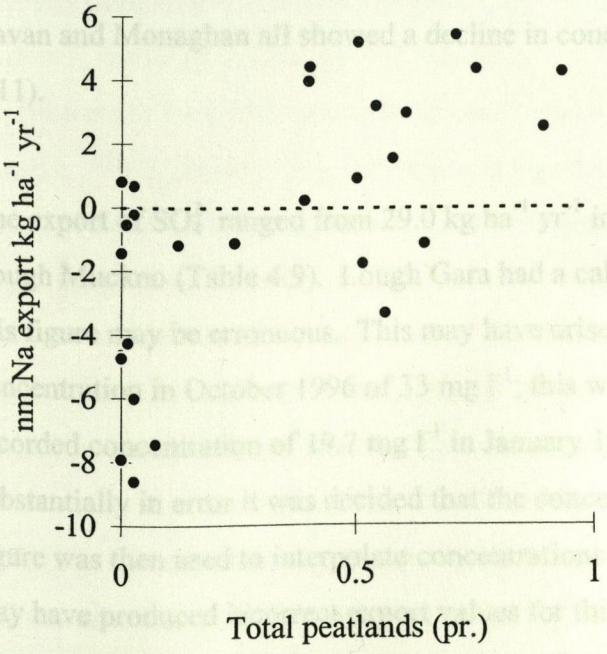


Figure 4.8 Relationship between non-marine Na^+ export (kg ha^{-1} yr^{-1}) and total peatlands (CORINE) (pr). n = 29 (Egish and Ramor excluded).

4.3.2 Sulphate

The mean concentration of SO_4^{2-} ranged from 2.73 mg l^{-1} in Lough Muckross to 19.44 mg l^{-1} in Lough Muckno (Table 4.9). Seasonal and between year variation in SO_4^{2-} did not appear to have a common pattern in the lakes (Figure 4.9). In Lough Gowna, concentrations had a curvilinear increase and decrease in 1996 whereas in 1997 concentrations were lower and declined linearly after an initial increase. In contrast, Lough Owel showed little variation seasonally or between years. In Lough Lickeen and Doolough, both located in County Clare, concentrations were similar in 1996 but differed in 1997. Lough Feeagh and Dan had similar concentrations and displayed little variation over the two years despite being located in the west and east of Ireland, respectively (Figure 4.9). Despite similar concentrations, the sources of SO_4^{2-} in these two upland lakes were likely to be different. This is seen in the higher percentage of non-marine sulphate in Lough Dan (70%) than in Lough Feeagh (39%) (Table 4.9). In fact, the percentage of SO_4^{2-} that was calculated as being of non-marine origin increased from west to east (Figure 4.10). Despite the lack of a general pattern in SO_4^{2-} variation it is noteworthy that lakes in Cavan and Monaghan all showed a decline in concentration from 1996 to 1997 (Figure 4.11).

The export of SO_4^{2-} ranged from 29.0 kg ha^{-1} yr^{-1} in Lough Easky to 80.4 kg ha^{-1} yr^{-1} in Lough Muckno (Table 4.9). Lough Gara had a calculated export of 147.1 kg ha^{-1} yr^{-1} but this figure may be erroneous. This may have arisen because of an unusually high SO_4^{2-} concentration in October 1996 of 33 mg l^{-1}; this was much higher than the subsequently recorded concentration of 19.7 mg l^{-1} in January 1997. As the ion balance was not substantially in error it was decided that the concentration may be plausible. However, this figure was then used to interpolate concentrations for November and December 1996 and may have produced incorrect export values for this lake as such a high concentration was unlikely to have been maintained over November and December when flushing was high. Owing to this uncertainty, Lough Gara is treated as an outlier in the analysis.

The variation in SO_4^{2-} export is hard to interpret as information on atmospheric deposition, a major source of SO_4^{2-}, is sparse. In addition, because SO_4^{2-} deposition has both marine and anthropogenic sources it cannot be inferred by distance from the Atlantic (easting) as was

done for Na^+ and Cl^-. However, in order to ascertain if broadly similar amounts of SO_4^{2-} were exported as were deposited from the atmosphere it was decided to examine some published measurements of atmospheric deposition. Table 4.10 compares export with the range of deposition calculated from a map of SO_4^{2-} concentration in Irish precipitation and at nearby (within 50 km) sites (Jordan, 1997; Farrell *et al.*, 1997). Export from 24 of the lakes was similar to or slightly below the range of atmospheric deposition (Jordan, 1997). The remaining lakes in Cavan and Monaghan exported substantially more SO_4^{2-} than was deposited by atmospheric deposition. Some of the ranges produced from Jordan's (1997) map of SO_4^{2-} concentration were large but values for nearby stations lead to similar conclusions (Table 4.10). Comparing the lakes in Cavan and Monaghan with the station at Clones it can be seen that these lakes had exports which were on average 40 kg ha^{-1} yr^{-1} higher than deposition at Clones. In contrast, one Cavan lake, Lough Mullagh, exported an amount of SO_4^{2-} which was close to that of atmospheric deposition (33.2 kg ha^{-1} yr^{-1}).

One of the problems with information on atmospheric deposition is that it is not strictly spatially comparable: stations are often quite far from catchments and may be at different altitudes. Other problems are that deposition varies annually and that estimated ranges of deposition are very wide owing to Ireland's sparse rainfall chemistry monitoring network (Jordan, 1997) (Table 4.10). Therefore, it was decided to compare the ratio of SO_4^{2-} to Cl^- in export with the ratio in deposition between regions. The ratio of SO_4^{2-} to Cl^- in atmospheric deposition may be less variable within a region than amounts deposited which will vary with altitude, rainfall, aspect, vegetation and other factors. If the ratio in export is similar to that in deposition then it is likely that SO_4^{2-} export was mainly derived from atmospheric deposition. Table 4.10 shows that even though exported amounts of SO_4^{2-} were broadly similar between lakes in Clare, Kerry and Wicklow the ratios were more distinctive of their county and were similar between export and deposition (Figure 4.12). It is therefore likely that in these lakes the SO_4^{2-} exported was almost entirely derived from atmospheric deposition. Once again the lakes in Cavan and Monaghan were an exception; here the ratios of SO_4^{2-} to Cl^- in export were substantially greater than those in deposition (Figure 4.12).

This indicates that there was an additional source of SO_4^{2-} in these catchments. Figure 4.13 shows that the lakes in Cavan and Monaghan which had substantially higher non-marine

SO_4^{2-} export also tended to have a high proportion of agriculture in their catchments. However, no linear trend in SO_4^{2-} export with agriculture is visible for all the catchments.

Table 4.9 Mean SO_4^{2-} concentration and export for the period July 1996 to June 1997. nm = non-marine.

Lake	mean mg l^{-1}	95% C.I.	mean nm mg l^{-1}	mean meq l^{-1}	mean nm meq l^{-1}	nm %	Export kg ha^{-1} yr^{-1}	nm export kg ha^{-1} yr^{-1}
Ballycullinan	7.22	1.49	3.66	0.150	0.076	51	34.5	19.5
Ballyquirke	7.82	0.38	4.46	0.163	0.093	57	52.6	33.1
Bray	4.26	0.13	3.20	0.089	0.067	75	30.2	22.8
Bunny	5.55	0.28	2.62	0.115	0.054	47	26.7	13.5
Caragh	2.80	0.29	0.90	0.058	0.019	32	45.8	14.7
Cullaun	7.79	0.24	4.78	0.162	0.099	61	35.2	22.0
Dan	4.06	0.34	2.86	0.085	0.060	70	43.9	31.6
Doolough	7.21	0.32	4.29	0.150	0.089	59	52.2	32.9
Dromore	8.67	0.89	5.49	0.181	0.114	63	36.2	23.6
Easky	2.97	0.32	1.47	0.062	0.031	49	29.0	14.8
Egish	17.73	0.50	15.56	0.369	0.324	88	72.0	63.4
Feeagh	4.18	0.20	1.63	0.087	0.034	39	41.9	18.0
Gara South	17.46	6.55	15.34	0.364	0.319	88	147.1	133.7
Gowna	15.05	1.03	13.12	0.313	0.273	87	70.1	61.1
Graney	6.25	0.69	4.19	0.130	0.087	67	32.7	22.5
Inchiquin	8.39	0.40	5.14	0.175	0.107	61	52.0	34.6
Leane	3.92	0.18	2.00	0.082	0.042	51	47.4	24.2
Lene	8.21	0.18	6.56	0.171	0.137	80	32.3	26.0
Lettercraffroe	4.57	0.40	1.94	0.095	0.040	42	33.4	15.1
Lickeen	9.26	0.64	5.67	0.193	0.118	61	30.2	19.1
Maumwee	3.42	0.46	1.22	0.071	0.025	36	49.9	20.2
Moher	6.66	0.47	3.46	0.139	0.072	52	52.8	30.4
Muckno	19.44	2.49	17.20	0.405	0.358	88	80.4	71.5
Muckross	2.73	0.33	1.07	0.057	0.022	39	42.9	16.9
Mullagh	8.14	1.53	6.13	0.170	0.128	75	33.2	24.9
Oughter	17.30	3.10	15.01	0.360	0.312	87	77.0	67.2
Owel	11.06	0.33	9.12	0.230	0.190	82	44.4	36.6
Pollaphuca	4.69	0.39	3.49	0.098	0.073	75	32.6	24.5
Ramor	15.40	0.68	13.32	0.321	0.277	86	68.0	59.5
Rea	7.61	0.26	4.99	0.159	0.104	65	39.7	26.4
Talt	3.80	0.58	2.00	0.079	0.042	53	31.4	17.2

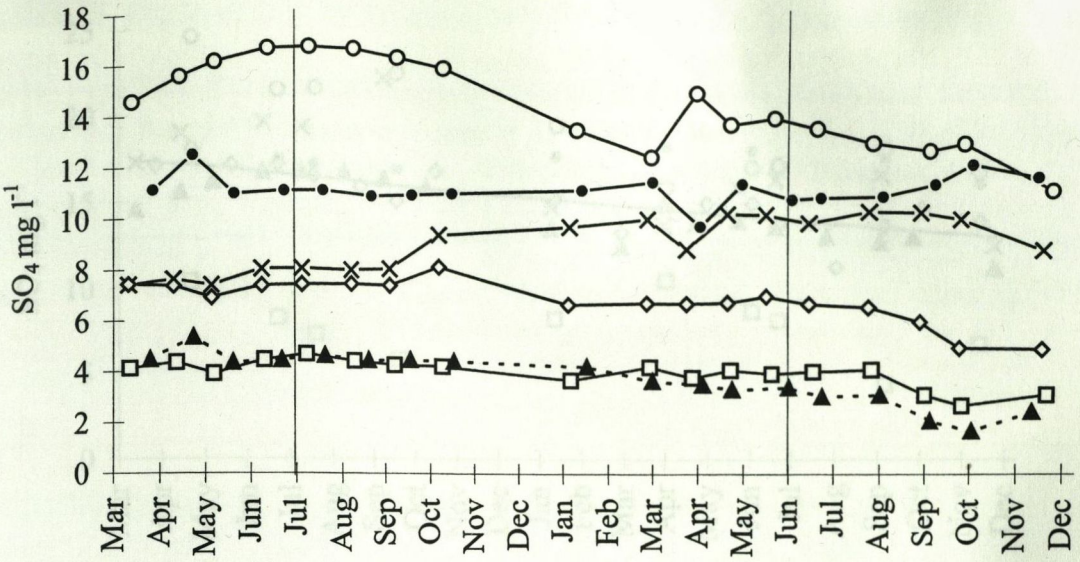


Figure 4.9 Seasonal variation in SO_4^{2-} between March 1996 and December 1997 in Lough Gowna (—O—), Owel (—●—), Lickeen (—×—), Doolough (—◇—), Feeagh (—⊟—) and Dan (- - -▲- - -). Vertical bars indicate period from which averages and exports were calculated.

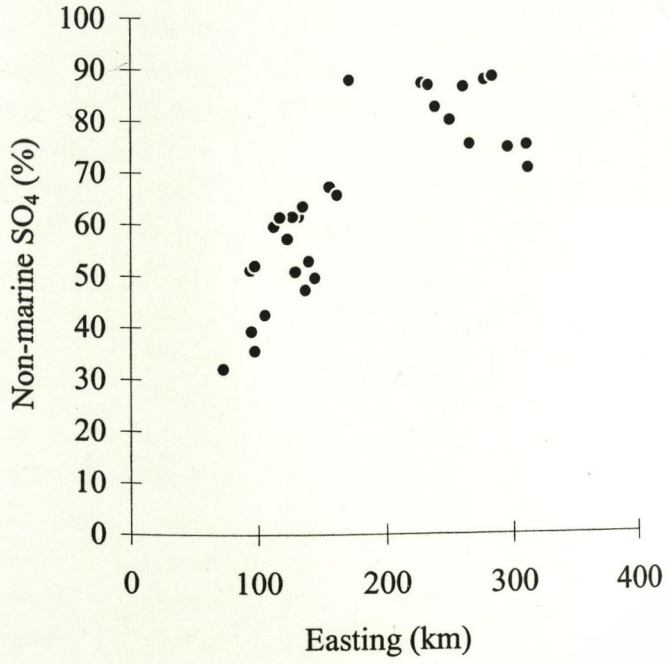


Figure 4.10 Relationship between the percentage of non-marine SO_4^{2-} and easting (km) (n = 31).

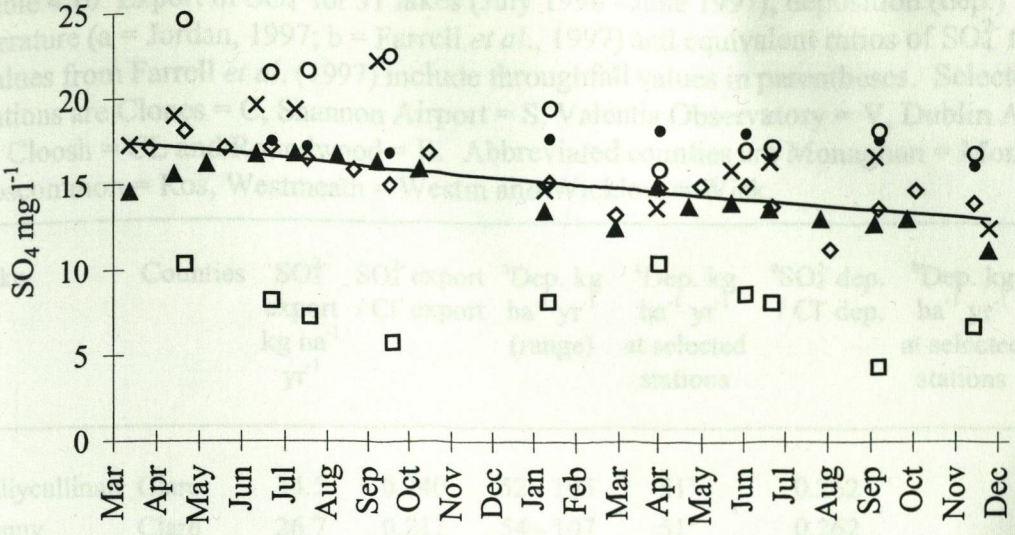


Figure 4.11 Decline in SO_4^{2-} (mg l^{-1}) concentration between 1996 and 1997 in the Cavan and Monaghan lakes: Egish (●), Muckno (○), Gowna (▲), Oughter (×), Ramor (◇) and Mullagh (□). Equation of line is $y = -0.0067x + 252.74$, $r^2 = 0.12$, $p = 0.002$, $n = 76$.

Table 4.10 Export of SO_4^{2-} for 31 lakes (July 1996 - June 1997), deposition (dep.) from literature (a = Jordan, 1997; b = Farrell *et al.*, 1997) and equivalent ratios of SO_4^{2-} to Cl^-. Values from Farrell *et al.* (1997) include throughfall values in parentheses. Selected stations are Clones = C, Shannon Airport = S, Valentia Observatory = V, Dublin Airport = D, Cloosh = CL and Roundwood = R. Abbreviated counties are Monaghan = Mon, Roscommon = Ros, Westmeath = Westm and Wicklow = Wick.

Lake	Counties	SO_4^{2-} export kg ha^{-1} yr^{-1}	SO_4^{2-} export / Cl^- export	[a]Dep. kg ha^{-1} yr^{-1} (range)	[a]Dep. kg ha^{-1} yr^{-1} at selected stations	[a]SO_4^{2-} dep. / Cl^- dep.	[b]Dep. kg ha^{-1} yr^{-1} at selected stations	[b]SO_4^{2-} dep. / Cl^- dep.
Ballycullinan	Clare	34.5	0.240	52 - 105	51[s]	0.262		
Bunny	Clare	26.7	0.211	54 - 107	51[s]	0.262		
Cullaun	Clare	35.2	0.277	53 - 105	51[s]	0.262		
Doolough	Clare	52.2	0.281	66 - 132	51[s]	0.262		
Dromore	Clare	36.2	0.298	51 - 101	51[s]	0.262		
Graney	Clare	32.7	0.333	45 - 56	51[s]	0.262		
Inchiquin	Clare	52.0	0.309	59 - 118	51[s]	0.262		
Lickeen	Clare	30.2	0.283	62 - 123	51[s]	0.262		
Ballyquirke	Galway	52.6	0.281	45 - 56			35 (57)[cl]	0.162 (0.169)
Lettercraffroe	Galway	33.4	0.190	60 - 75			35 (57)[cl]	0.162 (0.169)
Maumwee	Galway	49.9	0.175	75 - 150			35 (57)cl	0.162 (0.169)
Rea	Galway	39.7	0.309	42 - 52				
Caragh	Kerry	45.8	0.153	55 - 73	51[v]	0.135		
Leane	Kerry	47.4	0.213	51 - 68	51[v]	0.135		
Muckross	Kerry	42.9	0.171	53 - 70	51[v]	0.135		
Feeagh	Mayo	41.9	0.182	83 - 167				
Moher	Mayo	52.8	0.246	74 - 149				
Easky	Sligo	29.0	0.212	65 - 81				
Talt	Sligo	31.4	0.230	59 - 74				
Lene	Westm.	32.3	0.529	27 - 36				
Owel	Westm.	44.4	0.593	27 - 36				
Bray	Wick.	30.2	0.425	47 - 63	39[d]	0.482	24 (63)[r]	0.376 (0.418)
Dan	Wick.	43.9	0.372	57 - 72	39[d]	0.482	24 (63)[r]	0.376 (0.418)
Pollaphuca	Wick.	32.6	0.415	40 - 54	39[d]	0.482	24 (63)[r]	0.376 (0.418)
Gowna	Cavan	70.1	0.809	27 - 37	27[c]	0.427		
Mullagh	Cavan	33.2	0.417	19 - 28	27[c]	0.427		
Oughter	Cavan	77.0	0.818	19 - 28	27[c]	0.427		
Ramor	Cavan	68.0	0.839	28 - 37	27[c]	0.427		
Egish	Mon.	72.0	0.872	19 - 29	27[c]	0.427		
Muckno	Mon.	80.4	0.944	20 - 29	27[c]	0.427		
Gara S.	Ros.	147.1	1.145	32 - 43				

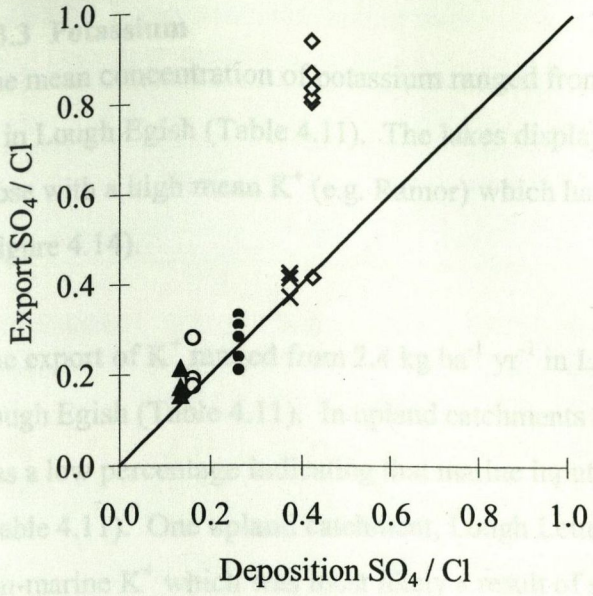


Figure 4.12 Relationship between the ratio of Cl^- to SO_4^{2-} (equivalents) in export and atmospheric deposition (bulk precipitation) in Counties Kerry (▲), Galway (O), Clare (●), Wicklow (X) and Cavan / Monaghan (◇) (n = 23). Line represents a 1:1 relationship. Atmospheric deposition data for Kerry, Cavan / Monaghan and Clare are from Jordan (1997), data from Galway and Wicklow are from Farrell *et al.* (1997).

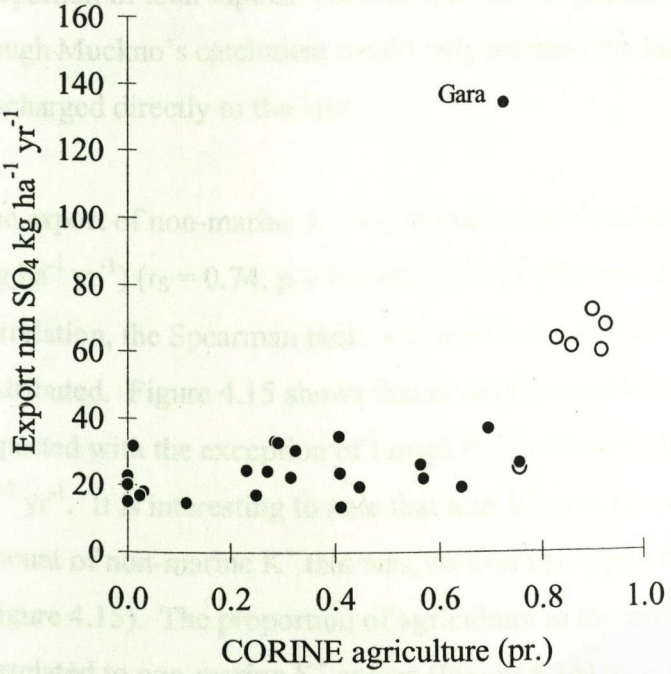


Figure 4.13 Relationship between export of non-marine SO_4^{2-} and the proportion of agriculture (CORINE) in the catchment. O = lakes in Cavan and Monaghan.

4.3.3 Potassium

The mean concentration of potassium ranged from 0.29 mg l^{-1} in Lough Easky to 3.96 mg l^{-1} in Lough Egish (Table 4.11). The lakes displayed little seasonal variation except for those with a high mean K^+ (e.g. Ramor) which had higher levels in winter than in summer (Figure 4.14).

The export of K^+ ranged from 2.4 kg ha^{-1} yr^{-1} in Lough Lettercraffroe to 16.2 kg ha^{-1} yr^{-1} in Lough Egish (Table 4.11). In upland catchments (e.g. Feeagh, Maumwee) non-marine K^+ was a low percentage indicating that marine inputs accounted for most of the K^+ exported (Table 4.11). One upland catchment, Lough Lettercraffroe, had a negative export of non-marine K^+ which was most likely a result of significant net retention of K^+ in the catchment.

Owing to their widespread use, K^+ fertilisers are likely to be a major influence on lake concentrations. To test this the input of K^+ to the catchments from anthropogenic sources was estimated. Table 4.12 indicates that K^+ application to pasture was the dominant input to most catchments. Inputs from the human population were generally a very small proportion of total inputs. For example, the K^+ produced by the human population in Lough Muckno's catchment would only increase the lake concentration by 0.12 mg l^{-1} if discharged directly to the lake.

The export of non-marine K^+ was strongly correlated to the total anthropogenic input of K^+ (kg ha^{-1} yr^{-1}) ($r_S = 0.74$, $p \leq 0.0001$, $n = 31$) (Figure 4.15). Here, a non-parametric correlation, the Spearman rank, was used because the variables were not normally distributed. Figure 4.15 shows that several groundwater lakes had lower K^+ export than expected with the exception of Lough Ballycullinan which had a very high export of 14 kg ha^{-1} yr^{-1}. It is interesting to note that four lakes in Cavan and Monaghan exported an amount of non-marine K^+ that was, on average, equivalent to 57% of fertiliser input (Figure 4.15). The proportion of agriculture in the catchment (CORINE) was also correlated to non-marine K^+ export (Figure 4.16) ($r_S = 0.86$, $p \leq 0.0001$, $n = 31$). A transformation (log x+2) of both variables improved their distribution and allowed a regression to be performed which was also highly significant ($r^2 = 0.73$, $p \leq 0.0001$, $n = 31$).

Table 4.11 Mean potassium concentration and export for the period July 1996 to June 1997. nm = non-marine.

Lake	mean mg l^{-1}	95% C.I.	mean nm mg l^{-1}	mean meq l^{-1}	mean nm meq l^{-1}	nm %	Export kg ha^{-1} yr^{-1}	nm export kg ha^{-1} yr^{-1}
Ballycullinan	2.96	0.29	2.44	0.076	0.062	82	14.0	11.8
Ballyquirke	1.13	0.05	0.63	0.029	0.016	56	7.0	4.2
Bray	0.37	0.01	0.21	0.009	0.005	57	2.5	1.4
Bunny	1.28	0.06	0.85	0.033	0.022	66	6.1	4.1
Caragh	0.40	0.05	0.12	0.010	0.003	29	6.5	1.9
Cullaun	1.73	0.11	1.29	0.044	0.033	74	7.7	5.7
Dan	0.28	0.01	0.11	0.007	0.003	38	2.9	1.1
Doolough	1.00	0.03	0.57	0.026	0.015	57	6.8	4.0
Dromore	1.55	0.06	0.91	0.035	0.023	66	6.5	4.7
Easky	0.29	0.09	0.06	0.007	0.002	23	3.1	1.0
Egish	3.96	0.23	3.64	0.101	0.093	92	16.2	15.0
Feeagh	0.55	0.02	0.17	0.014	0.004	31	5.3	1.8
Gara South	1.28	0.43	0.97	0.033	0.025	76	10.2	8.2
Gowna	2.54	0.07	2.26	0.065	0.058	89	12.4	11.1
Graney	0.82	0.06	0.52	0.021	0.013	63	4.3	2.8
Inchiquin	1.15	0.05	0.68	0.030	0.017	59	7.1	4.6
Leane	0.76	0.02	0.48	0.020	0.012	63	9.2	5.8
Lene	0.97	0.02	0.72	0.025	0.018	75	3.7	2.8
Lettercraffroe	0.32	0.03	-0.07	0.008	-0.002	-21	2.4	-0.3
Lickeen	1.60	0.05	1.07	0.041	0.027	67	4.7	3.1
Maumwee	0.38	0.10	0.06	0.010	0.002	16	5.4	1.0
Moher	1.19	0.03	0.72	0.030	0.018	60	9.0	5.7
Muckno	3.80	0.14	3.47	0.097	0.089	91	15.8	14.5
Muckross	0.32	0.03	0.07	0.008	0.002	23	5.0	1.2
Mullagh	2.10	0.18	1.80	0.054	0.046	86	8.6	7.3
Oughter	3.42	0.53	3.08	0.087	0.079	90	15.6	14.2
Owel	1.09	0.02	0.80	0.028	0.021	74	4.3	3.1
Pollaphuca	0.54	0.01	0.37	0.014	0.009	68	3.8	2.6
Ramor	3.61	0.20	3.30	0.092	0.085	92	15.6	14.3
Rea	1.27	0.03	0.89	0.033	0.023	70	6.7	4.7
Talt	0.67	0.03	0.41	0.017	0.010	61	5.5	3.4

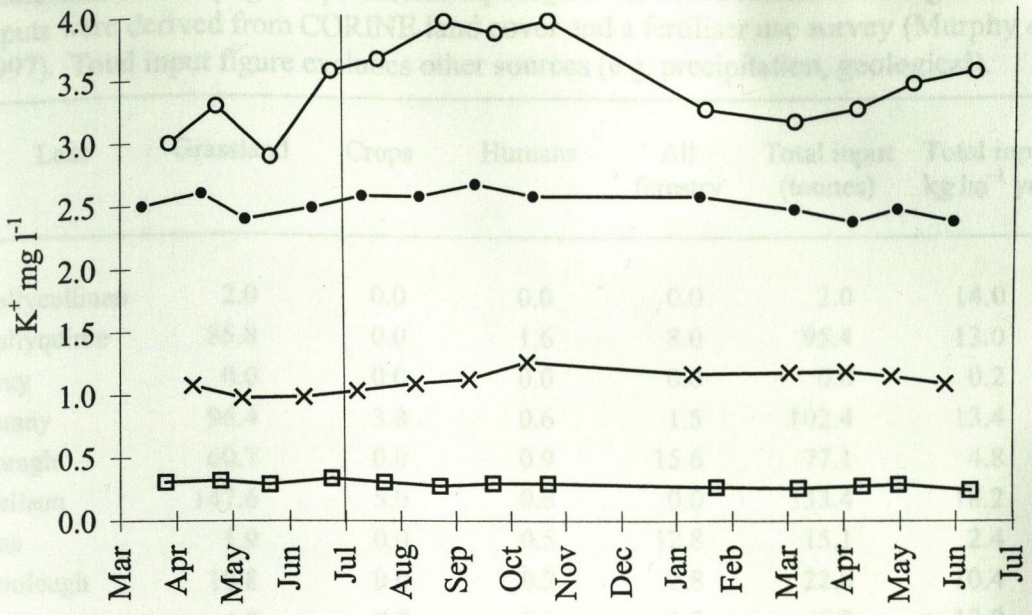


Figure 4.14 Seasonal variation in K^+ (mg l^{-1}) in Lough Ramor (—O—), Gowna (—●—), Inchiquin (—×—) and Dan (—⊟—) between March 1996 and July 1997. Vertical bars indicate period from which averages and exports were calculated.

Table 4.12 Anthropogenic potassium inputs (tonnes) in the catchments. Agricultural inputs were derived from CORINE land cover and a fertiliser use survey (Murphy *et al.*, 1997). Total input figure excludes other sources (e.g. precipitation, geological).

Lake	Grassland	Crops	Humans	All forestry	Total input (tonnes)	Total input kg ha^{-1} yr^{-1}
Ballycullinan	2.0	0.0	0.0	0.0	2.0	14.0
Ballyquirke	85.8	0.0	1.6	8.0	95.4	13.0
Bray	0.0	0.0	0.0	0.0	0.0	0.2
Bunny	96.4	3.8	0.6	1.5	102.4	13.4
Caragh	60.7	0.0	0.9	15.6	77.1	4.8
Cullaun	147.6	5.0	0.8	0.0	153.4	18.2
Dan	1.9	0.0	0.5	12.8	15.1	2.4
Doolough	19.8	0.0	0.2	2.8	22.8	10.4
Dromore	4.0	0.0	0.1	1.9	6.0	18.9
Easky	0.0	0.0	0.1	0.0	0.1	0.1
Egish	17.6	0.0	0.3	0.0	17.9	22.8
Feeagh	10.1	0.0	0.5	40.4	51.0	5.1
Gara South	365.6	0.0	2.1	0.6	368.3	19.9
Gowna	308.4	1.9	3.0	5.1	318.4	24.8
Graney	108.7	0.0	0.7	62.9	172.4	15.4
Inchiquin	188.2	0.0	1.0	4.4	193.5	13.0
Leane	489.3	26.1	16.5	90.0	622.0	11.3
Lene	18.5	7.9	0.7	0.0	27.1	23.2
Lettercraffroe	0.0	0.0	0.1	3.4	3.4	8.9
Lickeen	16.3	0.0	0.1	0.0	16.4	20.1
Maumwee	0.0	0.0	0.0	0.0	0.0	0.0
Moher	10.0	0.0	0.1	1.4	11.5	12.3
Muckno	391.8	0.0	2.6	11.1	405.6	25.2
Muckross	4.8	0.0	0.6	17.8	23.1	3.8
Mullagh	2.4	0.0	0.1	0.0	2.5	21.8
Oughter	3843.5	4.9	39.1	35.2	3922.7	26.5
Owel	101.7	9.0	3.6	3.8	118.1	25.1
Pollaphuca	164.0	144.1	5.1	87.8	401.0	13.2
Ramor	644.9	4.8	6.6	10.4	666.7	26.5
Rea	41.5	1.5	0.3	0.1	43.5	32.1
Talt	3.0	0.0	0.0	0.0	3.0	6.3

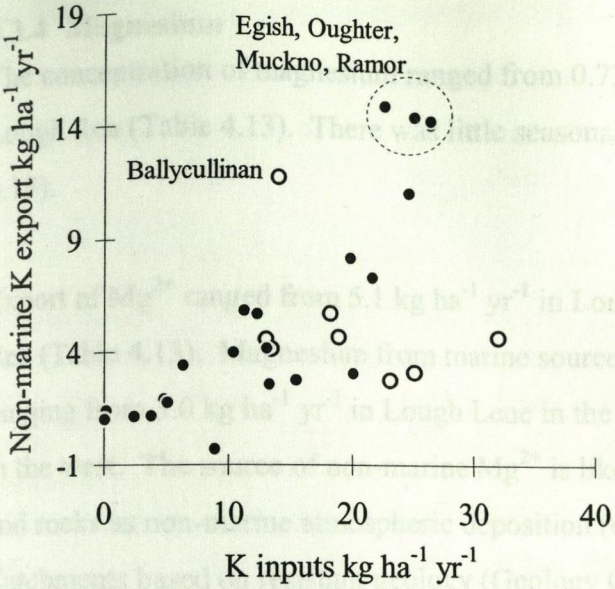


Figure 4.15 Relationship between non-marine potassium export and anthropogenic potassium input in groundwater lakes (O) and non-groundwater (●) lakes.

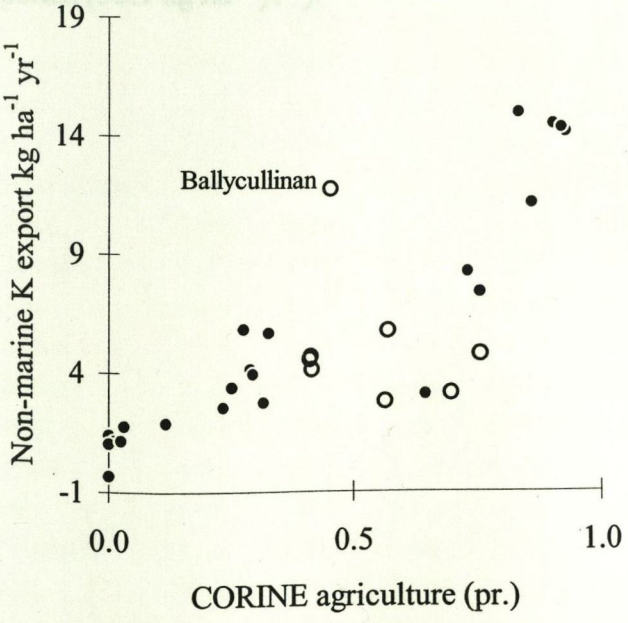


Figure 4.16 Relationship between non-marine potassium export and the proportion of agriculture (CORINE) in groundwater lakes (O) and non-groundwater (●) lakes.

4.3.4 Magnesium

The concentration of magnesium ranged from 0.73 mg l^{-1} in Lough Bray to 7.34 mg l^{-1} in Lough Rea (Table 4.13). There was little seasonal variation in Mg^{2+} in most lakes (Figure 4.17).

Export of Mg^{2+} ranged from 5.1 kg ha^{-1} yr^{-1} in Lough Bray to 39.3 kg ha^{-1} yr^{-1} in Lough Rea (Table 4.13). Magnesium from marine sources formed a large proportion of export ranging from 3.0 kg ha^{-1} yr^{-1} in Lough Lene in the east to 14.8 kg ha^{-1} yr^{-1} in Lough Caragh in the west. The source of non-marine Mg^{2+} is likely to be from the weathering of soils and rocks as non-marine atmospheric deposition (e.g. dust) is small (Jordan, 1997). Catchments based on resistant geology (Geology Group 3 in Table 4.14) exported the least non-marine Mg^{2+} of 5.3 kg ha^{-1} yr^{-1} (S.D. = 2.7) (Table 4.14). The other groups, limestone and Silurian/Ordovician greywacke exported an average of 11.6 kg nm Mg^{2+} ha^{-1} yr^{-1} (S.D. = 2.8, excluding Lough Rea) and 12.6 kg nm Mg^{2+} ha^{-1} yr^{-1} (S.D. = 3.3) (Table 4.14). Lough Rea was noteworthy in that an exceptional amount of non-marine Mg^{2+} was exported (32.9 kg ha^{-1} yr^{-1}).

Table 4.13 Mean magnesium concentration and export for the period July 1996 to June 1997. nm = non-marine.

Lake	mean mg l^{-1}	95% C.I.	mean nm mg l^{-1}	mean meq l^{-1}	mean nm meq l^{-1}	nm %	Export kg ha^{-1} yr^{-1}	nm export kg ha^{-1} yr^{-1}
Ballycullinan	4.58	0.19	2.88	0.377	0.237	63	20.3	13.1
Ballyquirke	2.48	0.13	0.88	0.204	0.072	35	14.6	5.3
Bray	0.73	0.01	0.22	0.060	0.018	30	5.1	1.6
Bunny	3.28	0.17	1.88	0.270	0.155	57	16.0	9.7
Caragh	1.29	0.17	0.38	0.106	0.032	30	21.1	6.3
Cullaun	4.60	0.12	3.16	0.378	0.260	69	20.7	14.4
Dan	0.83	0.01	0.25	0.068	0.021	31	8.7	2.8
Doolough	2.25	0.06	0.85	0.185	0.070	38	15.8	6.6
Dromore	3.84	0.91	2.32	0.316	0.191	60	18.1	12.1
Easky	0.86	0.24	0.15	0.071	0.012	17	9.4	2.6
Egish	3.20	0.09	2.16	0.263	0.178	68	13.1	9.1
Feeagh	1.99	0.09	0.77	0.163	0.063	39	19.0	7.6
Gara South	3.72	0.35	2.70	0.306	0.222	73	21.6	15.3
Gowna	4.22	0.12	3.30	0.347	0.271	78	20.2	15.9
Graney	2.12	0.11	1.14	0.175	0.094	54	11.6	6.7
Inchiquin	2.66	0.07	1.11	0.218	0.091	42	15.1	6.7
Leane	1.77	0.16	0.85	0.145	0.070	48	21.4	10.3
Lene	3.68	0.04	2.89	0.302	0.238	79	14.5	11.5
Lettercraffroe	1.48	0.17	0.22	0.122	0.018	15	10.7	2.0
Lickeen	2.49	0.08	0.78	0.205	0.064	31	7.9	2.6
Maumwee	1.23	0.34	0.18	0.101	0.015	15	17.5	3.3
Moher	2.50	0.10	0.97	0.206	0.080	39	18.4	7.8
Muckno	3.74	0.13	2.67	0.308	0.220	71	15.4	11.1
Muckross	1.17	0.07	0.38	0.096	0.031	33	18.4	6.0
Mullagh	4.68	0.26	3.72	0.385	0.306	79	19.8	15.8
Oughter	4.26	0.26	3.17	0.350	0.260	74	18.6	14.0
Owel	3.42	0.03	2.50	0.281	0.205	73	13.4	9.7
Pollaphuca	1.43	0.09	0.86	0.118	0.071	60	9.8	5.9
Ramor	4.39	0.26	3.40	0.361	0.279	77	18.6	14.6
Rea	7.34	0.13	6.09	0.604	0.500	83	39.3	32.9
Talt	1.99	0.07	1.13	0.163	0.093	57	16.0	9.2

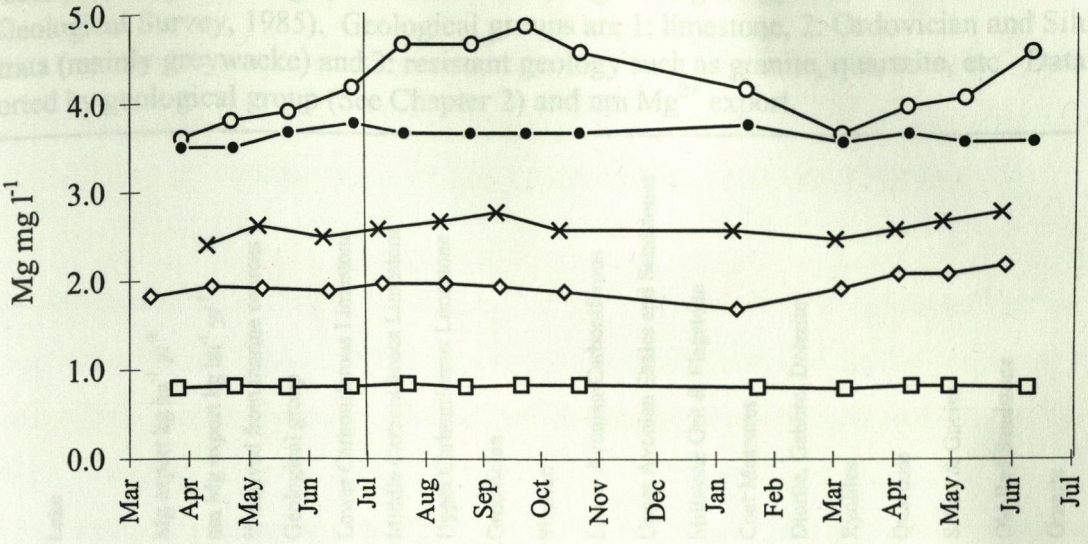


Figure 4.17 Variation in Mg^{2+} (mg l^{-1}) between March 1996 and June 1997 in Lough Ramor (—O—), Lene (—●—), Inchiquin (—×—), Feeagh (—◇—) and Dan (—⊟—). Vertical bars indicate periods when means and exports were calculated.

Table 4.14 Export of Mg^{2+}, non marine (nm) Mg^{2+} and geology of the 31 catchments (Geological Survey, 1985). Geological groups are 1: limestone, 2: Ordovician and Silurian strata (mainly greywacke) and 3: resistant geology such as granite, quartzite, etc. Data are sorted by geological group (See Chapter 2) and nm Mg^{2+} export.

Lake	Mg export kg ha^{-1} yr^{-1}	nm Mg export kg ha^{-1} yr^{-1}	% derived from marine sources	Geological group	Lower Carboniferous Limestone	Middle Carboniferous Limestone	Upper Carboniferous Limestone	Ordovician	Silurian	Lower Avonian/Carboniferous	Upper Avonian Shales and Sandstones	Millstone Grit & Flagstone	Coal Measures	Diorite, Gabbro, Dolerite	Ryolites	Quartzite	Schist & Gneiss	Old Red Sandstone	Granite
Inchiquin	15.1	6.7	55	1	0.78						0.15	0.07							
Bunny	16.0	9.7	39	1	1.00		0.00												
Owel	13.4	9.7	28	1		1.00													
Lene	14.5	11.5	21	1		1.00													
Dromore	18.1	12.1	33	1	0.69	0.31													
Gara S.	21.6	15.3	29	1			0.93			0.07									
Ballycullinan	20.3	13.1	35	1	1.00														
Cullaun	20.7	14.4	30	1	1.00														
Rea	39.3	32.9	16	1			0.99			0.01									
Moher	18.4	7.8	58	2				0.47	0.53										
Egish	13.1	9.1	31	2				0.02	0.98										
Muckno	15.4	11.1	28	2				0.02	0.98										
Oughter	18.6	14.0	25	2		0.08	0.09	0.31	0.46					0.05		0.00	0.01		0.03
Ramor	18.6	14.6	22	2			0.00	0.02	0.98										
Gowna	20.2	15.9	21	2			0.11	0.23	0.62	0.02			0.02						
Mullagh	19.8	15.8	20	2					1.00										
Bray	5.1	1.6	69	3															1.00
Lettercraffroe	10.7	2.0	81	3															1.00
Easky	9.4	2.6	72	3													0.58		0.42
Dan	8.7	2.8	67	3				0.21											0.79
Maumwee	17.5	3.3	81	3												0.58			0.42
Lickeen	7.9	2.6	67	3							0.51	0.49							
Ballyquirke	14.6	5.3	64	3			0.28										0.10		0.61
Muckross	18.4	6.0	67	3		0.00	0.03						0.00					0.97	
Caragh	21.1	6.3	70	3			0.01											0.99	
Pollaphuca	9.8	5.9	40	3				0.19						0.01					0.80
Doolough	15.8	6.6	58	3								0.46	0.54						
Feeagh	19.0	7.6	60	3						0.01						0.44	0.44	0.11	
Graney	11.6	6.7	42	3					0.34	0.02								0.64	
Talt	16.0	9.2	42	3													0.67		0.33
Leane	21.4	10.3	52	3		0.00	0.09				0.01	0.05	0.23		0.03			0.58	

4.3.5 Calcium and alkalinity

The average calcium concentration ranged from 0.9 mg l^{-1} in Lough Bray to 66.6 mg l^{-1} in Lough Ballycullinan (Table 4.15). A decline in Ca^{2+} concentration in summer was noted in lakes with high concentrations such as Lough Inchiquin and Lene (Figure 4.18).

The export of calcium ranged from 6.5 kg ha^{-1} yr^{-1} in Lough Bray to 429 kg ha^{-1} yr^{-1} in Lough Gara South (Table 4.15). Only a relatively small amount of the Ca^{2+} exported was derived from marine sources: 1.0 kg ha^{-1} yr^{-1} in Lough Lene in the east to 4.7 kg ha^{-1} yr^{-1} in Lough Caragh in the west. As would be expected the export of non-marine Ca^{2+} was highly dependent on catchment geology. Catchments located on limestone exported the most (average = 258, S.D. = 91 kg nm Ca ha^{-1} yr^{-1}), those on Ordovician and Silurian greywacke exported an intermediate amount (average = 86, S.D. = 25 kg nm Ca ha^{-1} yr^{-1}) and those on resistant geology the least (average = 50, S.D. = 55 kg nm Ca ha^{-1} yr^{-1}) (Table 4.16).

Ratios of non-marine Mg^{2+} to Ca^{2+} in freshwater should reflect catchment geology. An examination of the ratio of non-marine Mg^{2+} to Ca^{2+} export showed it to be considerably lower in limestone catchments (average = 0.048, S.D. = 0.018, excluding Lough Rea) than Ordovician/Silurian greywacke catchments (average = 0.153, S.D. = 0.043). Catchments underlain by resistant geology had more variable ratios (average = 0.179, S.D. = 0.096) (Table 4.16).

The mean alkalinity of the lakes ranged from -0.8 mg l^{-1} $CaCO_3$ in Lough Bray to 171.8 mg l^{-1} $CaCO_3$ in Lough Ballycullinan (Table 4.17). Alkalinity would be expected to have a similar relationship with catchment characteristics as Ca^{2+} as its mainly derived from the dissolution of $CaCO_3$.

Table 4.15 Mean calcium concentration and export for the period July 1996 to June 1997. nm = non-marine.

Lake	mean mg l^{-1}	95% C.I.	mean nm mg l^{-1}	mean meq l^{-1}	mean nm meq l^{-1}	nm %	Export kg ha^{-1} yr^{-1}	nm export kg ha^{-1} yr^{-1}
Ballycullinan	66.6	9.9	66.1	3.325	3.298	99	313.6	311.3
Ballyquirke	22.1	2.5	21.6	1.104	1.079	98	119.5	116.5
Bray	0.9	0.0	0.8	0.046	0.038	82	6.5	5.3
Bunny	47.5	10.0	47.0	2.368	2.346	99	255.5	253.5
Caragh	2.0	0.2	1.8	0.102	0.088	86	33.4	28.7
Cullaun	57.9	3.2	57.5	2.891	2.868	99	267.1	265.1
Dan	1.2	0.0	1.0	0.059	0.050	85	12.3	10.4
Doolough	3.3	0.1	2.8	0.163	0.141	86	22.9	19.9
Dromore	51.9	18.2	51.4	2.590	2.566	99	256.8	254.9
Easky	1.3	0.4	1.1	0.066	0.055	83	14.9	12.7
Egish	18.7	0.3	18.4	0.933	0.917	98	77.4	76.1
Feeagh	3.0	0.2	2.6	0.147	0.128	87	29.1	25.4
Gara South	65.9	9.3	65.6	3.288	3.272	100	429.4	427.4
Gowna	25.1	0.9	24.8	1.254	1.240	99	118.9	117.5
Graney	10.8	0.7	10.4	0.537	0.521	97	58.3	56.7
Inchiquin	55.3	2.4	54.8	2.761	2.737	99	328.9	326.3
Leane	8.1	1.2	7.8	0.403	0.388	96	97.6	94.1
Lene	36.8	1.1	36.5	1.835	1.823	99	146.2	145.2
Lettercraffroe	1.5	0.1	1.1	0.073	0.053	73	10.8	8.0
Lickeen	10.1	0.4	9.5	0.502	0.474	95	31.7	30.1
Maumwee	1.6	0.3	1.3	0.080	0.064	79	24.0	19.5
Moher	7.2	0.5	6.7	0.357	0.333	93	52.3	48.9
Muckno	22.9	0.4	22.5	1.141	1.124	99	93.4	92.1
Muckross	2.7	0.1	2.4	0.133	0.121	91	42.1	38.1
Mullagh	16.6	1.2	16.3	0.826	0.811	98	70.1	68.9
Oughter	26.6	4.8	26.3	1.328	1.311	99	119.3	117.8
Owel	35.9	3.5	35.6	1.793	1.778	99	151.5	150.4
Pollaphuca	10.4	1.2	10.3	0.521	0.512	98	69.7	68.5
Ramor	18.7	1.0	18.4	0.933	0.917	98	79.0	77.7
Rea	33.9	6.0	33.5	1.690	1.670	99	185.7	183.7
Talt	25.7	4.8	25.4	1.280	1.267	99	212.2	210.1

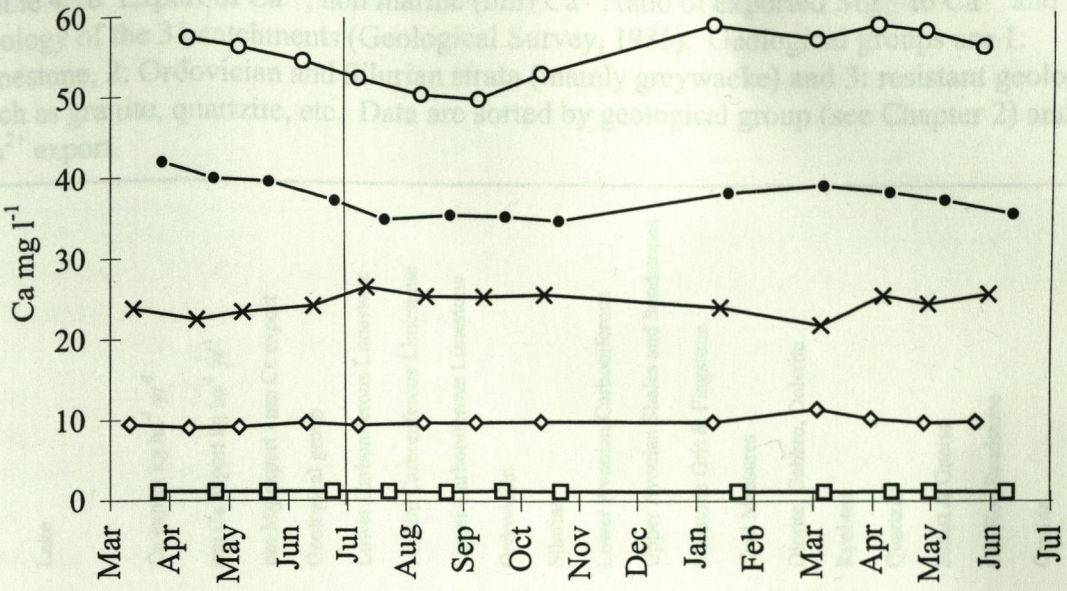


Figure 4.18 Variation in Ca^{2+} (mg l^{-1}) between March 1996 and June 1997 in Lough Inchiquin (—O—), Lene (—●—), Gowna (—×—), Lickeen (—◇—) and Dan (—⊟—). Vertical bars indicate periods when means and exports were calculated.

Table 4.16 Export of Ca^{2+}, non marine (nm) Ca^{2+}, ratio of exported Mg^{2+} to Ca^{2+} and geology of the 31 catchments (Geological Survey, 1985). Geological groups are 1: limestone, 2: Ordovician and Silurian strata (mainly greywacke) and 3: resistant geology such as granite, quartzite, etc. Data are sorted by geological group (see Chapter 2) and nm Ca^{2+} export.

Lake	Ca export kg ha^{-1} yr^{-1}	nm Ca export kg ha^{-1} yr^{-1}	nm Mg export / nm Ca export	Geological group	Lower Carboniferous Limestone	Middle Carboniferous Limestone	Upper Carboniferous Limestone	Ordovician	Silurian	Lower Avonian/Carboniferous	Upper Avonian Shales and Sandstones	Millstone Grit & Flagstone	Coal Measures	Diorite, Gabbro, Dolerite	Ryolites	Quartzite	Schist & Gneiss	Old Red Sandstone	Granite
Lene	146.2	145.2	0.08	1		1.00													
Owel	151.5	150.4	0.06	1		1.00													
Rea	185.7	183.7	0.18	1			0.99			0.01									
Bunny	255.5	253.5	0.04	1	1.00		0.00												
Cullaun	267.1	265.1	0.05	1	1.00														
Dromore	256.8	254.9	0.05	1	0.69	0.31													
Inchiquin	328.9	326.3	0.02	1	0.78						0.15	0.07							
Ballycullinan	313.6	311.3	0.04	1	1.00														
Gara S.	429.4	427.4	0.04	1			0.93			0.07									
Moher	52.3	48.9	0.16	2				0.47	0.53										
Mullagh	70.1	68.9	0.23	2					1.00										
Egish	77.4	76.1	0.12	2				0.02	0.98										
Ramor	79.0	77.7	0.19	2			0.00	0.02	0.98										
Muckno	93.4	92.1	0.12	2				0.02	0.98										
Gowna	118.9	117.5	0.14	2			0.11	0.23	0.62	0.02			0.02						
Oughter	119.3	117.8	0.12	2		0.08	0.09	0.31	0.46					0.05		0.00	0.01		0.03
Bray	6.5	5.3	0.30	3															1.00
Lettercraffroe	10.8	8.0	0.25	3															1.00
Dan	12.3	10.4	0.27	3				0.21											0.79
Easky	14.9	12.7	0.20	3													0.58		0.42
Maumwee	24.0	19.5	0.17	3												0.58			0.42
Doolough	22.9	19.9	0.33	3								0.46	0.54						
Feeagh	29.1	25.4	0.30	3						0.01						0.44	0.44	0.11	
Caragh	33.4	28.7	0.22	3			0.01											0.99	
Muckross	42.1	38.1	0.16	3		0.00	0.03						0.00					0.97	
Lickeen	31.7	30.1	0.09	3							0.51	0.49							
Graney	58.3	56.7	0.12	3					0.34	0.02								0.64	
Pollaphuca	69.7	68.5	0.09	3				0.19						0.01					0.80
Leane	97.6	94.1	0.11	3		0.00	0.09				0.01	0.05	0.23		0.03			0.58	
Ballyquirke	119.5	116.5	0.05	3			0.28										0.10		0.61
Talt	212.2	210.1	0.04	3													0.67		0.33

Table 4.17 Mean alkalinity for the period July 1996 to June 1997.

Lake	mean mg l^{-1} $CaCO_3$	95% C.I.	mean HCO_3^- meq l^{-1}
Ballycullinan	171.8	18.7	3.436
Ballyquirke	53.0	7.6	1.060
Bray	-0.8	0.4	-0.016
Bunny	120.4	21.0	2.409
Caragh	3.3	0.9	0.065
Cullaun	148.3	6.5	2.967
Dan	-0.4	0.3	-0.009
Doolough	4.8	0.8	0.096
Dromore	150.5	11.8	3.010
Easky	1.8	0.7	0.036
Egish	67.5	5.6	1.349
Feeagh	5.9	0.8	0.118
Gara South	153.4	22.8	3.069
Gowna	62.2	3.1	1.245
Graney	25.9	3.2	0.517
Inchiquin	131.3	3.6	2.626
Leane	20.1	5.0	0.402
Lene	96.8	2.2	1.937
Lettercraffroe	0.6	0.5	0.012
Lickeen	20.0	1.3	0.400
Maumwee	2.0	0.6	0.040
Moher	16.0	2.6	0.319
Muckno	43.9	2.5	0.879
Muckross	5.7	0.7	0.113
Mullagh	52.2	5.4	1.044
Oughter	68.5	6.2	1.369
Owel	93.3	4.8	1.866
Pollaphuca	23.8	3.9	0.476
Ramor	51.8	7.1	1.037
Rea	104.2	15.0	2.083
Talt	73.8	0.9	1.475

4.3.6 Silicon

The concentration of silica-silicon (SiO_2-Si) ranged from less than 0.003 mg l^{-1} in Lough Maumwee to 3.67 mg l^{-1} in Lough Egish (Table 4.18). Seasonal variation was more marked in lakes of high trophic status such as Lough Ramor compared with lakes of a lower trophic status such as Lough Dan (Figure 4.19). The explanation for the seasonal variation is the incorporation of Si into diatom frustules and their subsequent sedimentation. Figure 4.20 shows that the seasonal variation in diatom numbers in Lough Muckno corresponded to the concentration of particulate Si.

The highest maxima of Si were recorded in lakes located on Silurian and Ordovician greywacke where the concentration, with the exception of Lough Moher, was greater than 2.2 mg l^{-1} (Table 4.19). The lower concentration in Lough Moher (1.36 mg l^{-1}) was most likely a result of dilution because of the higher net precipitation in this catchment (Table 4.19). Lakes located on limestone had intermediate concentrations ranging from 0.96 to 2.14 mg l^{-1}, excluding Lough Ballycullinan which had a high maximum concentration of 2.92 mg l^{-1}. Concentrations in lakes located on resistant geology were wide-ranging but were mostly lower than lakes located on other rock types (Table 4.19).

Some indication of export of Si to the lakes may be obtained by comparing maximum winter concentration and net rainfall in the catchment. Where both concentration and net precipitation are high then export of Si to the lake will be high. Table 4.19 shows that as the concentration is very high in the greywacke lakes (Group 2) they will export the most even though the net precipitation is quite low. For example, even though Lough Maumwee had a net precipitation 3.4 times greater than Lough Egish, export to Lough Egish was still likely to be considerably higher because maximum Si concentration was 13.6 times that in Lough Maumwee. Using this approach it can be seen from Table 4.19 that three lakes located on Wicklow granite (Lough Dan, Pollaphuca and Bray) may have received Si inputs comparable to lakes located on greywacke. In contrast, despite also being located on granite, Lough Lettercraffroe had a much lower maximum Si concentration (0.42 mg l^{-1}) (Table 4.19).

Table 4.18 Summary of silica-silicon (SiO_2-Si) concentrations (mg l^{-1}) recorded between March 1996 and December 1997.

Lake	Average	95% C.I.	n	Max	Min	Range
Ballycullinan	0.99	0.57	10	2.92	0.02	2.90
Ballyquirke	0.66	0.19	17	1.51	0.05	1.46
Bray	1.81	0.03	10	1.88	1.71	0.17
Bunny	0.52	0.18	10	0.96	0.14	0.82
Caragh	0.32	0.11	9	0.56	0.13	0.42
Cullaun	0.61	0.16	10	1.04	0.36	0.68
Dan	1.32	0.07	18	1.56	1.03	0.53
Doolough	0.33	0.09	18	0.73	0.02	0.71
Dromore	0.71	0.29	10	1.63	0.17	1.46
Easky	0.37	0.09	10	0.55	0.04	0.51
Egish	1.42	0.64	9	3.67	0.05	3.62
Feeagh	0.65	0.03	18	0.80	0.51	0.29
Gara S.	0.86	0.56	9	1.85	0.01	1.84
Gowna	0.97	0.35	18	3.12	0.17	2.95
Graney	0.59	0.18	10	1.03	0.27	0.76
Inchiquin	0.43	0.16	17	1.07	0.05	1.02
Leane	0.48	0.18	9	0.88	0.08	0.80
Lene	0.94	0.29	18	1.92	0.08	1.84
Lettercraffroe	0.14	0.08	10	0.42	0.02	0.40
Lickeen	0.35	0.07	18	0.61	0.12	0.49
Maumwee	0.11	0.06	10	0.27	< 0.003	0.27
Moher	0.58	0.19	18	1.36	0.07	1.29
Muckno	0.66	0.51	10	2.26	0.01	2.25
Muckross	0.32	0.07	9	0.46	0.21	0.25
Mullagh	1.25	0.61	10	2.55	0.12	2.43
Oughter	1.03	0.56	11	2.62	0.27	2.35
Owel	0.55	0.13	18	1.08	0.13	0.95
Pollaphuca	0.96	0.22	10	1.65	0.50	1.15
Ramor	1.44	0.57	18	3.55	0.01	3.54
Rea	1.26	0.34	10	2.14	0.55	1.59
Talt	1.13	0.06	10	1.27	1.01	0.26

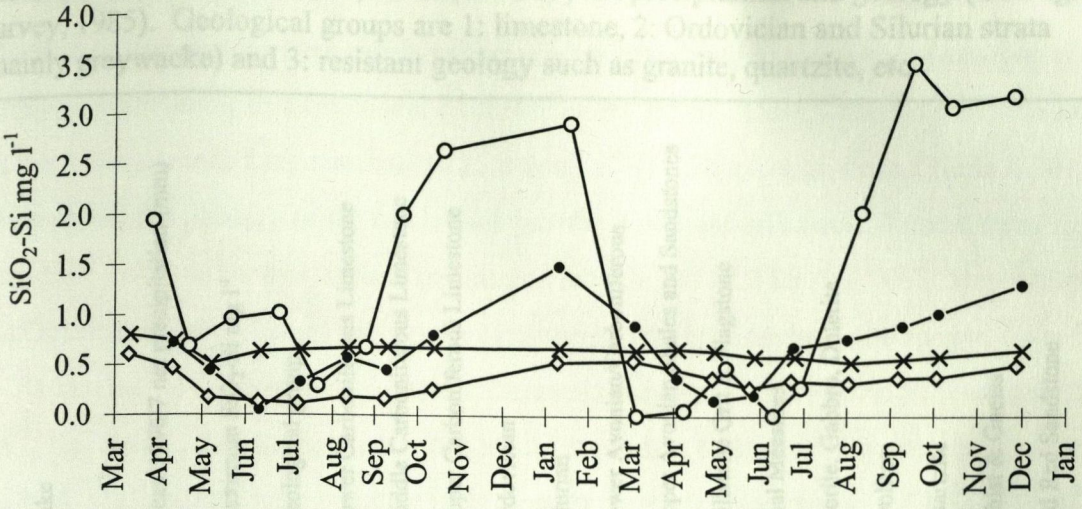


Figure 4.19 Variation in SiO_2-Si between March 1996 and December 1997 in Lough Ramor (—O—), Ballyquirke (—•—), Feeagh (—×—) and Lickeen (—◇—).

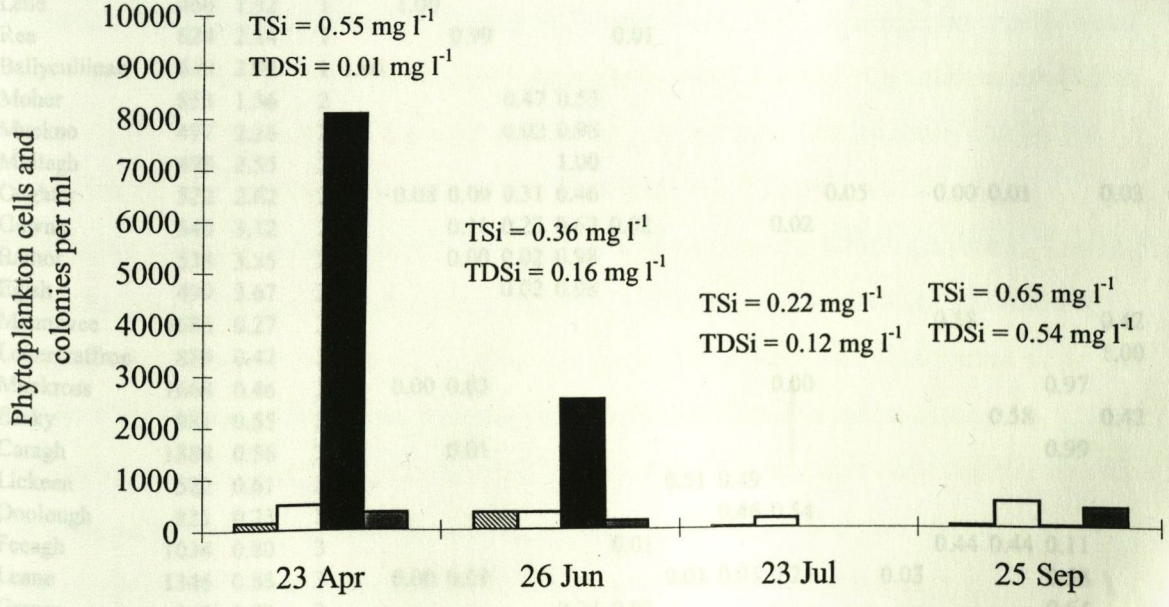


Figure 4.20 Variation in Cyanophyta (▨), Chlorophyta (□), Bacillariophyceae (■) and Cryptophyta (■) (cells and colonies ml^{-1}) at four dates between April and September 1996 in Lough Muckno. Concentrations of total silica (TSi) and total dissolved silica (TDSi) are detailed above columns (mg l^{-1}).

Table 4.19 Maximum SiO_2-Si, mean (1996/97) net precipitation and geology (Geological Survey, 1985). Geological groups are 1: limestone, 2: Ordovician and Silurian strata (mainly greywacke) and 3: resistant geology such as granite, quartzite, etc.

Lake	Mean 1996/7 net precipitation (mm)	Maximum SiO_2-Si mg l^{-1}	Geological group	Lower Carboniferous Limestone	Middle Carboniferous Limestone	Upper Carboniferous Limestone	Ordovician	Silurian	Lower Avonian/Carboniferous	Upper Avonian Shales and Sandstones	Millstone Grit & Flagstone	Coal Measures	Diorite, Gabbro, Dolerite	Ryolites	Quartzite	Schist & Gneiss	Old Red Sandstone	Granite
Bunny	658	0.96	1	1.00		0.00												
Cullaun	631	1.04	1	1.00														
Inchiquin	762	1.07	1	0.78						0.15	0.07							
Owel	455	1.08	1		1.00													
Dromore	577	1.63	1	0.69	0.31													
Gara S.	672	1.85	1			0.93			0.07									
Lene	466	1.92	1		1.00													
Rea	624	2.14	1			0.99			0.01									
Ballycullinan	619	2.92	1	1.00														
Moher	853	1.36	2				0.47	0.53										
Muckno	497	2.26	2				0.02	0.98										
Mullagh	498	2.55	2					1.00										
Oughter	522	2.62	2		0.08	0.09	0.31	0.46					0.05		0.00	0.01		0.03
Gowna	540	3.12	2			0.11	0.23	0.62	0.02			0.02						
Ramor	538	3.55	2			0.00	0.02	0.98										
Egish	499	3.67	2				0.02	0.98										
Maumwee	1686	0.27	3												0.58			0.42
Lettercraffroe	889	0.42	3															1.00
Muckross	1668	0.46	3		0.00	0.03						0.00					0.97	
Easky	981	0.55	3													0.58		0.42
Caragh	1888	0.56	3			0.01											0.99	
Lickeen	522	0.61	3							0.51	0.49							
Doolough	821	0.73	3								0.46	0.54						
Feeagh	1034	0.80	3						0.01						0.44	0.44	0.11	
Leane	1346	0.88	3		0.00	0.09				0.01	0.05	0.23		0.03			0.58	
Graney	645	1.03	3					0.34	0.02								0.64	
Talt	818	1.27	3													0.67		0.33
Ballyquirke	778	1.51	3			0.28										0.10		0.61
Dan	1412	1.56	3				0.21											0.79
Pollaphuca	936	1.65	3				0.19						0.01					0.80
Bray	1007	1.88	3															1.00

4.3.7 Chemical weathering

The sum of non-marine base cation export (C_B) is often used to indicate the amount of chemical weathering in a catchment (Johnson *et al.*, 1994). The C_B ranged from 0.6 keq ha^{-1} yr^{-1} from Lough Lettercraffroe to 22.8 keq ha^{-1} yr^{-1} from Lough Gara (Table 4.20). Once again, the geology of the catchment was the dominant influence. Export from limestone catchments was highest and ranged from 8.3 to 22.8 keq ha^{-1} yr^{-1}. Export from the Ordovician and Silurian greywacke catchments was intermediate and ranged from 3.2 to 7.4 keq ha^{-1} yr^{-1}. Admittedly, these catchments may have a non-geological source of Ca^{2+}, Na^{+} and K^{+} (i.e. agricultural) that would invalidate estimates of weathering by this method. Catchments with resistant rock types exported between 0.6 - 11.5 keq ha^{-1} yr^{-1}.

The variation in C_B between catchments with resistant rock types was examined. From this group, defined as Group 3 in Chapter 2, Lough Ballyquirke and Talt were excluded. This was because 28% of the Lough Ballyquirke drainage area consists of limestone which may have a disproportionately large effect on its C_B (Table 4.20). In Lough Talt no limestone was present in the solid geology (Harney *et al.*, 1996) although site visits found limestone indicating the presence of drift deposits to which the high C_B must be attributed (Table 4.20). A regression of C_B with catchment area (m^2) divided by mean catchment relief yielded an r^2 of 0.94 ($p \leq 0.0001$, $n = 13$, Figure 4.21) and shows that large catchments with low relief exported more than small catchments with high relief. The high r^2 may be caused by three catchments which had a high catchment area (m^2) divided by mean catchment relief (Figure 4.21), although these points were well distributed along the x-axis. Calculation of leverages, a measure of influence of individual x cases on a regression, revealed that Lough Leane had a leverage of 0.6 which is only slightly above the value of 0.5 which may cause concern (Velleman, 1997). Other catchment characteristics did not explain additional variation in multiple regression.

Other catchment characteristics also had high correlations with the C_B from the lakes located on resistant geology (Lough Talt and Ballyquirke excluded). These included the flow path ($r_S = 0.87$, $p = 0.0001$), catchment area ($r_S = 0.85$, $p = 0.0002$), slope ($r_S = -0.73$, $p = 0.0046$) and crenulation of catchment perimeter ($r_S = 0.64$, $p = 0.0185$).

Three mechanisms mainly determine the chemical composition of the Earth's surface water: precipitation inputs, rock and soil weathering and evaporation/crystallisation. Evaporation/crystallisation is mainly of importance in saline lakes and oceans. Gibbs (1970) developed a model to visualise the relative importance of the three mechanisms in determining a waters chemistry. This is achieved by plotting total dissolved solids against the ratio of Na^+ to the sum of Na^+ and Ca^{2+}. This is plotted in Figure 4.22 where total dissolved solids (mg l^{-1}) was estimated as being 2/3 of conductivity ($\mu s\ cm^{-1}$) (Flanagan, 1990). The principal is that if the composition of a water is influenced mainly by precipitation rather than rock and soil weathering it will have a high concentration of Na^+ and a small concentration of Ca^{2+} and thus a high ratio. The lakes located on resistant rock types (crosses in Figure 4.22) mainly fell into this category. Their chemistry may therefore be said to be more influenced by precipitation inputs than rock and soil weathering. In contrast, the chemistry of the limestone lakes may be said to be principally influenced by rock weathering (open circles in Figure 4.22). In these lakes the low ratio ($Na^+ / Ca^{2+} + Na^+$) is caused by the high rates of chemical weathering of $CaCO_3$ relative to inputs of Na^+ from precipitation.

Lough Egish had a higher ratio than the other lakes located on Silurian and Ordovician greywacke as a result of anthropogenic inputs of Na^+ (Figure 4.22). Similarly, Lough Moher was also located on greywacke and had a high ratio (> 0.6) but the explanation in this case may be its unique location in the West of Ireland where deposition of Na^+ is higher.

Table 4.20 Total non-marine base cation export (keq ha^{-1} yr^{-1}) and geology (Geological Survey, 1985). Geological groups are 1: limestone, 2: Ordovician and Silurian strata (mainly greywacke) and 3: resistant geology such as granite, quartzite, etc.

Lake	Sum nm base cation export keq ha^{-1} yr^{-1}	Geological group	Lower Carboniferous Limestone	Middle Carboniferous Limestone	Upper Carboniferous Limestone	Ordovician	Silurian	Lower Avonian/Carboniferous	Upper Avonian Shales and Sandstones	Millstone Grit & Flagstone	Coal Measures	Diorite, Gabbro, Dolerite	Ryolites	Quartzite	Schist & Gneiss	Old Red Sandstone	Granite
Lene	8.3	1		1.00													
Owel	8.4	1		1.00													
Rea	12.0	1			0.99			0.01									
Bunny	13.6	1	1.00		0.00												
Dromore	13.8	1	0.69	0.31													
Cullaun	14.6	1	1.00														
Inchiquin	17.0	1	0.78						0.15	0.07							
Ballycullinan	16.9	1	1.00														
Gara S.	22.8	1			0.93			0.07									
Moher	3.2	2				0.47	0.53										
Mullagh	5.0	2					1.00										
Ramor	5.9	2			0.00	0.02	0.98										
Muckno	5.9	2				0.02	0.98										
Gowna	7.5	2			0.11	0.23	0.62	0.02			0.02						
Egish	7.0	2				0.02	0.98										
Oughter	7.4	2		0.08	0.09	0.31	0.46					0.05		0.00	0.01		0.03
Lettercraffroe	0.6	3															1.00
Bray	0.6	3															1.00
Dan	1.0	3				0.21											0.79
Easky	1.0	3													0.58		0.42
Maumwee	1.5	3												0.58			0.42
Doolough	1.7	3								0.46	0.54						
Carragh	2.0	3			0.01											0.99	
Feeagh	2.1	3						0.01						0.44	0.44	0.11	
Lickeen	1.8	3							0.51	0.49							
Muckross	2.7	3		0.00	0.03						0.00					0.97	
Graney	3.6	3					0.34	0.02								0.64	
Pollaphuca	4.2	3				0.19						0.01					0.80
Leane	5.7	3		0.00	0.09				0.01	0.05	0.23		0.03			0.58	
Ballyquirke	6.4	3			0.28										0.10		0.61
Talt	11.5	3													0.67		0.33

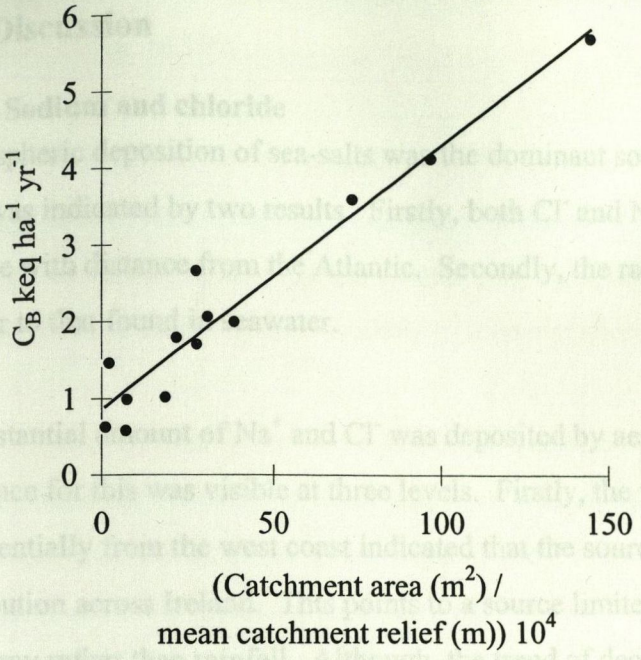


Figure 4.21 Relationship between C_B (total non-marine base cation export in keq ha^{-1} yr^{-1}) and (catchment area (m^2) / mean catchment relief (m)) 10^4. Equation: $y = 0.0347x + 0.8542$ ($r^2 = 0.94$, $p \leq 0.0001$, $n = 13$).

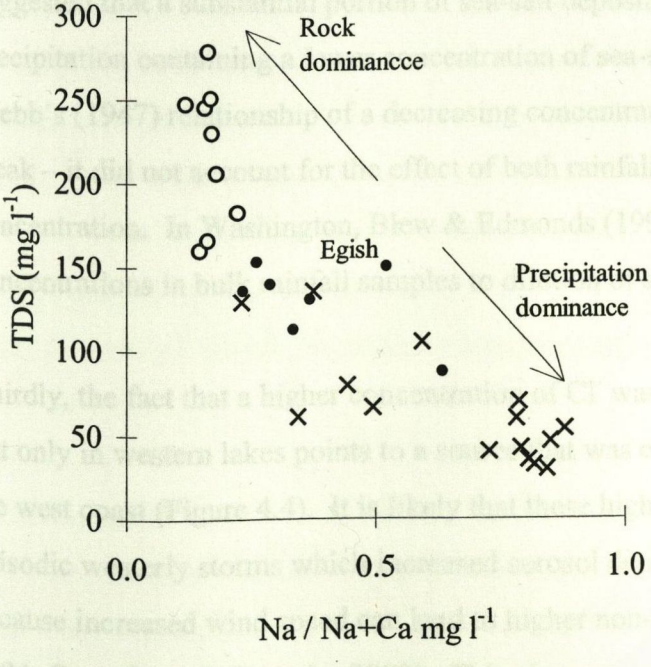


Figure 4.22 Relationship between mean (July 1996 to June 1997) total dissolved solids (mg l^{-1}) and $Na^+ / Na^+ + Ca^{2+}$ in lakes on limestone (O), Ordovician and Silurian greywacke (●) and resistant geology (X).

4.4 Discussion

4.4.1 Sodium and chloride

Atmospheric deposition of sea-salts was the dominant source of Na^+ and Cl^- in the lakes. This was indicated by two results. Firstly, both Cl^- and Na^+ export had an exponential decline with distance from the Atlantic. Secondly, the ratio of Na^+ to Cl^- in the lakes was similar to that found in seawater.

A substantial amount of Na^+ and Cl^- was deposited by aerosols as well as by rainfall. Evidence for this was visible at three levels. Firstly, the fact that Cl^- export decreased exponentially from the west coast indicated that the source of Cl^- was limited in its distribution across Ireland. This points to a source limited to the west coast such as sea-spray rather than rainfall. Although, the trend of decreasing export eastwards would also be influenced by the general decline of rainfall from west to east.

Secondly, precipitation was a highly significant negative factor in describing Cl^- concentration when it was included in a multiple regression with easting (Table 4.6). This suggested that a substantial portion of sea-salt deposition was from aerosols and that precipitation containing a lower concentration of sea-salts diluted this. This explains why Webb's (1947) relationship of a decreasing concentration of Cl^- from west to east was weak – it did not account for the effect of both rainfall amount and easting on Cl^- concentration. In Washington, Blew & Edmonds (1995) partly attributed lower Cl^- concentrations in bulk rainfall samples to dilution of sea-salts by rainfall.

Thirdly, the fact that a higher concentration of Cl^- was observed in the first half of 1997 but only in western lakes points to a source that was episodic in magnitude and limited to the west coast (Figure 4.4). It is likely that these higher concentrations were caused by episodic westerly storms which increased aerosol deposition of sea-salts. This was likely because increased wind speed can lead to higher non-wet deposition (Ross & Lindberg, 1994; Gustafsson & Franzén, 2000). This phenomenon has been previously observed in Ireland. Allott *et al.* (1997) associated higher Cl^- concentrations in western streams with specific weather events such as storms and gales arising over the Atlantic Ocean. Farrell *et*

al. (1998) found that a single storm in Western Ireland accounted for 45% of annual deposition of Na^+ in 1991.

The positive influence of mean catchment relief (lake height minus mean catchment boundary height) on Cl^- export in multiple regression with easting (Table 4.7) was probably because of increased deposition owing to higher wind speeds at higher altitudes and also because a higher relief is likely to intercept more marine aerosols.

In line with the results of this study, Gustafsson & Franzén (2000) found that deposition of sea-salts from marine aerosols decreased from west to east across southern Sweden. This was measured by a transect of gauze filters deployed during dry westerlies. The rate at which deposition decreases with distance from the sea varies between countries. Blew & Edmonds (1995) found that deposition stabilised 24 km from the Pacific Ocean compared to approximately 156 km in this study. Differences in penetration of aerosols inland is likely to be determined by wind speed at the coast and air mass type (Gustafsson & Franzén, 2000). In contrast, in Northern Ireland, Wu & Gibson (1996) did not find a significant relationship between Na^+ and Cl^- concentration in 615 lakes and distance from the sea; instead negative relationships were found with altitude. However, distance from the sea may not be an adequate measure of marine influence in Northern Ireland. This is because sea-salt deposition may be occurring from both westerly and northerly directions and therefore, a single measure of distance from the sea may not adequately describe the different sources and their relative importance. The negative relationship found between altitude and Na^+ and Cl^- concentration would be consistent with aerosol sea-salt deposition being diluted by high rainfall at high altitudes compared to a concentration mechanism at lower altitudes.

Assuming all Cl^- was derived from sea-salt, an average of 98% of Na^+ exported could be accounted for by sea salt deposition (Table 4.8). This figure excludes Lough Egish and Ramor both of which had a higher export of Na^+ relative to Cl^-. The additional source of Na^+ in these lakes was most likely anthropogenic. Lough Egish receives discharges from an adjacent Lakeland Dairies plant. Lough Ramor receives effluent from both a dairy and a sewage treatment plant. Sodium was, as expected, strongly co-linear with Cl^- and was mainly controlled by the same factors (sea-salt deposition). However, in some catchments

(other than Egish and Ramor) there were noticeable amounts of non-marine Na^+ exported (Table 4.8). Almost all of these catchments had a high proportion of peatlands. This indicates that the source may have been marine Na^+ that was previously adsorbed to the peat soils owing to their high cation exchange capacity. Adsorption of marine Na^+ deposited during westerly storms has been found to act as a store from which subsequent leaching may take place (Allott *et al.*, 1997). As this release will be in excess of the ratio to Cl^- in seawater it will inadvertently be calculated as being of non-marine origin. However, it can be noted that eastern peatland catchments exported similar amounts of non-marine Na^+ as those in the west (Table 4.8). If the non-marine export is to be attributed to prior deposition of marine Na^+ then it would be expected that western catchments would have a higher export. Perhaps there was a higher Na^+ contribution from geology in the eastern lakes (Bray, Dan and Pollaphuca) and this would be supported by their elevated Si concentrations which are indicative of higher weathering (Thornton & Dise, 1998) (Table 4.19). Further work over a long time period with collateral precipitation analysis may be necessary to determine the relative importance of desorption and catchment geology as a source of the non-marine Na^+ measured.

It is important to be cognisant of the fact that a large proportion of sea-salt deposition takes place by aerosols and that there are episodes of substantial deposition. Wu & Gibson (1996) compared rainfall Na^+ concentration with that of lakes and where lake concentrations were larger it was taken to be indicative of geological contribution of Na^+. They proposed a modification of Gibbs's (1970) classification of the world's waters which would compare lake Na^+ concentration with that of precipitation and therefore indicate the contribution of non-marine sodium from catchment geology. However, results from this study would indicate that such an approach would be problematic. Owing to the episodic nature of sea-salt deposition this approach may only work when precipitation data is concurrent with chemistry data of the lakes. In addition, data on precipitation chemistry may also need to be catchment specific. The reason for this is that the relative amounts of both wet and aerosol deposition to catchments may make lake concentrations in some regions very variable. For example, concentrations in County Clare ranged from 10.5 mg l^{-1} Na^+ in Lough Dromore and Bunny to 14.7 mg l^{-1} Na^+ in Lough Lickeen. The high concentration in Lough Lickeen was probably because of the low net precipitation recorded (357 mm) compared with Dromore and Bunny (497 and 567 mm). Aerosol

deposition of sea-salts and low precipitation in Lough Lickeen led to higher concentrations being recorded although actual export was lower. If Lough Lickeen's high Na^+ concentration was compared with regional data on precipitation chemistry it would erroneously indicate a high contribution of Na^+ from geology. Therefore on reasons of practicality Wu & Gibson's (1996) approach may not work although it is theoretically superior to Gibbs (1970).

Previous work on Na^+ and Cl^- export or deposition in Ireland is limited. One useful study was that done by Jordan (1997) who reported bulk rainfall deposition of Na^+ and Cl^- at 15 locations in Ireland. Table 4.21 shows that export was broadly similar to deposition at two nearby stations. In fact, as neither net retention or loss of Cl^- would be expected then differences in Table 4.21 are probably owing to station location, precipitation, and annual variation in deposition (Farrell *et al.*, 1998, Figure 4.4). As deposition and export of Cl^- should balance and given the inaccuracies in bulk precipitation measurements (Ross & Lindberg, 1994), the Cl^- export values in this study may represent the best estimates of atmospheric sea-salt deposition in Ireland. However, these estimates are also subject to error from both analytical measurement and also in estimating rather than measuring runoff. The combined error from these sources was estimated to be plus or minus 4% in Section 4.2.

Inputs of Na^+ and Cl^- in atmospheric deposition do not always balance catchment exports. Smith (1976) reported a higher export of Na^+ (95.7 kg ha^{-1} yr^{-1}) compared with inputs from atmospheric deposition (37.4 kg ha^{-1} yr^{-1}) in the river Maine catchment in Northern Ireland. Chloride export was also high (135.2 kg ha^{-1} yr^{-1}). Measurements of Na^+ in sewage indicated that this was not an important source (1 kg ha^{-1} yr^{-1}). The higher Cl^- concentrations were attributed to a higher density of cattle. However, this study indicated that input of Cl^- from cattle might not be a substantial source in catchments. This was indicated by the low variation in Cl^- export from intensively farmed areas (Cavan, Monaghan) even though they had a high variation in stocking density and N and P concentrations. One possibility for the discrepancy between studies may be additions of road salt as this was suggested by Gibson *et al.* (1995a) as a source of elevated Na^+ concentrations in lakes in Northern Ireland.

Gibson *et al.* (1995b) estimated that 19 kg ha^{-1} yr^{-1} of non-marine sodium was exported from an upland basalt catchment in Northern Ireland. This was based on export net of measured atmospheric deposition. This is much higher than non-marine exports calculated in this study (mean = 2.9 kg ha^{-1} yr^{-1}, S.D. = 1.8, n = 14). Possible reasons for this may be higher rate of weathering of Na from the basalt geology, underestimation of actual deposition which is inherent in bulk deposition measurements (Ross & Lindberg, 1994) or analytical problems (the ratio of Na^+ to Cl^- in atmospheric deposition was 0.774 which is lower than that of seawater (0.862, Keene *et al.*, 1986).

Table 4.21 Deposition of Na^+ and Cl^- (Jordan, 1997) and export from lakes in Wicklow (n = 3) and Clare (n = 8). All figures are in kg ha^{-1} yr^{-1}.

	Shannon airport deposition	Clare lakes export (range)	Dublin airport deposition	Wicklow lakes export (range)
Cl^-	143.4	85.7 - 148.9	60.9	62.2 - 93.0
Na^+	84.8	54.3 - 88.0	36.6	41.2 - 59.5

4.4.2 Sulphate

The lack of a clear seasonal variation in SO_4^{2-} indicates that there was little retention in the lakes. If there was a substantial retention of SO_4^{2-} a decline in summer should have been observed (Figure 4.9). This is supported by Lennox *et al.* (2000) who calculated that only 7.8% of annual input was retained in Lough Neagh in Northern Ireland. Mitchell *et al.* (1996) also assumed losses of S within lakes would not markedly affect S budgets. Therefore, the lack of substantial internal loss adds validity to the calculation of export from mid-lake samples. Information on SO_4^{2-} export will prove useful in Ireland, as Murphy (1991) has identified poor knowledge of leaching losses as an impediment to providing effective recommendations for fertiliser addition.

The percentage of SO_4^{2-} of non-marine origin in the lakes increased from west to east across Ireland (Figure 4.10). This relationship was probably caused by the higher anthropogenic atmospheric deposition in the east (Jordan, 1997) and, in the case of lakes in Cavan and Monaghan, an additional non-marine source within the catchment.

Export of SO_4^{2-} was similar to atmospheric deposition except for the lakes in Cavan and Monaghan. This was indicated by both the amounts and ratios of SO_4^{2-} to Cl^- being similar between deposition and export. The ratio of SO_4^{2-} to Cl^- was used because it was likely to be less variable than bulk deposition locally. If the ratio in export was higher or lower than in deposition it would indicate that the catchment was either a source or a sink for SO_4^{2-}. Comparisons with bulk deposition alone may be invalid because of the high degree of inter-annual variation in deposition, a sparse monitoring network and high local variation owing to altitude, vegetation, aspect, and other factors. Comparable results have been found by Reynolds *et al.* (1997) who found that atmospheric SO_4^{2-} inputs matched outputs in two grassland and two forest catchments in the Welsh uplands. However, one catchment exported 34.2 kg SO_4^{2-} ha^{-1} yr^{-1} more than atmospheric inputs which was attributed to either land management or bedrock mineralisation. In contrast, Gibson *et al.* (1995b) found a net retention of 5.1 kg SO_4^{2-} ha^{-1} yr^{-1} in an upland blanket peat catchment in Northern Ireland. Upland lakes in this study appeared to have similar ratios of SO_4^{2-} to Cl^- in atmospheric deposition and export indicating that inputs broadly matched outputs (Figure 4.12). An accurate estimation of a catchment's SO_4^{2-} fluxes would require deposition measurements in each catchment and should include measurements of organic sulphur (Houle *et al.*, 1995). It is clear, however, that lakes in Cavan and Monaghan had a substantial net export of SO_4^{2-} (Figure 4.12).

The export of SO_4^{2-} in Cavan and Monaghan exceeded atmospheric deposition at Clones by an average of 40 kg ha^{-1} yr^{-1}. This indicated that there was an additional source of SO_4^{2-} in these catchments. Moreover, this elevated SO_4^{2-} appears to be a recent phenomenon. Table 4.22 shows that the average SO_4^{2-} to Cl^- ratio in lakes in Cavan and Monaghan was 0.383 in 1973-4 compared with 0.808 in 1996-7. The ratio in 1973-4 was close to that in atmospheric deposition at nearby Clones (0.427), which indicates that in the past outputs were similar to atmospheric inputs. It is noteworthy that Lough Owel and Lene in the eastern midlands and Lough Gara in the western north midlands also had higher ratios in 1996-7 whereas other lakes had similar ratios in 1996-7 as in 1973-4.

As the elevated SO_4^{2-} export in Cavan and Monaghan appears to be a recent event then a geological source may be discounted. In any case the contribution from greywacke which

is dominant in Cavan and Monaghan (Morris, 1984) is small, being about 3.8 kg SO_4^{2-} ha^{-1} yr^{-1} (Giusti, 1999). There are two possible explanations for the higher SO_4^{2-} in Cavan and Monaghan: either direct losses of fertiliser S or more likely, increased mineralisation following the drought in 1995 (Mac Cárthaigh, 1996).

In 1989 20,000 tons of S was applied in Ireland, which equates to 12.5 kg SO_4^{2-} ha^{-1} yr^{-1} (assuming 47,862 km^2 farmed). This is too low to account for export in Cavan and Monaghan which was on average 40 kg ha^{-1} yr^{-1} higher than atmospheric deposition, although, direct losses may be sufficient if the recommended 75 kg SO_4^{2-} ha^{-1} yr^{-1} was applied in the Cavan - Monaghan region (Murphy, 1991). However, this would assume an unrealistically high leaching rate of S fertiliser (Sakadevan *et al.*, 1993). Unfortunately, information on S fertiliser usage was not available on a regional basis. The ratio of SO_4^{2-} to Cl^- in 1973-4 was similar to that in atmospheric deposition in Cavan and Monaghan lakes. At first, it may be thought that this was because S fertiliser addition was at a minimum of 8,000 tons in 1975 (Murphy, 1991). However, this seems counter-intuitive because in 1969 S fertiliser use amounted to 37,000 tons and was substantially higher prior to 1969 when sulphate fertilisers such as ammonium sulphate and superphosphate were more widely used (Murphy, 1991; Hanley, 1969). Therefore an increased loss of SO_4^{2-} for some years after application should have resulted in the SO_4^{2-} to Cl^- ratio being higher in 1973-4 if direct losses of fertiliser were important. In addition, no general trend in non-marine export was found with the proportion of agriculture in the catchment (Figure 4.13). If direct losses were responsible then a linear increase with agriculture would be expected.

Increased mineralisation, caused by the 1995 drought, is proposed as the most likely mechanism that led to elevated SO_4^{2-} (Mac Cárthaigh, 1996). Mineralisation is known to account for more than 75% of S leached, even on S fertilised grasslands (Sakadevan *et al.*, 1993); Aerobic conditions, caused by drought, would increase mineralisation of organic S. The lakes with higher SO_4^{2-}:Cl^- in 1996-7 than in 1973-4 were mainly in areas that would be prone to drought: the East-Midlands (Cavan, Monaghan and Westmeath) which receive the lowest precipitation of the 31 catchments (Table 4.22) (Chapter 2). Additional evidence that supports a mineralisation mechanism is the significant ($p = 0.002$) decline in SO_4^{2-} in lakes in Cavan and Monaghan following the 1995 drought from March 1996 to December 1997 (Figure 4.11). This indicates that the high SO_4^{2-} concentrations in Cavan

and Monaghan were the result of an isolated event such as a drought. If direct losses of fertiliser S were responsible then SO_4^{2-} concentrations would have been similar in both 1996 and 1997.

A substantially higher SO_4^{2-} to Cl^- ratio was observed in Cavan and Monaghan (0.808) than in Westmeath (0.549) despite a more prolonged drought in Westmeath (Mac Cárthaigh, 1996). This may be explained by soils in Cavan and Monaghan having a higher amount of organic S than those in Westmeath which consequently led to more SO_4^{2-} being mineralised. The Cavan and Monaghan region is one of the most intensive farming regions in Ireland and prior to 1969 large amounts of S would have been applied in the form of ammonium sulphate and superphosphate (Hanley, 1969). Past fertiliser additions are important, as Freney & Williams (1983) have shown that after 50 years of pasture establishment and regular additions of sulphur fertiliser, the amount of total sulphur in pasture soils can more than double. Sakadevan *et al.* (1993) found that pasture with a history of fertiliser application tended to export higher amounts of SO_4^{2-}, mainly by mineralisation of soil organic matter.

Therefore, the explanation for the higher export in Cavan and Monaghan may be that past agricultural inputs resulted in a high store of organic S of which a large amount was mineralised in the drought of 1995. Direct losses may have been of minor importance.

Lennox *et al.* (2000) examined SO_4^{2-} loadings to Lough Neagh in Northern Ireland from 1988-1997 and found that loading increased following dry summers and reached a maximum in 1996. Export to Lough Neagh ranged from 94 to 142 kg SO_4^{2-} ha^{-1} yr^{-1} (mean = 115 kg SO_4^{2-} ha^{-1} yr^{-1}) between 1988 and 1997 which is consistently higher than atmospheric deposition of 33.3 kg SO_4^{2-} ha^{-1} yr^{-1} recorded at Parkgate by Jordan (1997). As Lennox *et al.* (2000) estimate current S fertiliser additions to be negligible then mineralisation of previously accumulated S must explain the large amounts of S exported. This partly contradicts the explanation above, which suggested that elevated S losses might be isolated events occurring in agricultural catchments in response to drought. It is possible that past fertiliser additions of S in Northern Ireland were greater than in the Republic and lead to consistently higher mineralisation.

Table 4.22 The ratio of SO_4^{2-} to Cl^- (meq l^{-1}) in lakes in 1973-4 (Flanagan & Toner, 1975) and 1996-7. Figures for 1973-4 are for one or two samples taken in summer and winter, figures for 1996-7 are means for the period March 1996 - December 1997.

Lake	County	SO_4^{2-} / Cl^- 1973-4	SO_4^{2-} / Cl^- 1996-7
Gowna	Cavan	0.262	0.781
Gowna	Cavan	0.410	
Ramor	Cavan	0.625	0.772
Egish	Monaghan	0.406	0.841
Egish	Monaghan	0.344	
Muckno	Monaghan	0.505	0.881
Muckno	Monaghan	0.394	
Oughter	Monaghan	0.304	0.764
Oughter	Monaghan	0.194	
	Average of Cavan and Monaghan	**0.383**	**0.808**
Lene	Westmeath	0.201	0.512
Owel	Westmeath	0.158	0.586
Owel	Westmeath	0.105	
Gara	Roscommon	0.332	0.780
Gara	Roscommon	0.295	
Graney	Clare	0.231	0.318
Inchiquin	Clare	0.590	0.279
Inchiquin	Clare	0.235	
Rea	Galway	0.347	0.304
Caragh	Kerry	0.246	0.148
Caragh	Kerry	0.092	
Leane	Kerry	0.158	0.212
Leane	Kerry	0.043	
Feeagh	Mayo	0.304	0.162
Feeagh	Mayo	0.295	
Easky	Sligo	0.470	0.206
Easky	Sligo	0.148	

4.4.3 Potassium

The wide variation in K^+ was a result of differences in inputs from marine, geological and agricultural sources. In upland catchments non-marine K^+ was a low percentage indicating that marine inputs accounted for most of the K^+ exported (Table 4.11). Lough Lettercraffroe had a negative export of non-marine K^+ indicating that a significant net retention of K^+ occurred. This catchment had the highest proportion of coniferous forestry (39%) which probably altered the mass balance of K^+. Most other upland catchments had a positive export of non-marine K^+ which was most likely derived from mineral weathering given the absence of agriculture.

To exclude marine sources the export of non-marine K^+ was calculated. This export should result from either mineral weathering or agricultural inputs. A linear relationship was found with both fertiliser input and the proportion of the catchment used for agriculture (CORINE). This indicated that agriculture was a major factor controlling K^+ export from the lakes in this study. Such a result is not surprising given the large amount of K^+ applied as fertiliser (Table 4.12, Murphy *et al.*, 1997).

In agricultural catchments the loss of non-marine K^+ was substantial, being 57% of fertiliser input in four Cavan lakes (Figure 4.15). Agricultural losses come from both direct fertiliser losses and desorption of K^+ previously applied to the soil. Potassium has increased in Irish soil from 20 mg kg^{-1} in 1950 to 108 mg kg^{-1} in 1994, which is likely a result of the low rate of removal of K^+ in farm produce and continued application of K (Figure 4.1, Culleton *et al.*, 1996; Coulter *et al.*, 1999). Although the rate of K^+ application has remained constant since 1970, it is thought that the increase in soil K^+ may result in a higher concentration in lakes over time. Table 4.23 shows that lakes in Cavan and Monaghan (Egish, Gowna, Muckno, Oughter and Ramor), where agriculture is most intensive, tended to have higher K^+ in 1996-7 than in 1973-4. A paired t-test indicated a significant increase in the Cavan and Monaghan lakes ($p = 0.042$, $n = 9$) but not in the other lakes ($p = 0.417$, $n = 18$). It is noteworthy that the increase in Cavan and Monaghan was not substantial in the context of the five-fold increase in soil K^+. A likely reason for this is the tendency for K^+ to be strongly adsorbed by clay minerals (O'Neill, 1993).

Large losses of K^+ fertiliser to freshwater have been reported previously by Cuttle and James (1995) who found that of 117 kg K ha^{-1} applied to an upland stagnogley Welsh pasture 104 kg K ha^{-1} was exported after four years compared with just 20 kg K ha^{-1} from an unfertilised control site.

Several lakes located on limestone and receiving groundwater drainage were found to export less K^+ than the other lakes in this study (Figure 4.15 & Figure 4.16). This may have been because of a greater adsorption capacity of their soils. Such a conclusion is supported by Culleton *et al.* (1996) and Coulter *et al.* (1999) who noted that limestone soils with clay minerals have fertility problems because of K^+ adsorption. One exception was Lough Ballycullinan, which although it received groundwater drainage had exceptionally high K^+ (Figure 4.15). This was most likely a result of a point source as P concentrations have increased since the 1980s (see Chapter 6).

In Northern Ireland Gibson *et al.* (1995a) surveyed 612 lakes and found the majority of lakes had a K^+ concentration less than 0.5 mg l^{-1}. Thirty-six of the lakes had concentrations greater than 4.5 mg l^{-1} and these lakes were situated in the lowlands and tended to be enriched with P and Cl^-. This supports a conclusion of increased leaching of K^+ from agricultural land. Previous work on K^+ export in Ireland is limited. Gibson *et al.* (1995b) found that an upland catchment exported 2.3 kg ha^{-1} yr^{-1} in Northern Ireland which was matched by inputs from atmospheric deposition. This figure is similar to values for upland lakes examined in this study, which ranged from 2.4 kg ha^{-1} yr^{-1} in Lough Lettercraffroe to 6.5 kg ha^{-1} yr^{-1} in Lough Caragh. Smith (1976) estimated export from the river Main in Northern Ireland as 11.7 kg K^+ ha^{-1} yr^{-1}, which is similar to agricultural catchments in this study such as Gowna (12.4 kg K^+ ha^{-1} yr^{-1}) and Ramor (15.6 kg K^+ ha^{-1} yr^{-1}).

Table 4.23 The concentration of K^+ (mg l^{-1}) in winter and summer in 1973-4 (Flanagan & Toner, 1975) and 1996-7. Concentrations from 1996-7 are from June 1996 and January 1997.

Season	Lake	K^+ (mg l^{-1}) 1973-4	K^+ (mg l^{-1}) 1996-7
Winter	Egish	4.5	3.9
Summer	Egish	3.2	3.9
Winter	Gowna	2.3	2.6
Winter	Muckno	3.2	4.0
Summer	Muckno	2.0	3.6
Winter	Oughter	2.5	3.1
Summer	Oughter	2.5	3.2
Winter	Ramor	3.6	3.3
Summer	Ramor	1.9	3.6
	Average of Cavan and Monaghan	**2.9**	**3.5**
Winter	Caragh	0.4	0.4
Summer	Caragh	0.4	0.4
Winter	Easky	0.5	0.3
Summer	Easky	0.5	0.4
Winter	Feeagh	0.4	0.5
Summer	Feeagh	0.8	0.5
Winter	Gara	1.4	1.6
Summer	Gara	1.4	0.4
Winter	Graney	1.0	0.8
Summer	Graney	1.0	0.8
Winter	Inchiquin	0.9	1.2
Summer	Inchiquin	0.9	1.0
Winter	Leane	0.8	0.8
Summer	Leane	0.7	0.8
Winter	Lene	0.9	0.9
Summer	Lene	1.0	1.0
Winter	Owel	0.9	1.1
Winter	Rea	1.3	1.3
	Average of other counties	**0.84**	**0.79**

4.4.4 Magnesium

Catchments dominated by rock types resistant to weathering exported less non-marine Mg^{2+} than those based on based on limestone or Silurian / Ordovician strata. It was interesting that limestone and Ordovician / Silurian greywacke catchments exported similar amounts of non-marine Mg^{2+}, even though the denudation rate of limestone was likely to be higher. The most likely reason for this is that the Mg^{2+} composition is higher in greywacke than in limestone. Table 4.24 indicates that greywacke can have over three times more Mg^{2+} than in some limestones. Lough Rea had an exceptionally high export of non-marine Mg^{2+} (32.9 kg nm Mg ha^{-1} yr^{-1}). The explanation for this might be the presence of dolomite or high-magnesium calcite in the catchment.

Table 4.24 Percentage of SiO_2, MgO, CaO and CO_2 in rocks. All figures are from Brownlow (1996) except for granitoid, which is from Giusti (1999).

	Greywacke	Lithographic Limestone	Fossiliferous limestone	Dolomite	Granitoid
SiO_2	68.84	1.15	0.29	3.24	65.06
MgO	1.94	0.56	0.70	20.84	2.87
CaO	2.23	53.8	55.53	29.58	2.79
CO_2	0.14	42.69	43.42	45.54	-

4.4.5 Calcium and alkalinity

The decline of Ca^{2+} in summer in lakes with high concentrations of Ca^{2+} was most likely a result of precipitation of $CaCO_3$, which is enhanced by increased photosynthetic uptake of CO_2 (Horne & Goldman, 1994). This proceeds as follows:

$$Ca^{2+} + 2HCO_3^- \rightleftarrows Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow H_2O + CO_2 \text{ (taken up by plants)}$$

As was expected, Ca^{2+} and alkalinity were mainly determined by catchment geology, the highest values being found on limestone. This is owing to the dissolution of $CaCO_3$, which is a high proportion of limestone (over 96% $CaCO_3$, Table 4.24).

The ratio of non-marine Mg^{2+} to Ca^{2+} was lower in lakes with limestone catchments than where the rock type was either Ordovician / Silurian greywacke or more resistant rock types (Table 4.16). This reflects the chemical composition of catchment rock types: limestone has a lower ratio of Mg^{2+} to Ca^{2+} than greywacke or resistant rock types such as granite (Table 4.24). Lough Rea was an exception and its higher ratio indicates the presence of dolomite or high magnesium calcite.

Gibson *et al.* (1995a) also noted consistent differences in the ratio of Mg^{2+} to Ca^{2+} concentration between limestone and Silurian strata in lakes in Northern Ireland. The ratio for limestone was 0.047 (based on a trimmed mean), that for Silurian strata was 0.283 and 0.268 for Ordovician. This is broadly similar to the Mg^{2+} to Ca^{2+} ratios of non-marine export found in this study (0.048 for limestone and 0.153 for Ordovician / Silurian greywacke). Discrepancies between the studies may be due to differences in calculation (concentration versus non-marine export), sample size, addition of lime and variation in calcareous overburden.

4.4.6 Silicon

Silicon concentration in the lakes was determined by rock type and weathering. The lakes on greywacke had higher concentrations of Si than those located on limestone or rock types resistant to weathering (Table 4.19). Some of the rock types have a similar content of Si (e.g. greywacke and granite Table 4.24); therefore, differences in Si in lakes must be because of differences in the rates of weathering and subsequent export. Giusti (1999) used denudation rates of 0.02 and 0.25 mm yr^{-1} for granite and greywacke respectively. However, the generality of such denudation rates may be questionable as three lakes located on granite in County Wicklow received a similar load of Si as the lakes located on greywacke (Table 4.19).

Lakes located in limestone catchments had similar or higher Si concentrations than lakes located in siliceous granite catchments (e.g. Lettercraffroe, Table 4.19). This may seem implausible given that limestone has only 1.15% Si compared with 65% in granite (Table 4.24). However, the average ratio of maximum Si to maximum Ca^{2+} in the lakes in limestone catchments was 0.028 (n = 9), which is close to the ratio of Si to Ca^{2+} in

limestone of 0.021 (Table 4.24). Therefore the higher weathering rate of limestone as indicated by the Ca^{2+} concentration is sufficient to account for the Si concentration. In addition, some limestones may have an additional source of Si in the form of chert, which is composed of silica (Hamilton *et al.*, 1990). The occurrence of localised chert in limestone may explain the high concentration of Si found in Lough Ballycullinan (Table 4.19). This is supported by Drew (1988) who has recorded the occurrence of chert in stratigraphic sequences in the locality.

In contrast, the average ratio of Si to Ca^{2+} in lakes located on greywacke was 0.138 (n = 7), which is much lower than the ratio of 30.9 found in greywacke (Table 4.24). Clearly, corresponding amounts of Si to Ca^{2+} are not exported in the greywacke catchments. Reasons for this may be that Ca^{2+} concentrations are derived from artificial inputs of lime or calcareous glacial overburden or that weathered Ca^{2+} is more easily exported than Si in greywacke. Meybeck *et al.* (1996) state that Si has a low soluble transport index and thus will not be easily exported.

4.4.7 Chemical weathering

Calculation of the sum of non-marine base cation export (C_B) gives a useful indication of the chemical weathering in a catchment which is important in soil formation and acid neutralisation (Johnson *et al.*, 1994). This study will not provide an estimate of landscape erosion because particulate export was not estimated, and this can account for as much as 88% of the mass discharged by rivers to oceans (Wollast & Mackenzie, 1983).

As would be expected the C_B was greatest in the catchments based on limestone geology. The Ordovician and Silurian greywacke catchments had an intermediate C_B while the lakes with catchments composed of rock types resistant to weathering had the least. Johnson *et al.* (1994) reviewed the export of base cations from small catchments in Europe and North America underlain by felsic bedrock (Si rich igneous rock). They found that in 28 catchments the export ranged from 0.16 to 2.29 keq ha^{-1} yr^{-1} and average export was 0.97 keq ha^{-1} yr^{-1} (S.D. = 0.58). Six of the catchments in this study that were considered to be small (under 23 km^2) had an average export of 1.19 keq ha^{-1} yr^{-1} (S.D. = 0.54) which is close to the figures of Johnson *et al.* (1994).

A highly significant positive relationship was found between C_B and catchment area (m^2) divided by mean catchment relief in 13 catchments located on resistant rock types (r^2 = 0.94, $p \leq 0.0001$, Figure 4.21). The independent parameter: catchment area (m^2) divided by mean catchment relief was developed specifically for use in this study from the concept of a relief ratio used for rivers which is calculated by dividing relief by a horizontal distance (Strahler, 1964). For lake catchments, it was thought more appropriate to use catchment area and using mean catchment relief as the denominator instead of numerator gave the parameter a better distribution. The positive relationship observed indicates that large catchments with low relief exported more than small catchments with high relief. This parameter may have described several environmental factors of importance to the export of base cations. These include catchment area, as large catchments would have longer flow paths to the lake whereby solute load would increase with distance travelled (Kähkönen, 1996). A low relief (calculated by subtraction of lake altitude from mean catchment boundary altitude) would also increase solute load. This is possible because lower relief means less kinetic energy for water movement which will increase the period of time the water is in contact with the rocks and soils, thereby increasing solute load. In addition, large catchments with low relief will have low slopes which may mean thicker soils (Young, 1972). Thicker soils provide more substrate for weathering reactions and therefore increase the solute load.

The high proportion of variance (94%) explained may be an overestimate of the performance of the predictor owing to the small sample size (n = 13) but it is not a result of a high leverage caused by extreme data points. Other factors which are likely to have some additional influence include: rock and soil type, atmospheric H^+ inputs, and uptake or release by vegetation. Most studies of chemical weathering, including this one, assume that there is negligible net uptake of cations by vegetation or changes in the soil pool (Johnson *et al.*, 1994).

Explaining a large proportion of the variation in C_B with one parameter (catchment area (m^2)/mean catchment relief (m)) is a large improvement on previous work. Thornton & Dise (1998) typify the previous discursive approach to this topic where variation in base cations are attributed to differences in soil depth and rock type. Johnson *et al.* (1994) were unsuccessful in using catchment H^+ input to explain C_B. Hydrogen ion input is likely to be

of secondary importance to the series of catchment characteristics embodied in the relief ratio used in this study. Future work may focus on increasing the sample size and analysing the importance of factors other than the relief ratio such as H^+ inputs, rock type and so on.

The model produced by Gibbs (1970) to describe the dominant processes controlling water chemistry was useful in separating the mechanisms controlling the chemistry of the 31 Irish lakes. The separation of the lakes into rock dominated and precipitation dominated chemistry matched the separation achieved by examination of catchment geology (Figure 4.22). In contrast, previous authors have criticised the Gibbs model (Eilers *et al*, 1992) because it fails to adequately describe very dilute lakes or lakes with very high marine inputs. The model assumes Ca^{2+} weathering to be indicative of mineral weathering and Na^+ to be indicative of precipitation inputs. This may not be the case when Na^+ is an important weathering product relative to Ca^{2+} or if there is minimal marine influence in precipitation.

4.5 Conclusions

Overall, the estimation of export of the major ions from mid-lake concentrations was worthwhile. The export estimates compared well with previous work and allowed new insights into the knowledge of terrestrial and limnetic systems. The main conclusions from this chapter are:

- The principal catchment influences on the export of the major ions were rock type, marine salts, agricultural practices and antecedent climatic conditions.
- Most lakes displayed little seasonal variation in the concentration of major ions. However, western Loughs had higher Cl^- concentrations in the first half of 1997, which were attributed to episodic westerly storms in winter.
- Previous work found only a poor relationship between Cl^- concentrations and distance from the Atlantic. This study also found a poor relationship with Cl^- concentration and easting which was attributed to variation in the relative amounts of rainfall and sea-spray deposited. Examination of the export of Cl^- rather than concentration showed a curvilinear trend with easting ($r^2 = 0.81$).

- The percentage of SO_4^{2-} calculated as being of non-marine origin increased from west to east. This was most likely in response to higher anthropogenic atmospheric deposition and, in the case of lakes in Counties Cavan and Monaghan, an additional catchment source of SO_4^{2-}.
- With the exception of Cavan and Monaghan, the similarity of the Cl^- to SO_4^{2-} ratio between atmospheric deposition and export indicated that SO_4^{2-} inputs and outputs were in balance. In Cavan and Monaghan, SO_4^{2-} export was substantially higher than atmospheric deposition and this was attributed to increased mineralisation of soil organic S following the drought of 1995.
- The export of non-marine potassium increased linearly with both the proportion of the catchment used for agriculture and fertiliser input indicating that agricultural practices were a major factor controlling K^+ export. In lakes in Cavan and Monaghan, evidence was found that K^+ had increased significantly since 1973-4, which was attributed to the national increase in soil K^+ rather than an increase in K^+ fertiliser application.
- Rock type was found to be a major influence on Mg^{2+} Ca^{2+} and Si.
- Chemical weathering, as indicated by the export of non-marine base cations, from catchments located on resistant rock types was highly correlated to catchment area (m^2) divided by mean catchment relief. This indicated that weathering is mainly controlled by the depth of soils and the duration of contact between water and the drainage area.

5. THE RELATIONSHIP BETWEEN LAKE COLOUR AND CATCHMENT CHARACTERISTICS.

5.1 Introduction

5.1.1 Nature and importance of colour

The brown discoloration present in fresh water is mainly caused by soluble refractory acid polymers. These are principally humic and fulvic acids which are derived from incomplete microbial degradation of organic material. These recalcitrant compounds are likely to be the most numerous macromolecular material on earth (Mitchell, 1990).

The presence of colour in potable supplies has a negative aesthetic effect and thus the European Community have set maximum admissible concentrations of 20 mg l^{-1} PtCo (European Community, 1992). Highly coloured waters are also considered less desirable for bathing (Smith *et al.*, 1995). A more serious problem is the formation of by-products when humic substances are chlorinated. These substances, such as trihalomethanes and 3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone, are considered to be possible carcinogens (Gray, 1994; Maugh, 1981; Watt *et al.*, 1996).

Humic substances can also contribute to the acidity of natural waters (Gorham *et al.*, 1986; Oliver *et al.*, 1983) as well as potentially reducing the availability and toxicity of certain metals such as copper, mercury and iron by complexation. However, the availability of iron to biota may sometimes be increased by humic substances (Steinberg & Muenster, 1985; Jackson & Hecky, 1980). The complexation of phosphorus by humic substances is important in nutrient dynamics. Iron containing humic substances may release PO_4^{3-} following photoreduction of ferric iron by UV light. This process can be reversed in darkness (Franko & Heath, 1979; Franko & Heath, 1982). McGarrigle & Kilmartin (1992) found that this process operated in Irish lakes to a variable extent. They also found evidence that the released P was assimilated by *Oscillatoria redekei*. Nechutová and Tichý (1970) found that the addition of humic substances to cultures of *Scenedesmus quadricauda* increased their biomass compared with cultures without humic substances. In addition, photochemical transformation of humic substances in dystrophic lakes can provide a substrate for bacterial growth (Lindell *et al.*, 1995). Such photochemical

reactions can significantly reduce the oxygen in surface waters (Lindell *et al.*, 1995) and Crisman *et al.* (1998) found colour to be the most highly correlated variable to oxygen in 55 lakes in Florida. Such a finding is untypical: Nürnberg (1995) found inter-annual variation in anoxia to be affected by DOC, but between lake variation in anoxia was principally explained by nutrients and lake shape. Colour may also be a significant negative factor affecting zoobenthic biomass, either owing to the chemical oxygen demand or through inhibition (Rasmussen & Kalff, 1987).

Colour can also regulate light attenuation in lakes (Effler *et al.*, 1985). Håkanson & Lindström (1997) used colour, total phosphorus and pH to explain the variation in Secchi depth. Increased colour leads to less light penetration which can result in a decrease in metalimnetic chlorophyll *a* but this is partially offset by an increase in epilimnetic chlorophyll *a* (Christensen *et al.*, 1995).

5.1.2 Geographic variation in colour

Previous work on 53 Irish lakes found that colour ranged from less than 5 to greater than 100 mg l^{-1} PtCo (Flanagan & Toner, 1975). In 337 lakes in the northern United States and Canada colour ranged from 2 to 251 mg l^{-1} PtCo (Rasmussen *et al.*, 1989). Håkanson (1993) reported a mean colour of 72 mg l^{-1} PtCo in 556 Swedish lakes. A survey of 978 lakes in Finland found a median colour of 100 and a range from 0 to 600 mg l^{-1} PtCo (Kortelainen, 1993).

5.1.3 Seasonal variation in colour

Colour in lakes tends to show a seasonal pattern, decreasing during spring and summer and increasing in autumn and winter (e.g. Tipping & Woof, 1983; Naden & McDonald, 1989; Townsend *et al.*, 1996). In Ireland, this seasonal variation has been documented for a limited number of lakes (Bowman *et al.*, 1993; Bowman, 1986; Bowman, 1996) and alternate sampling in summer and winter has indicated a similar seasonal pattern in 53 lakes (Flanagan & Toner, 1975).

To explain the seasonal variation in colour, Naden & McDonald (1989) introduced the concept of a store of colour in the catchment. This store is developed during the summer

through increased microbial activity and may then be released following precipitation in autumn. Naden & McDonald (1989) found that the timing of colour release is dependent on precipitation and can occur as early as August. The duration of this flush of colour was found to vary from 39 to 194 days and ended between November and February over an eight year period in the Upper Nidd catchment in England. As the store of colour is removed in autumn, subsequent winter precipitation will not remove as much colour. Grieve (1984) presented evidence of this by plotting the residuals of a discharge - DOM relationship against time. Precipitation in autumn removed more colour (positive residuals) than similar precipitation in winter (negative residuals). During spring and summer the main trend is a decrease in lake water colour. This decrease is mainly the result of adsorption onto surfaces or cleavage by UV irradiation (Steinberg & Muenster, 1985). Engstrom (1987) noted that an initial high loss of labile humic substances as indicated by colour was followed by a more gradual decline. The decline in colour was greater at high temperatures and light levels (22°C, 100 $\mu E\ m^{-2}\ s^{-1}$) with an average loss rate of 0.48 yr^{-1}. In contrast, the decline at lower temperatures (4°C) and darkness was 0.16 yr^{-1}. Engstrom (1987) found that initial colour and conductivity were not significant factors influencing loss rates. Whereas Steinberg & Muenster (1985) noted that dissolved organic matter can be co-precipitated by calcium carbonate but that high concentrations of fulvic acid can prevent precipitation of calcium carbonate by sorbing to the spiral dislocation of the calcite crystal and forcing it to grow slower.

5.1.4 Inter-annual variation in colour

Colour can vary substantially between years in freshwaters owing to climatic variability. Townsend *et al.* (1996) found average colour in two Australian reservoirs to be dependent on annual retention time over three wet seasons. Shorter retention times led to higher colour. Similarly, Andersson *et al.* (1991) attributed an upward trend in colour in Swedish freshwaters over 20 years to increased precipitation. Naden & McDonald (1989) developed a model to explain variation in colour for an eight year period in the Upper Nidd catchment in North Yorkshire. Monthly colour was high if flushing was high; however, a low precipitation either 7-8 months or 15-16 months previously also led to increased colour. This was supported experimentally by Mitchell & McDonald (1992) who demonstrated that peat cores released more colour if they were subjected to drought. However, the release of colour was dependent on sufficient rewetting of the peat and it was

estimated that sufficient rewetting in nature could take up to a year. The mechanism by which low moisture content of soils increases colour is likely to be increased micro-organism respiration owing to increases in temperature and aerobic conditions (Mitchell & McDonald, 1992; Swift *et al.*, 1979). Colour production has been shown to be microbially mediated as the addition of antibiotic solutions to soil decreases respiration and extractable colour (McDonald *et al.*, 1991 cited in Mitchell & McDonald, 1992). Scott *et al.* (1998) noted DOC to increase following dry periods (four weeks) but when the bog pools dried completely for eight weeks a smaller summer and autumn concentration of DOC was observed. It was postulated that extremes of drying possibly reduced DOC production. However, the following year DOC concentrations were substantially higher. This may indicate that insufficient rewetting delayed release of colour producing substances. Apsite & Klavins (1998) found colour to decline between 1977 and 1995 in Latvian rivers. This was attributed to changes in management of the catchment rather than climate. The gradual decline in colour followed land drainage schemes initiated in the 1940s.

5.1.5 Empirical models to explain colour

The high variation of humic substances found in lakes and rivers has led to many attempts to explain it. Explanations are often based on colour or estimations of carbon such as TOC or DOC, which are strongly correlated with colour (Kortelainen, 1993; Rasmussen *et al.*, 1989; Meili, 1992). One of the principal predictors of colour is soil type, usually the proportion of peat rich soils as these have a high carbon export relative to mineral soils (Urban *et al.*, 1989). If peatlands are planted with Sitka spruce they tend to develop a higher store of colour than unforested peatlands and this may be released after harvest (Reynolds *et al.*, 1996). In addition, mineral soils not only have a lower organic content but they also tend to adsorb DOC (McDowell & Likens, 1988). Engstrom (1987) noted that lakes with catchments containing greater than 25% open peatlands had higher colour than lakes situated on well-drained forest soils. In Northern Finland, the percentage of peatland in catchments explained 49% of the variation in DOC in a sample of 183 lakes. Better correlations were found in the north - possibly as a result of the reduced level of disturbance such as drainage (Kortelainen, 1993). In a study of 45 streams draining three catchments in North Yorkshire the percentage of catchment area covered by blanket peat explained 44% of the variation in colour. Three streams had very high colour and were noted to be subject to recent drainage and burning for grouse moor management (Mitchell

& McDonald, 1995). In southern Quebéc the percentage of wetland (bog, fen, swamp and beaver pond) showed the strongest relationship (r^2 0.26 to 0.67) to stream DOC in 42 catchments (Eckhardt & Moore, 1990). Rasmussen *et al.* (1989) found no relationship between the proportion of wetlands and colour in 337 lakes from northern USA and Canada. Instead a multiple regression model that included drainage ratio (drainage area/lake area), slope, maximum depth, and lake area explained between 50 and 80% of the variation in four regions. It was noted that the inclusion of slope in the model may have partly accounted for the variation in wetlands. Exchanging water residence time for drainage ratio explained less variance but was still significant.

Water residence time and drainage ratio are co-linear because lakes with a large drainage ratio have short residence times. Both these variables are related to colour in two ways. Firstly, lakes with a drainage ratio less than 20 will have lower colour because of dilution by precipitation directly onto the lake surface (Schindler, 1971; Engstrom, 1987). Secondly, a shorter residence time will increase colour because the store of colour accumulated in the catchment during the summer is quickly transported to the lake (Free *et al.*, 2000). A short residence time also means that there is less reduction of colour by photolysis (Rasmussen *et al.*, 1989). Meili (1992) and Townsend *et al.* (1996) noted a negative relationship between colour and water residence time indicating the allochthonous nature of colour. Schindler (1971) found a positive relationship between catchment area divided by lake volume and colour but noted that the relationship may only be valid for catchments with similar soils and vegetation. Tipping *et al.* (1988) observed positive relationships between colour and discharge for five Cumbrian streams. However, the seasonal pattern was one of initial high increase in colour with discharge after summer, whereas subsequent discharges did not produce similar peaks in colour. This is in accordance with the concept of a store of colour - flushing should initially release this store but similar flushing later in the winter may not produce similar colour as the store will have already been exported from the catchment. Hope *et al.* (1996) also noted that lakes with high DOC tended to have high drainage ratios and percentages of peatlands. In contrast, Eckhardt & Moore (1990) found a significant relationship between discharge and DOC in catchments without wetlands compared to those with wetlands in southern Québec.

The percentage of peatland and either the residence time or the ratio of catchment to lake area are the most common variables used to explain colour. Slope is also frequently used either alone or in combination with other catchment characteristics. Rasmussen *et al.* (1989) found slope to be negatively correlated with colour in a multiple regression containing drainage ratio, maximum depth and lake area. The influence of maximum depth and lake area was probably owing to their relationship to retention time. The negative influence of slope was attributed to its relationship with the thickness of the organic soil horizon. Steep slopes are likely to have thin organic horizons and thus water will be filtered through the mineral horizons below which will adsorb the colour (Rasmussen *et al.*, 1989). Houle *et al.* (1995) found that three estimates of slope were all significantly correlated with lake colour ($r^2 = 0.47$ to 0.51, $n = 50$). However, the best model used the inverse maximum lake depth and flow path (Equation 5.1) to explain 69% of the variation in colour. Inverse maximum depth was replaceable with retention time. Flow path had a positive relationship with colour.

$$\text{Flow path} = \log_e[(\text{drainage area in km}^2/\text{lake perimeter in km}) / \text{Slope}^\circ] \qquad 5.1$$

Higher flow path values and colour tended to be found in catchments with low slopes with a large drainage area in relation to the lake perimeter. The inclusion of drainage area to lake perimeter is probably similar to other attempts that used drainage ratio as lake perimeter is related to lake area.

Mitchell & McDonald (1995) found that the percentage of total channel length in areas of catchment with slopes less than 5° was positively correlated with stream colour ($r^2 = 0.38$, $n = 48$), the probable reason being that a lower slope will allow more time for dissolution of decomposition products. Longer total channel lengths promote a low water table which allows more colour production through aerobic decomposition. The high drainage density also facilitates rapid transport of the colour during autumn. Mitchell & McDonald (1995) used this slope factor along with the percentage of peat in the catchment to explain 60% of the variance in colour. Removal of three outlying streams improved the percentage of variance explained to 82%. Eckhardt & Moore (1990) found that slope was co-linear with the percentage of wetland and soil drainage. Soil drainage explained 12-39% and slope 11-38% of the variation in stream DOC concentrations over five sampling dates.

However, the percentage of peatland alone was used to explain between 29 and 67% of the variation in DOC.

Kortelainen (1993) sampled 970 lakes in Finland and found that latitude, proportion of peatland in the catchment, catchment area/lake area, proportion of upstream lakes and proportion of fields explained 55% of the variation in TOC. Latitude was important as there was less colour in northern lakes owing to reduced microbial degradation at lower temperatures. Southern areas also tended to have a lower slope and therefore a separate regression for northern areas alone of TOC against percentage of peatlands explained 49% of the variation. The proportion of upstream lakes had a negative influence on TOC. Upstream lakes will reduce colour by interception of precipitation on the lake surface (less colour than if than if the precipitation fell on the drainage area) and through photolysis. Upstream lakes will also reduce the annual variation in colour as flushing of the study lake takes place by outflow from upstream lakes. Rasmussen *et al.* (1989) noted that downstream lakes had lower colour and separately analysed headwater lakes (i.e. lakes with < 25% of drainage area flowing through upstream lakes). The parameter [(drainage area / upstream lakes) / total drainage area] helped explain the lower colour of downstream lakes in a multiple regression.

5.1.6 Other sources of colour

Dissolved organic matter has also been attributed to autochthonous as well as allochthonous sources. Tipping *et al.* (1988) noted that DOC was higher during the summer in eight Cumbrian lakes. The lakes also showed a trend of increasing DOC with increasing productivity. This series of lakes was reported to have mean chlorophyll *a* concentrations ranging from 0.8 to 21.8 $\mu g\ l^{-1}$ but only one lake had a concentration above 10 $\mu g\ l^{-1}$ (Talling, 1999). It was noted that autochthonous DOC produced during the summer may not absorb at the wavelength (A_{340}) used for colour measurement. Evidence for this was a poor relationship between DOC and absorbance at 340 nm in summer but a good relationship in winter. Thus, estimating catchment derived humic substances by absorbance may be better than by DOC which will include a lot of carbon derived from algal exudates. Meili (1992) estimated that in unpolluted softwater lakes with a colour of 50 $mg\ l^{-1}$ Pt more than half of the organic carbon is allochthonous humic substances. Lakes with greater than 200 $mg\ l^{-1}$ Pt may have over 90% derived from allochthonous

sources. These estimates are likely to be very approximate as they are based on the relative proportions of nutrients in organic matter.

Colour can also be derived from the sediments. Tipping & Woof (1983) noted higher concentrations of humic substances and absorbance in the anoxic hypolimnion of Esthwaite Water in England. The increased concentrations were attributed to decomposition of organic matter in the sediments or increased solubility under anoxia. However, the volume of the hypolimnion and concentrations of humic substances therein were too small to account for the increase during autumn which they attributed to allochthonous sources. Townsend *et al.* (1996) also found that higher colour in the hypolimnion had a negligible contribution to lake colour. Aquatic macrophytes can increase the concentration of dissolved organic matter in lakes. Otsuki & Wetzel (1974) observed that 63 - 83% of total DOC input could be accounted for by autolysis of *Scirpus subterminalis*. Måns *et al.* (1998) found both absorbance (A_{250} and A_{365}) and DOC increased with time owing to the decay of *Phragmites australis*.

5.1.7 Specific aims

The specific aims of this chapter are:

- To use data from 189 lakes to indicate what proportion of Irish lakes are highly coloured.
- Examine the pattern and reasons for the seasonal variation in colour.
- To identify the main factors controlling the inter-annual variation in colour.
- To estimate the export of colour (following the estimation of the concentration of DOC from colour).
- Explain the variation in colour and export of DOC among lakes using catchment characteristics.
- To examine some of the effects of colour in Irish lakes, specifically its role in reducing transparency and dissolved oxygen concentrations.

5.2 Materials and Methods

The location of lakes and calculation of catchment characteristics were described in Chapter 2. Sampling frequency, methods of collection and storage of samples were described in Chapter 3. Additional catchment characteristics were determined solely for use in this chapter (Table 5.1). These were determined by a re-expression of data presented in Chapter 2 (soils data and CORINE land cover data) and Chapter 3 (lake volume, lake area).

Colour was measured by first filtering 100 ml of sample through a Whattman GF/C filter paper as a rinse. Following this, 25 ml of filtrate was placed into a sample cuvette and read at 455 nm using filtered (GF/C) de-ionised water as a blank. The concentration in mg l^{-1} PtCo was estimated directly by the HACH DR2000 spectrophotometer and adjusted for any difference between cuvettes, (HACH, 1991). Three replicate readings were taken. Two reference waters were purchased for quality assurance and measured values were within 95% confidence limits of the certified mean (Appendix 10).

Mean DOC was estimated from mean colour using the equation: 0.074 · colour (mg l^{-1} PtCo) + 2.265 (Rasmussen *et al.*, 1989). Approximate export of DOC was calculated by multiplying the average DOC for 1997 by the product of flushing and volume, which was then divided by catchment area.

Table 5.1 Additional catchment characteristics determined for prediction of colour. G.I.S. = Geographic Information System.

Catchment parameters	Calculation and Source
Peat soils (ha) / lake volume (m^3)	(General soils map & G.I.S.).
Peat soils (ha) / lake area (ha)	(General soils map & G.I.S.), (Kortelainen, 1993).
Peat soils (ha) / total lake area (ha)	(General soils map, 1:50,000 O.S. maps & G.I.S.).
Peat bogs unexploited (ha) / lake area (ha)	(CORINE & G.I.S.)
Total peatland area (ha) / lake area (ha)	(CORINE & G.I.S.)

The monthly flushing rate in Lough Ballyquirke was estimated:

Estimated flushing rate for month = [(Net rainfall for month (m) - Accumulated soil moisture deficit from previous months (m) (if any)) · Catchment area (m^2)] / Lake volume (m^3)

These estimates are likely to be only approximate as the actual runoff may be influenced by factors such the soil type and rainfall intensity. In addition examining monthly changes in lake chemistry with respect to monthly flushing may be too coarse a temporal scale to observe patterns. For example it is possible that a lake would be sampled early in a month but for most rainfall to occur later in the month and therefore any change in chemistry may only be observed in the following month. On an annual scale Gibson *et al.* (1995b) have estimated the error that may arise from estimating outflow using net precipitation rather than measured discharge as 3% in an upland catchment on basalt in Northern Ireland.

Statistical analysis was done using Excel® version 5.0 and Data Desk® version 6.1. Correlation between variables was determined using the non-parametric Spearman Rank correlation. The probability values of the Spearman rank correlation coefficients (r_S) were approximated according to Daly *et al.* (1995). Where necessary, transformations were applied to improve data distribution prior to incorporation into regression models. Many different transformations were calculated; mostly those recommended for lake chemistry, lake morphometry and catchment characteristics by Håkanson and Lindström (1997). The most suitable transformation was then selected with reference to the level of normality achieved by the transformation as judged by the closeness of the mean to median ratio to one and by histograms. Multiple regression models were constructed with regard to the procedures outlined by Velleman (1997).

5.3 Results

5.3.1 Range of colour found in Irish lakes

The survey of 187 lakes revealed that colour ranged from 4 - 258 mg l^{-1} PtCo. Median colour was 36 mg l^{-1} PtCo (Figure 5.1). These samples were collected during summer when colour concentrations were likely to be at a minimum. Figure 5.1 shows that a large proportion of the lakes sampled were highly coloured (50% ≥ 36, 25% ≥ 57, 10% ≥ 86 mg l^{-1} PtCo).

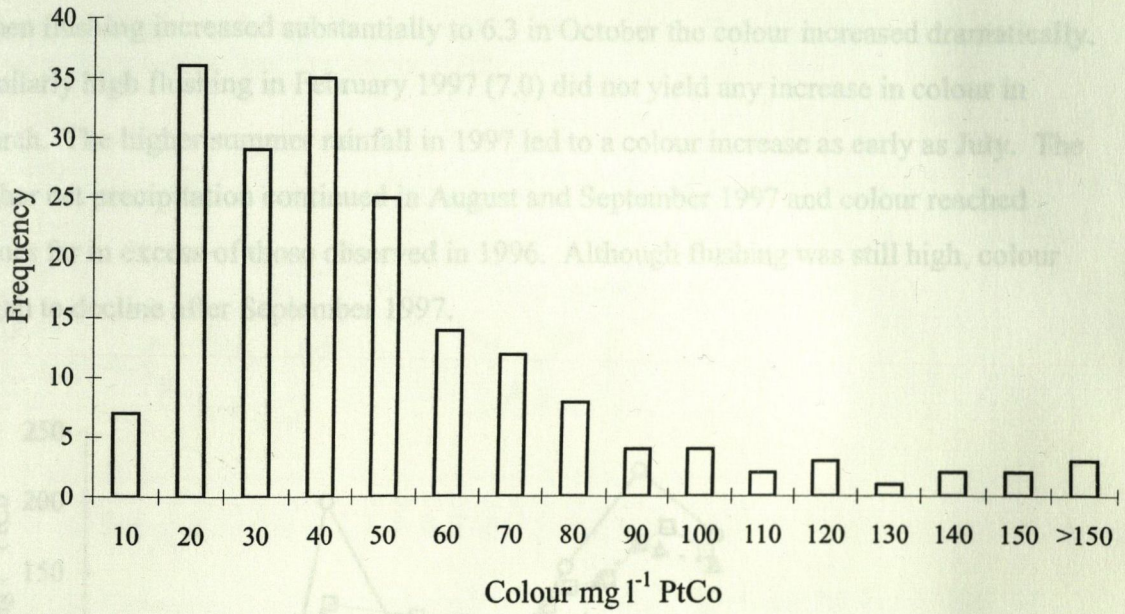


Figure 5.1. Histogram of colour (mg l^{-1} PtCo) from 187 lakes sampled from July to October 1996 and May to July 1997.

5.3.2 Seasonal variation in colour

A distinct seasonal variation in colour was evident in most of the core group of 31 lakes (Figure 5.2 to Figure 5.11). Colour was lowest in summer and highest in autumn and winter. The rate of decline in colour may be quantified in lakes that had negligible summer flushing. Lough Lickeen, Ballyquirke, Inchiquin and Gowna all had zero estimated flushing over a period of at least three months. Lough Inchiquin and Ballyquirke are likely to have significant groundwater input which may invalidate an estimate of the loss rate of colour (Chapter 2; Irvine *et al.*, 1998a). Lough Gowna showed an initial increase in colour and a regression of colour with time was not significant ($r^2 = 0.50$, p =

0.50, n = 3) (Figure 5.12). Lough Lickeen may therefore provide the most valid estimate of loss rate. The loss rate for Lough Lickeen was determined by linear regression (r^2 = 0.99, p = ≤ 0.0001, n = 6) and was estimated as -0.17 mg l^{-1} PtCo day^{-1} or 0.26% of initial colour per day. This equates to an annual loss rate of 95% of initial colour in Lough Lickeen.

After the summer decline in colour the occurrence and timing of the seasonal increase was controlled by net precipitation. Lough Ballyquirke is used to examine this. Figure 5.13 shows that as flushing decreased in the summer of 1996 there was a decline in colour. When flushing increased substantially to 6.3 in October the colour increased dramatically. Similarly high flushing in February 1997 (7.0) did not yield any increase in colour in March. The higher summer rainfall in 1997 led to a colour increase as early as July. The higher net precipitation continued in August and September 1997 and colour reached values far in excess of those observed in 1996. Although flushing was still high, colour began to decline after September 1997.

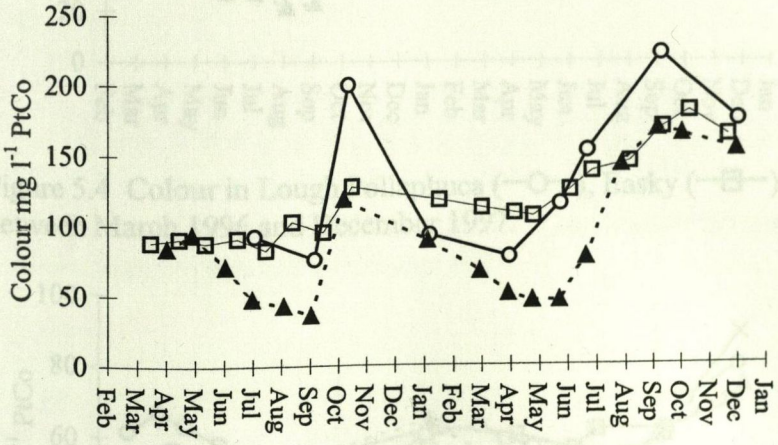


Figure 5.2 Colour in Lough Gara South (—O—), Dan (—⊟—) and Ballyquirke (- - -▲- - -) between March 1996 and December 1997.

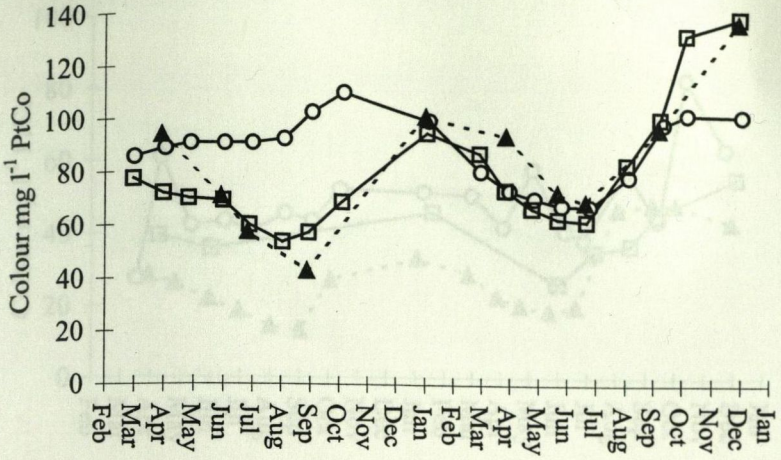


Figure 5.3 Colour in Lough Feeagh (—O—), Doolough (—□—) and Graney (- - -▲- - -) between March 1996 and December 1997.

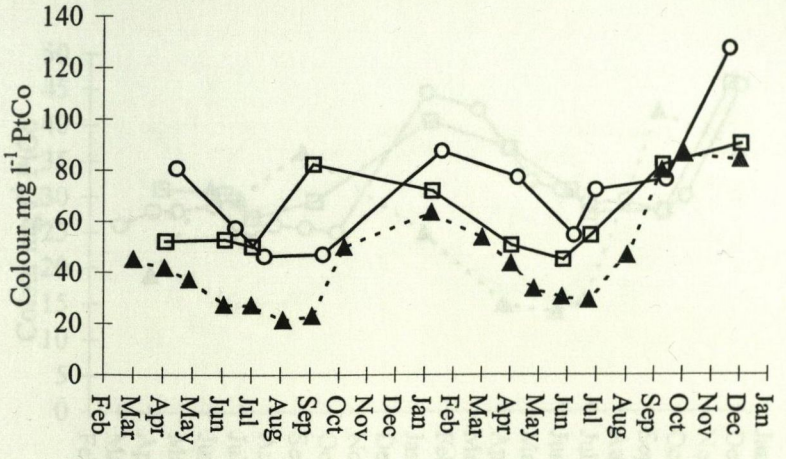


Figure 5.4 Colour in Lough Pollaphuca (—O—), Easky (—□—) and Moher (- - -▲- - -) between March 1996 and December 1997.

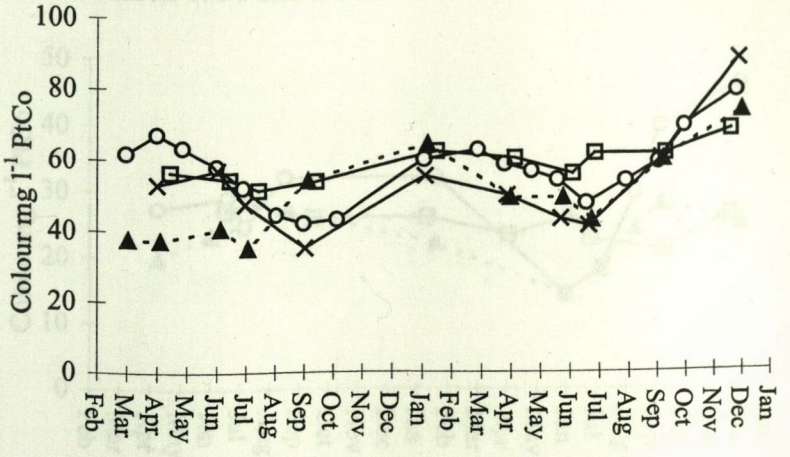


Figure 5.5 Colour in Lough Lickeen (—O—), Bray (—□—), Oughter (- - -▲- - -) and Lettercraffroe (—×—) between March 1996 and December 1997.

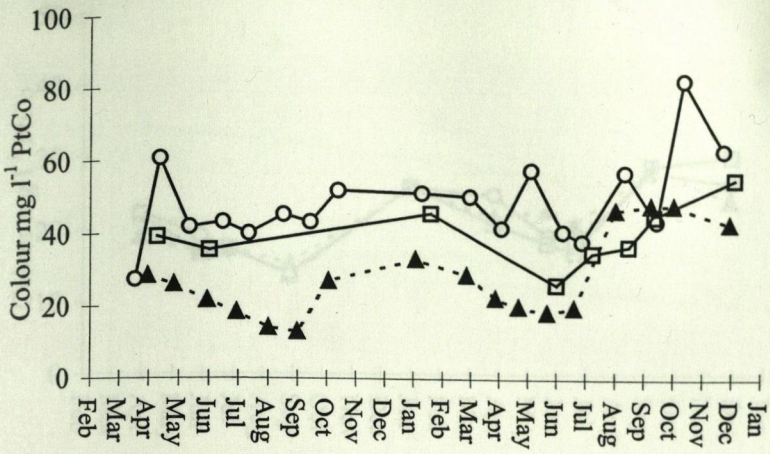


Figure 5.6 Colour in Lough Ramor (—O—), Leane (—⊟—) and Inchiquin (- - -▲- - -) between March 1996 and December 1997.

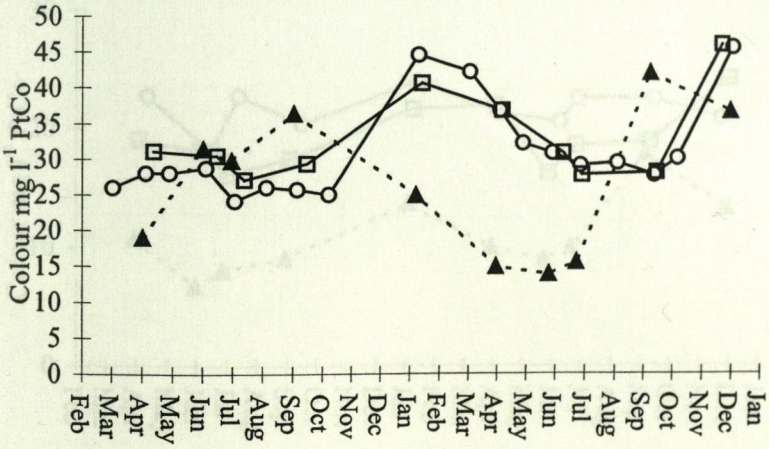


Figure 5.7 Colour in Lough Gowna (—O—), Muckno (—⊟—) and Maumwee (- - -▲- - -) between March 1996 and December 1997.

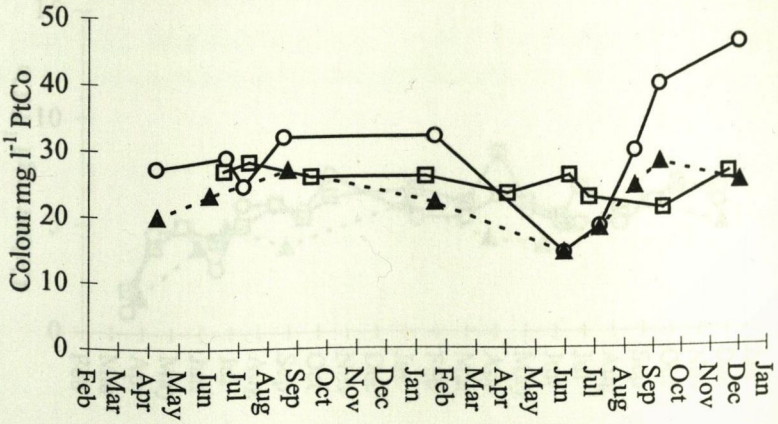


Figure 5.8 Colour in Lough Caragh (—O—), Egish (—⊟—) and Muckross (- - -▲- - -) between April 1996 and December 1997.

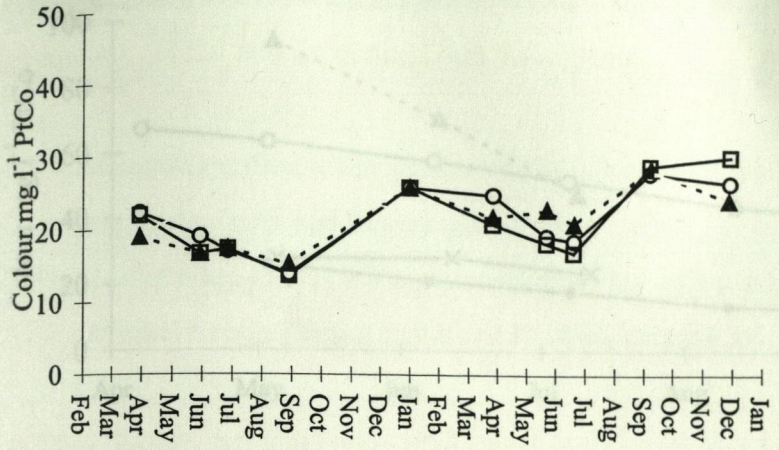


Figure 5.9 Colour in Lough Cullaun (—O—), Dromore (—⊟—) and Ballycullinan (· · ·▲· · ·) between April 1996 and December 1997.

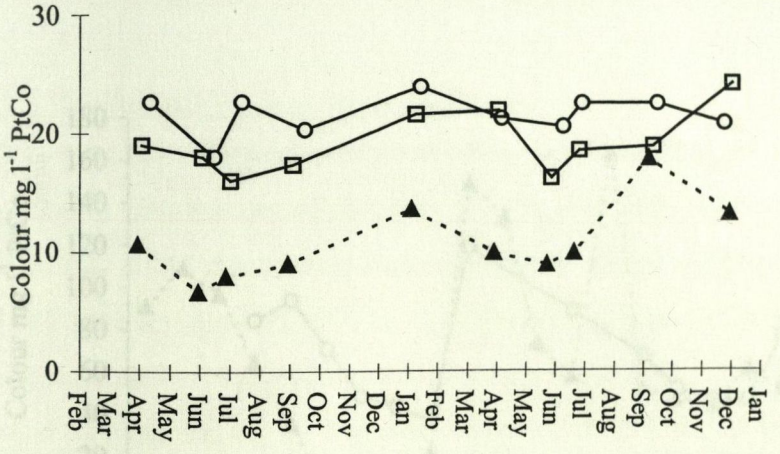


Figure 5.10 Colour in Lough Mullagh (—O—), Talt (—⊟—) and Bunny (· · ·▲· · ·) between April 1996 and December 1997.

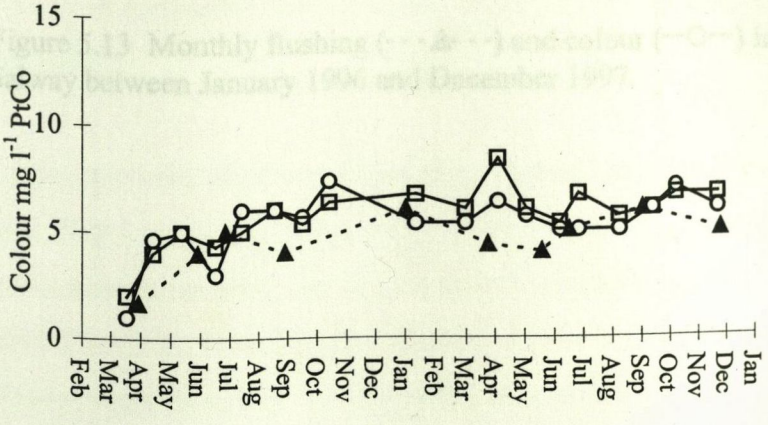


Figure 5.11 Colour in Lough Lene (—O—), Owel (—⊟—) and Rea (· · ·▲· · ·) between March 1996 and December 1997.

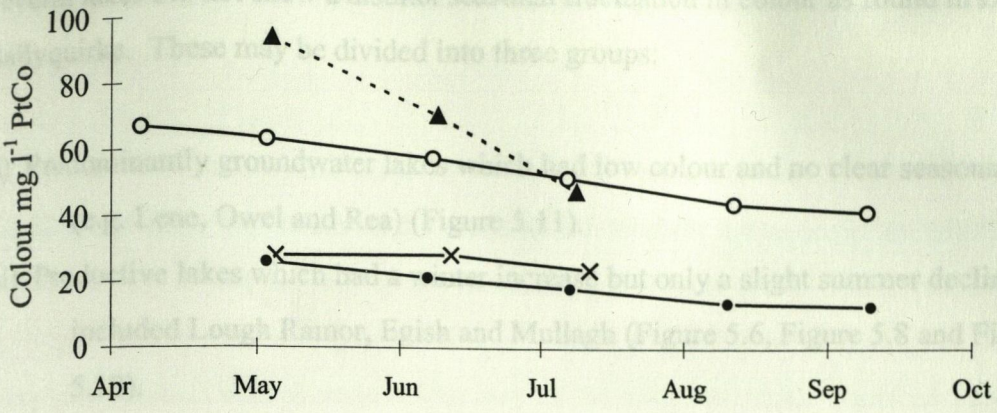


Figure 5.12 Loss of colour in lakes with low summer flushing. Lickeen = —O—, slope = -0.17, Ballyquirke = · · ·▲· · ·, slope = -0.72, Inchiquin = —●—, slope = -0.11 and Gowna = —×—, slope = -0.06.

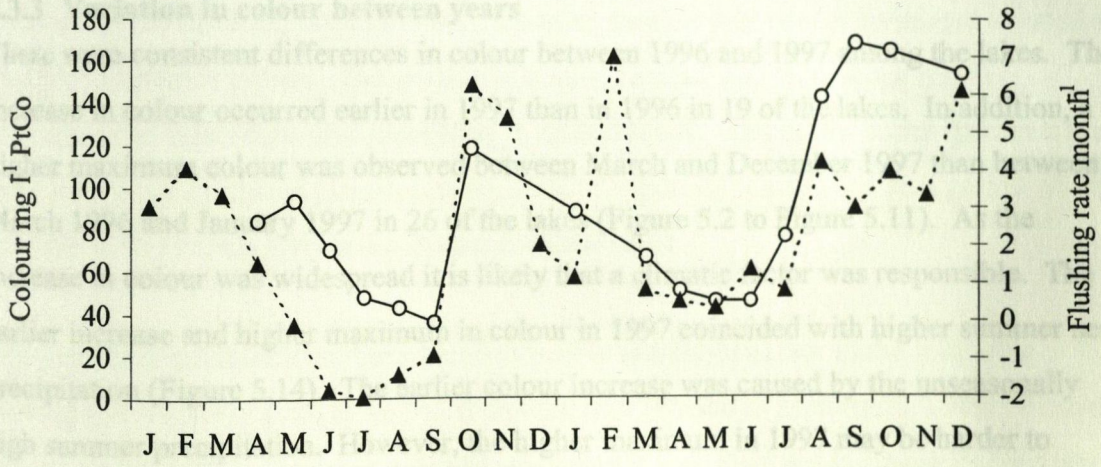


Figure 5.13 Monthly flushing (· · ·▲· · ·) and colour (—O—) in Lough Ballyquirke Co. Galway between January 1996 and December 1997.

Several lakes did not show a distinct seasonal fluctuation in colour as found in Lough Ballyquirke. These may be divided into three groups:

(i) Predominantly groundwater lakes which had low colour and no clear seasonal trend (e.g. Lene, Owel and Rea) (Figure 5.11).

(ii) Productive lakes which had a winter increase but only a slight summer decline. These included Lough Ramor, Egish and Mullagh (Figure 5.6, Figure 5.8 and Figure 5.10).

(iii) Deep, highly coloured lakes which had a winter increase but only a slight summer decline such as Lough Dan, Feeagh and Bray (Figure 5.2, Figure 5.3 and Figure 5.5).

5.3.3 Variation in colour between years

There were consistent differences in colour between 1996 and 1997 among the lakes. The increase in colour occurred earlier in 1997 than in 1996 in 19 of the lakes. In addition, a higher maximum colour was observed between March and December 1997 than between March 1996 and January 1997 in 26 of the lakes (Figure 5.2 to Figure 5.11). As the increase in colour was widespread it is likely that a climatic factor was responsible. The earlier increase and higher maximum in colour in 1997 coincided with higher summer net precipitation (Figure 5.14). The earlier colour increase was caused by the unseasonally high summer precipitation. However, the higher maximum in 1997 may be harder to explain. It is possible that the timing of the rainfall - in early summer - may be responsible.

To examine inter-annual variation in more detail, data from the period January 1988 to June 1999 from Lough Pollaphuca was examined. The data-set was collected at the Liffey works water treatment plant in County Kildare (National Grid Reference N 935 094), (Pers. Comm. C. McGahey & J. Earlie). Figure 5.15 and Figure 5.16 show that the timing of the increase in colour was dependent on increased precipitation, which generally occurred during autumn and winter. However, high precipitation (119 and 170 mm) during May and June 1993 led to interruption of the normal summer decline and colour

increased markedly. This may be similar to 1997 when summer rainfall increased colour earlier than usual.

The export of DOC was calculated for a 12-month period between June and May and was found to be highly dependent on the precipitation total for the same period which explained 94% of the variation ($p \leq 0.0001$, $n = 11$) (Figure 5.17). The average colour was also significantly related to precipitation ($r^2 = 0.61$, $p = 0.004$, $n = 11$), (Figure 5.17). The relationship found with average colour may be the most statistically valid because DOC load and annual precipitation are not strictly independent variables because rainfall was used to estimate lake flushing (Stronge *et al.*, 1997).

The high percentage of variation explained in the precipitation - export relationship (94%, Figure 5.17) may at first indicate that the total annual rainfall as a physical means of colour transport is the most important factor. However, another mechanism correlated to rainfall may also influence colour. The amount of annual rainfall also reflects the relative importance of infiltration and adsorption to mineral soils. Thus a low annual precipitation represents both a reduced physical mechanism of export of colour but also a period where infiltration to mineral soils and adsorption would occur.

Dry periods in summer have been found to lead to increased colour in the following autumn and winter or even up to 15-16 months later (Naden & McDonald, 1989; Mitchell & McDonald, 1992). However, no such relationship was observed in Lough Pollaphuca. The lowest summer precipitation was recorded in 1995 and was not followed by any marked increase in colour (Figure 5.15, Figure 5.16).

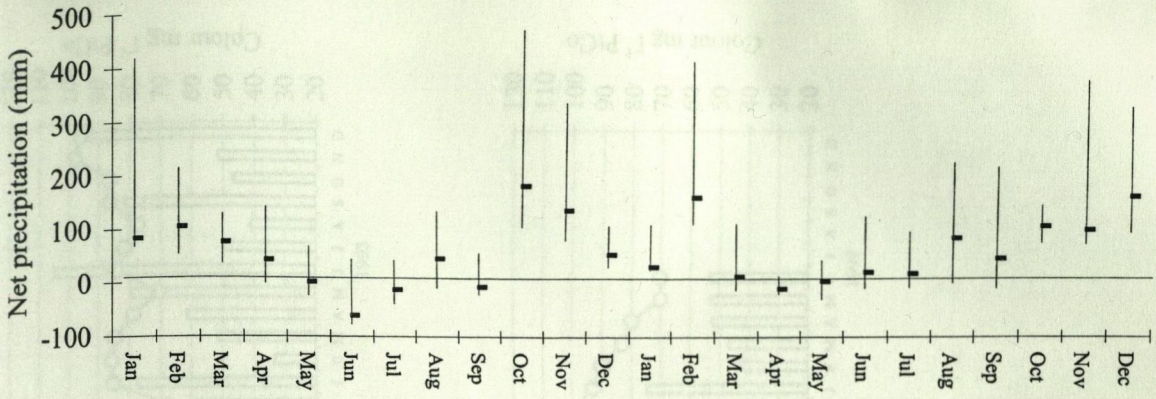


Figure 5.14 Monthly net precipitation or soil moisture deficit in 31 catchments. Vertical bars mark the maximum and minimum, horizontal bar indicates median.

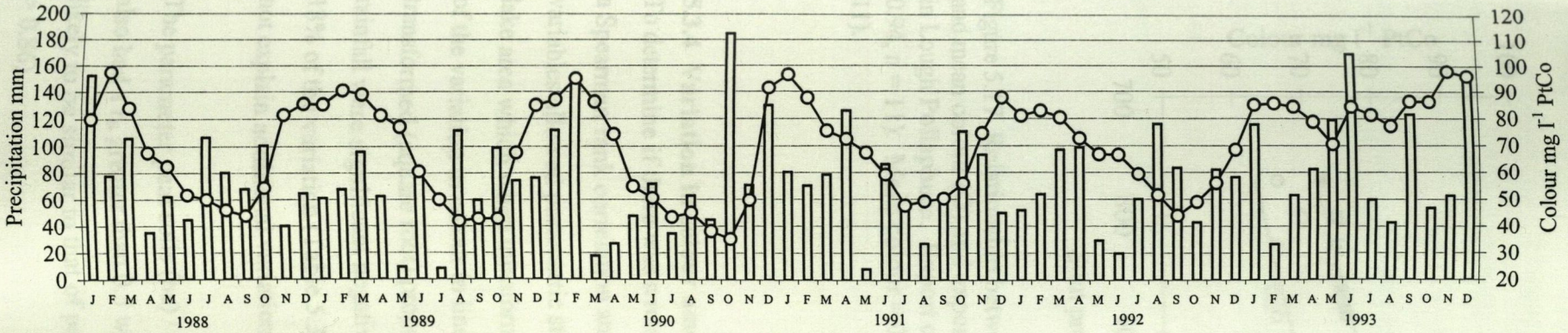


Figure 5.15 Colour (—O—) and precipitation (□) in Lough Pollaphuca between 1988 and 1993.

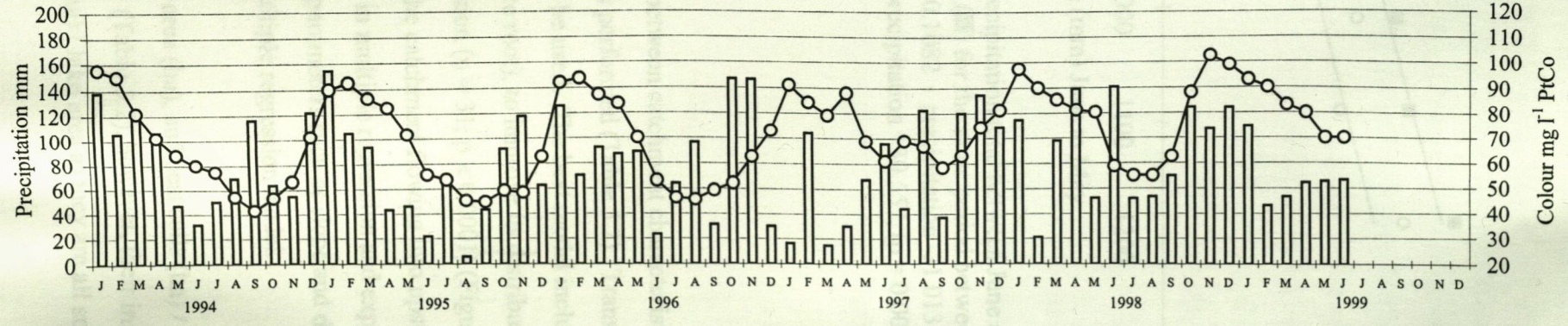


Figure 5.16 Colour (—O—) and precipitation (□) in Lough Pollaphuca between 1994 and 1999.

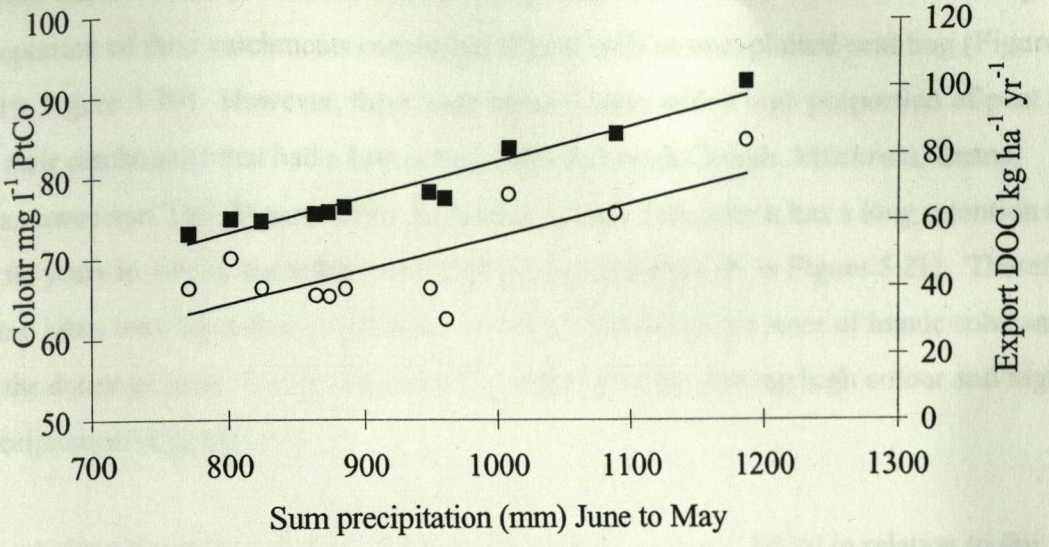


Figure 5.17 Relationship between the precipitation total between June and May (inclusive) and mean colour (O) and export of DOC (■) for the same period between 1988 and 1999 in Lough Pollaphuca. Export of DOC = 0.1082 · precipitation -31.013, ($p \leq 0.0001$, $r^2 = 0.94$, n = 11). Mean colour = 0.0422 · precipitation +30.557, ($p = 0.004$, $r^2 = 0.61$, n = 11).

5.3.4 Variation in colour among lakes

To determine if there was a relationship between catchment characteristics and lake colour a Spearman rank correlation analysis was performed (Table 5.2). Transformation of variables allowed parametric statistics to be used. The best model included peat soils (ha) / lake area which when transformed (square root), to improve its distribution, explained 54% of the variation in colour in linear regression ($n = 31$, $p \leq 0.0001$) (Figure 5.18). The transformed (square root) proportion of the catchment flowing into upstream lakes and net rainfall were significant negative factors in multiple regression and explained a further 18% of the variation (Table 5.3). Other parameters such as slope and drainage density did not explain additional variation in the multiple regression model.

The parameter peat soils (ha) / total lake area (ha), and peat soils (ha) / lake volume (m^3) also had a r_S greater than 0.5 with colour (Table 5.2), however, their influence on colour is likely to be similar to that of peat soils (ha) / lake area as they are all strongly co-linear ($r_S > 0.86$).

There was a tendency for lakes with colour greater than 60 mg l^{-1} PtCo to have a higher proportion of their catchments consisting of peat soils or unexploited peat bog (Figure 5.19, Figure 5.20). However, there were several lakes with a high proportion of peat soils in their catchments that had a low colour, namely Lough Caragh, Muckross, Leane, Maumwee and Talt (Figure 5.19). Excluding Lough Talt, which has a long retention time (2.04 years in 1997), these lakes had high net precipitation (✕ in Figure 5.21). Therefore, these lakes may have lower colour as a result of dilution of the store of humic substances in the drainage area. Lough Dan was an exception to this, having high colour and high net precipitation (Figure 5.21).

Lough Gara (south basin) had a high colour (mean 134 mg l^{-1} PtCo) in relation to the proportion of peat soils in the catchment (0.35) (Figure 5.19). Initially, the extensive beds of macrophytes dominated by *Scirpus lacustris* were believed to be responsible for the high colour (Irvine *et al.*, 1998b). However, this is unlikely as a high colour (201 mg l^{-1} PtCo) was observed during October 1996 when the lake was being flushed once every two days.

Table 5.2 Spearman rank correlation coefficients (r_S) between colour and catchment variables for 31 lakes. Only $r_S \geq \pm 0.355$, $p \leq 0.05$ are shown.

Catchment variables	r_S
Peat soils (ha) / total lake area (ha)	0.763
Peat soils (ha) / lake volume	0.718
Peat soils (ha) / lake area (ha)	0.704
Peat soils (ha) / retention time (yrs)	0.689
Peat bogs unexploited	0.570
Drainage density	0.553
Coniferous forest (pr.)	0.548
Peat soils (pr.)	0.508
Ruggedness number	0.479
Natural grasslands (pr.)	0.444
Lake altitude - mean catchment perimeter altitude (m)	0.414
Fresh water (pr.)	-0.406
1960-1990 retention time	-0.379
Catchment area / lake area	0.371
Lake altitude - max. catchment perimeter altitude (m)	0.371
Mean distance to catchment boundary (km)	0.367

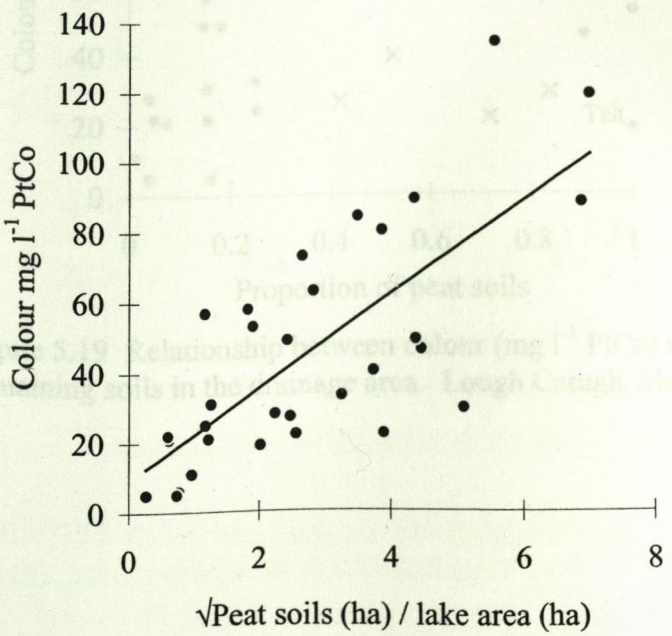


Figure 5.18 Relationship between colour and transformed (√) peat soils (ha) / lake area (ha). Equation: $y = 13.157x + 9.0752$, $r^2 = 0.54$, $p \leq 0.0001$, $n = 31$.

Table 5.3 Multiple regression for mean lake colour. Proportion is denoted by pr. Variables are significant ($p \leq 0.014$), $n = 31$.

Step	Variable	r^2	Model
1	√ (peat soils (ha) / lake area (ha)	0.54	colour = 9.075 + 13.157 · √ (peat soils (ha) / lake area (ha)
2	√ pr catchment flowing into upstream lakes	0.65	colour = 14.151 + 16.515 · √ (peat soils (ha) / lake area (ha) - 45.417 · √ pr catchment flowing into upstream lakes
3	Mean net rain (96-97)	0.72	colour = 28.745 + 19.459 · √ (peat soils (ha) / lake area (ha) - 48.730 · √ pr catchment flowing into upstream lakes - 0.026 · mean net rain (mm)

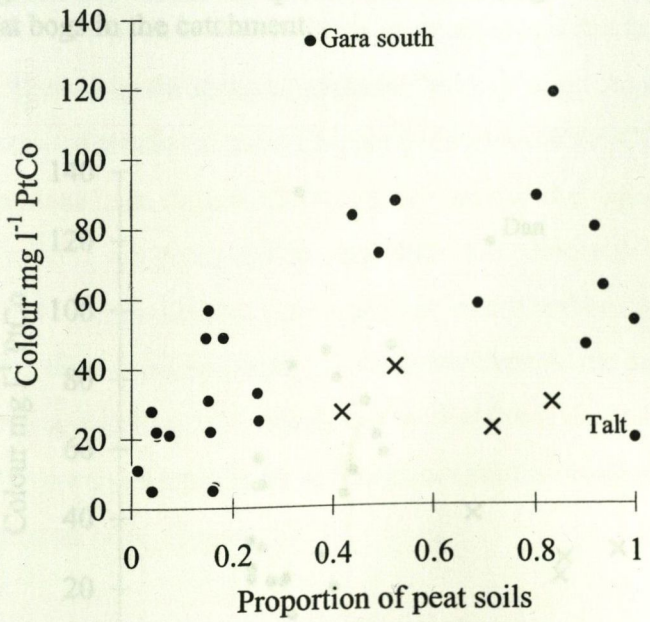


Figure 5.19 Relationship between colour (mg l^{-1} PtCo) and the proportion of peat containing soils in the drainage area. Lough Caragh, Maumwee, Leane and Muckross (×).

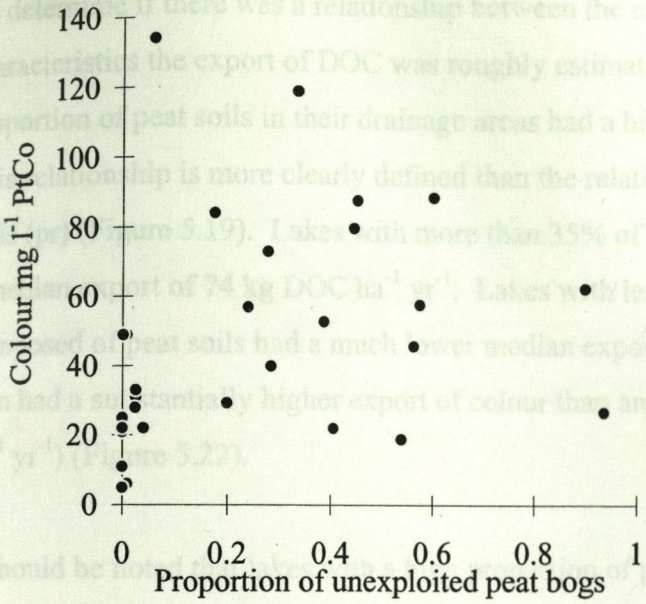


Figure 5.20 Relationship between colour (mg l^{-1} PtCo) and the proportion of unexploited peat bogs in the catchment.

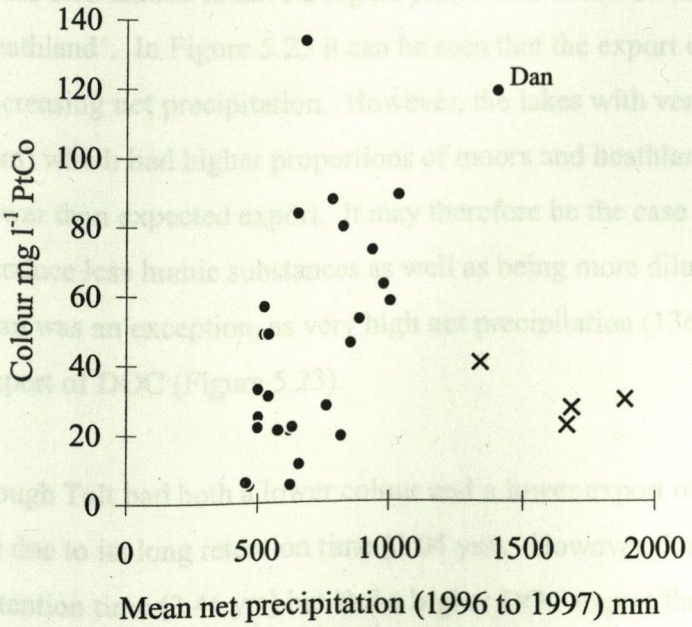


Figure 5.21 Colour and mean net precipitation (1996 and 1997) in the study lakes. Lough Caragh, Maumwee, Leane and Muckross (×).

To determine if there was a relationship between the export of colour and catchment characteristics the export of DOC was roughly estimated for 1997. Lakes with a large proportion of peat soils in their drainage areas had a higher export of DOC (Figure 5.22). This relationship is more clearly defined than the relationship between colour and peat soils (pr) (Figure 5.19). Lakes with more than 35% of peat soils in their drainage area had a median export of 74 kg DOC ha^{-1} yr^{-1}. Lakes with less than 25% of the catchment composed of peat soils had a much lower median export of 28 kg DOC ha^{-1} yr^{-1}. Lough Dan had a substantially higher export of colour than any of the other lakes (169 kg DOC ha^{-1} yr^{-1}) (Figure 5.22).

It should be noted that lakes with a high proportion of peat soils in their catchments but which had a low colour appeared to have similar export as other lakes, namely Lough Caragh, Muckross, Leane and Maumwee (✕ in Figure 5.19 and Figure 5.22). This indicates that their lower colour may have been due to dilution of the 'store' of humic substances as the amounts exported were similar. As well as having high rainfall these lakes also tended to have a higher proportion of the CORINE category 'moors and heathland'. In Figure 5.23 it can be seen that the export of DOC generally increased with increasing net precipitation. However, the lakes with very high net precipitation (>1340 mm) which had higher proportions of moors and heathlands or bare rocks (Table 5.4) had lower than expected export. It may therefore be the case that 'moors and heathlands' produce less humic substances as well as being more diluted by the higher rainfall. Lough Dan was an exception, as very high net precipitation (1361 mm) did result in very high export of DOC (Figure 5.23).

Lough Talt had both a lower colour and a lower export of DOC than expected and this may be due to its long retention time (2.04 yrs). However, Lough Bray also had a long retention time (3.46 yrs) but had a higher DOC export than Lough Talt (Figure 5.19, Figure 5.22).

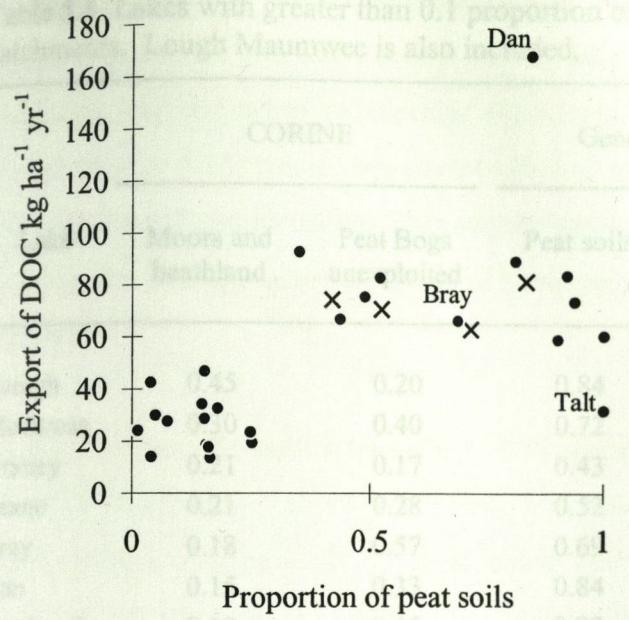


Figure 5.22 Export of DOC (kg DOC ha^{-1} yr^{-1}) in 1997 and the proportion of peat soils in the catchment. Lough Caragh, Maumwee, Leane and Muckross (X).

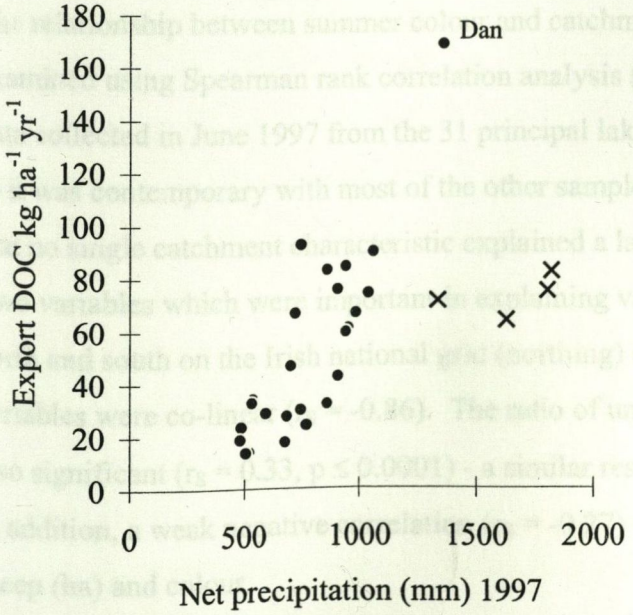


Figure 5.23 Relationship between export of DOC (kg DOC ha^{-1} yr^{-1}) in 1997 and net precipitation (1997). Lough Muckross, Maumwee, Leane and Caragh (X).

Table 5.4 Lakes with greater than 0.1 proportion of moors and heathland in their catchments. Lough Maumwee is also included.

	CORINE		General soil map		
Lake	Moors and heathland	Peat Bogs unexploited	Peat soils	Lithosols	Net rain 1997 (mm)
Caragh	0.45	0.20	0.84	0.16	1831
Muckross	0.30	0.40	0.72	0.26	1634
Graney	0.21	0.17	0.43	0.00	716
Leane	0.21	0.28	0.52	0.09	1340
Bray	0.18	0.57	0.69	0.31	986
Dan	0.15	0.33	0.84	0.16	1361
Doolough	0.13	0.45	0.92	0.00	938
Pollaphuca	0.12	0.28	0.49	0.17	901
Maumwee	0.00	0.93	0.42	0.58	1813

The relationship between summer colour and catchment characteristics for 187 lakes was examined using Spearman rank correlation analysis (Table 5.5). The 187 lakes included data collected in June 1997 from the 31 principal lakes in the study. June 1997 was used as it was contemporary with most of the other samples. All r_S were below 0.5 indicating that no single catchment characteristic explained a large amount of variation in colour. Two variables which were important in explaining variation in colour included the location north and south on the Irish national grid (northing) and annual mean sunshine hours, these variables were co-linear ($r_S = -0.86$). The ratio of unexploited peat bogs to lake area was also significant ($r_S = 0.33$, $p \leq 0.0001$) - a similar result to that observed for the 31 lakes. In addition, a weak negative correlation ($r_S = -0.27$) was observed between the density of sheep (ha) and colour.

The relationship between the log (x + 1) transformed ratio of total peatland area to lake area and colour was weak (Figure 5.24). One of the reasons why there was not a clearer relationship in the 187 lakes may be owing to the confounding influence of variable rainfall across catchments and the uncertain contribution to colour from the 'moors and heathlands' category discussed for the 31 lakes (Figure 5.21). A curvilinear relationship

found between colour and precipitation may be evidence of this (Figure 5.25). This relationship may be one where colour initially increases with rainfall, both because of increasing peatland extent and elevated export with high rainfall. At around 1600 mm rainfall (Figure 5.25) colour then starts to decline as both rainfall and the presence of moors and heathland increases. This may be because of dilution of the store of colour and possibly also because of lower release of humic substances from the moors and heathland category.

The significance of sunshine hours ($r_S = -0.29$, $p \leq 0.0001$) and northing ($r_S = 0.39$, $p \leq 0.0001$) is interesting (Table 5.5). The negative relationship may suggest that as irradiation increases from north to south in Ireland, colour decreases as a result of photolysis. However, not all of the 187 lakes were sampled at the same time, and therefore lakes that were sampled late in the summer could have had lower colour owing to a longer period for photolysis to take place. To reduce the effect of this, the relationship between colour and sunshine hours is examined for a 47 day period when 132 lakes were sampled (Figure 5.26). During this period a significant negative relationship was found ($r^2 = 0.08$, $p \leq 0.0001$).

Table 5.5 Spearman rank correlation coefficients (r_S) between colour and catchment variables for 187 lakes. Only $r_S \geq \pm 0.144$, $p \leq 0.05$ are shown. Total peatland area refers to the sum of the CORINE groups peat bogs, peat bogs exploited, peat bogs unexploited and moors and heathland.

Catchment variables	r_S
Northing	0.39
Peat bogs unexploited (ha) / lake area (ha)	0.33
Peat bogs unexploited (pr.)	0.29
Annual mean sunshine hours	-0.29
Sheep (ha^{-1})	-0.27
Total peatland area / lake area	0.24
Catchment area / lake area	0.20
Moors and heath (pr.)	-0.18
Total peatland area (pr.)	0.17

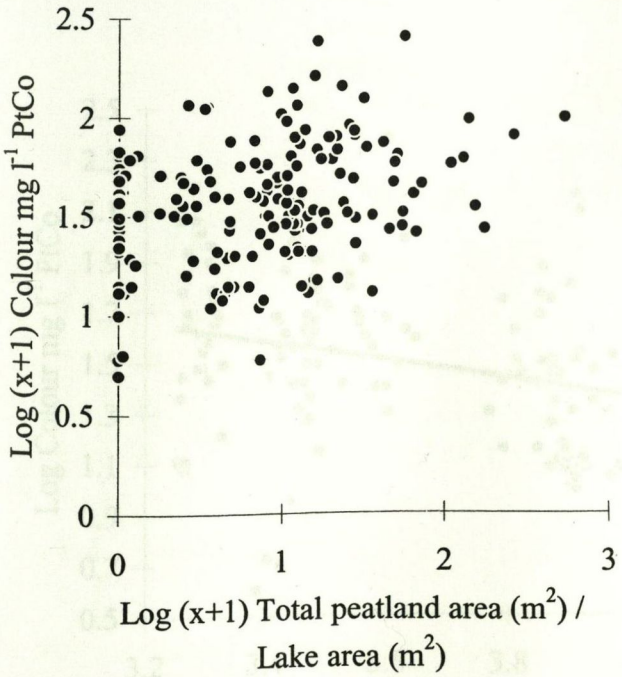


Figure 5.24 Relationship between transformed (log x + 1) colour and transformed (log x + 1) ratio of total peatland area (m^2) to lake area (m^2), (n = 187).

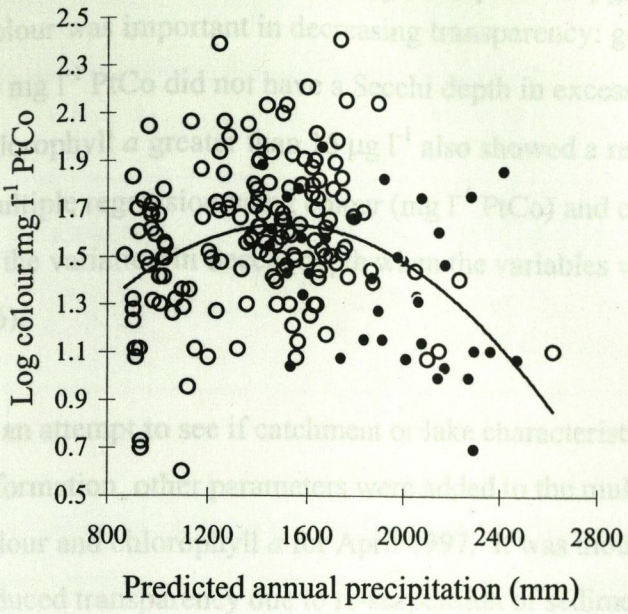


Figure 5.25 Relationship between transformed (log) colour and predicted annual precipitation (mm) in 187 lakes. ● = catchments with greater than 25% moors and heathland. A polynomial trendline is fitted to the data, equation $y = -6E\text{-}07x^2 + 0.0019x + 0.182$, $r^2 = 0.14$. Precipitation was predicted using the model of Goodale *et al.* (1998).

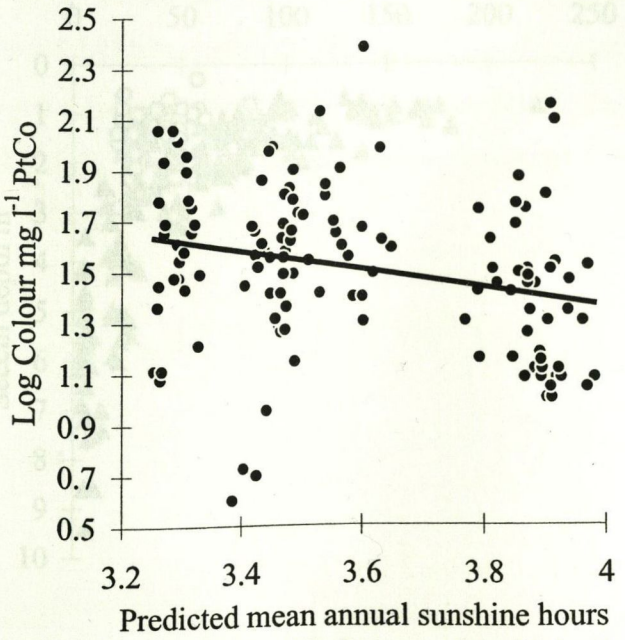


Figure 5.26 Relationship between colour and predicted mean annual sunshine hours in 132 lakes sampled between 31/5/97 and 13/7/97. Equation $y = -0.3658x + 2.8245$, $r^2 = 0.08$, $p \leq 0.0001$.

5.3.5 Effect of colour on transparency and oxygen

Colour was important in decreasing transparency: generally lakes with colour greater than 50 mg l^{-1} PtCo did not have a Secchi depth in excess of 3 m (Figure 5.27). Lakes with chlorophyll *a* greater than 15 µg l^{-1} also showed a reduced Secchi depth (O in Figure 5.27). Multiple regression using colour (mg l^{-1} PtCo) and chlorophyll *a* (µg l^{-1}) explained 82.1% of the variation in Secchi depth when the variables were transformed (Log x + 1), (Table 5.6).

In an attempt to see if catchment or lake characteristics could add additional explanatory information, other parameters were added to the multiple regression of Secchi depth, colour and chlorophyll *a* for April 1997. It was thought that shallow lakes may have had a reduced transparency due to re-suspension of sediments, however, a potential indicator of this - transformed (log x+1) mean depth divided by the square root of area (Nürnberg, 1995) did not explain any additional variation in multiple regression ($p = 0.204$).

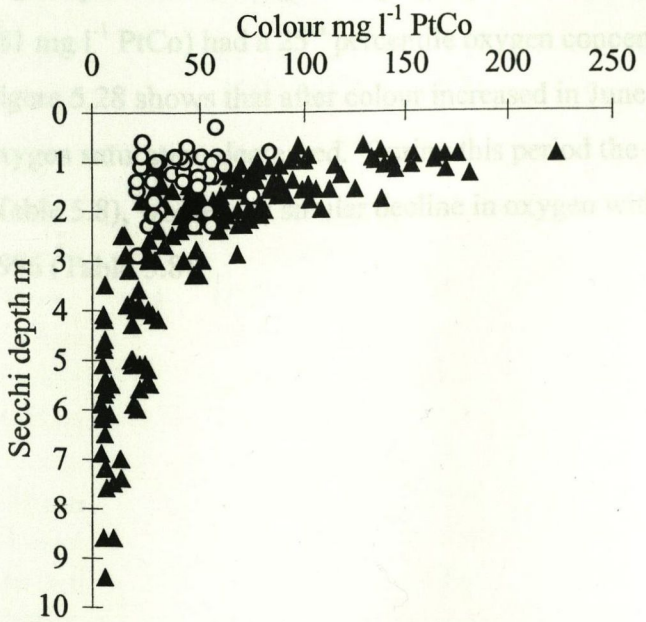


Figure 5.27 The relationship between Secchi depth (m) and colour (mg l^{-1} PtCo) when chlorophyll *a* was greater than 15 µg l^{-1} (O) (n = 38) or less than 15 µg l^{-1} (▲) (n = 175). Data are for the period January 1997 to December 1997.

Table 5.6 Multiple regression model for log (x + 1) Secchi depth (m), (January to December 1997), (n = 213), $p \leq 0.0001$.

Step	Variable	r^2	Model
1	Colour	0.63	1.1576 -0.403267 · log (x + 1) colour
2	Chlorophyll *a* μg l^{-1}	0.82	1.34495 -0.414109 · log (x + 1) colour -0.205299 · log (x + 1) chlorophyll *a* μg l^{-1}

To identify lakes that had significant deoxygenation the lower 25th percentile of each oxygen profile was determined. This should correspond to the oxygen concentration at the lower quarter of the depth at the sampling station. Lakes where the 25th percentile of dissolved oxygen was less than 5 mg l^{-1} are presented in Table 5.7. This concentration was chosen because the EC freshwater fish directive (78/659/EEC) states lower limits of 6 and 4 mg l^{-1} oxygen for salmonid and cyprinid waters (N.R.A, 1994). Two highly coloured oligotrophic lakes, Lough Feeagh (range 68 - 111 mg l^{-1} PtCo) and Lough Dan (range 83 - 181 mg l^{-1} PtCo) had a 25th percentile oxygen concentration below 5 mg l^{-1} (Table 5.7). Figure 5.28 shows that after colour increased in June 1997 in Lough Dan the percentage oxygen saturation decreased. During this period the decline in oxygen was greater at depth (Table 5.8), whereas, a similar decline in oxygen with depth was not noted previously in 1996 (Table 5.8).

Table 5.7 Occasions when the lower 25th percentile of the oxygen profile was less than 5 mg l^{-1}. Median and 75th percentile oxygen concentrations are also presented.

Lake	Date	75%	50%	25%
Ballycullinan	10/06/96	10.5	6.3	0.1
Ballycullinan	08/07/96	13.7	6.9	0.2
Ballycullinan	09/09/96	6.7	0.0	0.0
Ballyquirke	04/06/97	8.4	6.9	4.3
Cullaun	09/09/96	9.2	5.6	0.0
Dan	22/10/97	9.1	9.1	5.0
Dromore	08/07/96	10.1	4.0	0.6
Dromore	09/09/96	7.0	3.3	0.1
Dromore	30/06/97	9.2	8.4	0.5
Dromore	16/09/97	8.2	8.0	4.8
Feeagh	13/09/96	8.7	8.4	4.5
Gowna	13/08/97	9.5	7.1	2.0
Inchiquin	10/07/96	10.4	7.0	5.0
Inchiquin	12/08/96	8.0	4.3	1.9
Inchiquin	11/09/96	7.1	0.9	0.1
Inchiquin	01/07/97	10.3	8.8	3.3
Inchiquin	11/08/97	7.8	6.7	0.1
Inchiquin	17/09/97	8.5	6.6	0.2
Lene	24/07/96	9.9	7.2	4.2
Lene	19/06/97	10.6	9.7	4.2
Lene	20/08/97	9.1	6.7	0.1
Lickeen	13/08/96	8.6	7.9	3.0
Moher	12/08/97	8.7	7.6	4.1
Muckno	26/06/96	8.5	6.1	1.1
Muckno	23/07/96	9.3	2.1	0.1
Muckno	25/09/96	8.5	7.4	0.1
Muckno	18/06/97	8.5	6.1	3.1
Muckno	08/07/97	9.3	8.1	2.0
Muckno	24/09/97	8.6	6.8	0.1
Mullagh	26/06/96	8.4	7.4	5.0
Mullagh	24/07/96	7.5	7.5	0.5
Oughter	15/09/96	6.6	3.7	2.6
Oughter	07/06/97	8.9	5.2	3.4

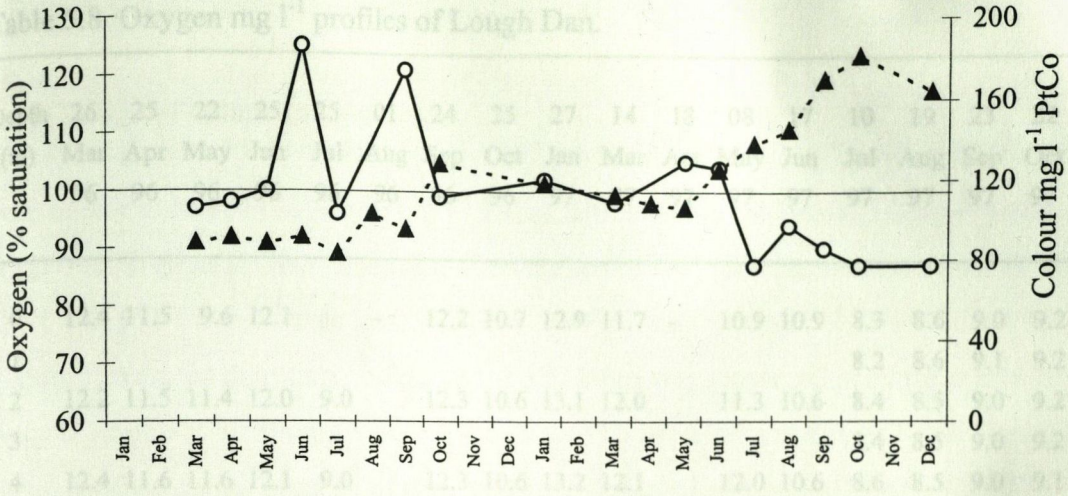


Figure 5.28 Colour (· · ·▲· · ·) and oxygen (—O—) in Lough Dan between March 1996 and December 1997. Colour was determined on 6 m integrated profiles, oxygen concentrations were averaged over 6 m.

Table 5.8 Oxygen mg l^{-1} profiles of Lough Dan.

Depth (m)	26 Mar 96	25 Apr 96	22 May 96	25 Jun 96	25 Jul 96	01 Aug 96	24 Sep 96	25 Oct 96	27 Jan 97	14 Mar 97	18 Apr 97	08 May 97	17 Jun 97	10 Jul 97	19 Aug 97	23 Sep 97	22 Oct 97	02 Dec 97
0	12.4	11.5	9.6	12.1		-	12.2	10.7	12.9	11.7	-	10.9	10.9	8.3	8.6	9.0	9.2	9.9
1														8.2	8.6	9.1	9.2	9.9
2	12.2	11.5	11.4	12.0	9.0		12.3	10.6	13.1	12.0		11.3	10.6	8.4	8.5	9.0	9.2	9.9
3														8.4	8.5	9.0	9.2	9.9
4	12.4	11.6	11.6	12.1	9.0		12.3	10.6	13.2	12.1		12.0	10.6	8.6	8.5	9.0	9.1	9.9
5														8.8	8.4	9.0	9.1	9.9
6	12.5	11.6	11.6	12.2	8.9		12.2	10.4	13.3	12.3		12.4	10.6	8.9	8.4	9.0	9.1	9.9
7														8.9	8.5	8.9	9.1	9.9
8	12.4	11.6	11.6	12.2	8.9		12.2	10.4	13.3	12.2		12.8	10.6	8.9	8.5	8.9	9.1	9.8
9				12.5										8.9	8.5	8.9	9.1	9.8
10	12.4	11.6	11.5	12.4	8.9		12.2	10.4	13.3	12.2		13.1	10.6	8.7	8.5	8.9	9.1	9.8
11													10.5	8.8	8.5	8.9	9.1	9.8
12	12.4	11.6	11.5	12.7	8.8		12.2	10.4	13.3	12.1		13.2	10.7	8.9	8.6	8.8	9.1	9.8
13													10.9		8.8	8.8	9.1	9.8
14	12.4	11.6	11.4	12.8	8.7		12.0	10.5	13.4	12.2		13.4	10.9	9.0	8.8	8.8	9.1	9.7
15															8.7	8.7		9.7
16	12.4	11.6	11.4	12.8	8.9		11.6	10.5	13.4	12.2		13.8	10.8	8.9	8.4	8.4	9.1	9.7
17							10.1								8.3	8.1	9.0	9.7
18	12.4	11.6	11.5	12.9	8.8		9.8	10.3	13.4	12.3		13.8	10.9	8.7	8.1	6.9	8.7	
19							9.6								7.9	6.7	8.4	
20	12.4	11.5	11.4	12.5	8.7		9.4	10.3	13.3	12.3		13.8	10.8	8.7	7.7	6.5	8.8	
21							9.3								7.4	6.4	8.4	
22	12.2	11.5	11.4	12.5	8.6		9.1	10.3	13.3	12.1		13.5	10.8	8.2	7.4		7.5	
23							8.8								7.1	5.9	6.8	
24	12.2	11.6	11.4	12.3	8.4		8.5	10.2	13.3	12.2		13.6	10.8	7.5	6.9	5.5	5.1	
25							8.2								6.6	5.5	4.5	
26	12.3	11.6	11.3	12.4	8.2		7.9	9.2	13.3	12.3		13.1	10.5	7.6	6.5	5.4	3.8	
27															6.3	4.9	3.7	
28	12.2	11.5	11.2	12.2	8.0				13.4	12.1		13.0	9.8	7.4	6.3	4.7	3.5	
29																4.5	3.2	
30	12.1	11.5	11.2	11.8	7.8				13.4	12.1		13.2	10.3	7.4		4.4	3.1	
31				12.0					13.3					7.3		4.4	3.1	
32	12.2		11.1		7.6											4.4	3.0	
33																4.4		

5.4 Discussion

5.4.1 Range of colour in Irish lakes

A wide range in colour was found in the 187 lakes. A significant proportion of the lakes were highly coloured (32% ≥ 50 mg l^{-1} PtCo), although the median of 36 mg l^{-1} PtCo was lower than in several other countries. Kortelainen (1993) found a median colour of 100 mg l^{-1} PtCo in 978 Finnish lakes and Håkanson (1993) found a mean colour of 72 in 556 Swedish lakes. In this study, colour of the 187 lakes was measured in summer and was likely to represent minimum values. It is likely that synoptic surveys of Nordic lakes had higher median colour because of their higher coverage of peatlands (Mitchell, 1990).

5.4.2 Seasonal variation in colour

It is clear that the majority of lakes examined had a distinct seasonal variation in colour. The summer decline in colour was linear over time in lakes with low flushing. The decline observed in Lough Lickeen corresponded to a factor of -0.95 yr^{-1}. A similar result was recorded by Jefferson-Curtis & Schindler (1997) who found a half time for colour (A_{350nm}) in lake enclosures of 166 days (corresponds to a factor of -1.099 yr^{-1}). Engstrom (1987), in a laboratory experiment, found that colour (optical density at 350 nm) in samples from 10 lakes declined by a factor of -0.24 to -0.78 yr^{-1} under cool white illumination at 100 μE m^{-2} s^{-1} (12 hrs light/dark) (~150 μmol m^{-2} s^{-1} (Moss, 1988)). Loss of colour in winter will be less visible because of the high flushing rates and low light levels.

Although substantial flushing led to an initial increase in colour in Lough Ballyquirke in 1996, subsequent flushing in late winter did not (Figure 5.13). There may be two reasons for this. Firstly, colour-producing substances accumulate through microbial activity to produce a "store" of colour (Mitchell & McDonald, 1992). This mainly occurs during the summer when temperatures are at a maximum. This store of colour is then removed by rainfall during autumn and early winter. As the store is finite, subsequent rainfall may not remove humic substances. Secondly, the store of colour may also be depleted over time by filtration through the subsoil. This removal of DOC by mineral soils is very efficient: McDowell & Likens (1988) recorded a 90% decrease in DOC after passing through a mineral soil. These factors may explain why the increased flushing in February 1997 did

not alter the pattern of colour decline evident after October 1996 in Lough Ballyquirke (Figure 5.13). Grieve (1984) also found evidence of seasonality in colour release in a moorland stream. Dissolved organic matter concentrations were higher during autumn than winter despite stream flow being similar.

Another factor that complicates the relationship between flushing and colour is the presence of upstream lakes in the catchment. Between May and June 1997 Ballyquirke was flushed more than once but colour only increased following continued flushing in July (Figure 5.13). It is probable that recharge of Lough Ballyquirke was initially derived from water in upstream lakes. There are 41 upstream lakes in Lough Ballyquirke's catchment which together are 3.98 times the surface area of Lough Ballyquirke. Colour in these lakes would have been subject to loss processes and would therefore be of lower colour than runoff from the drainage area. Rasmussen *et al.* (1989) also noted that downstream lakes had less colour than upstream lakes.

As photolysis plays a role in lowering of colour in lakes it may be expected that deeper lakes would tend to have a smaller loss during summer (Engstrom, 1987). Lough Dan (mean depth 13 m) does appear to have a slower decline in colour when compared to other lakes (Figure 5.2). However, in 1997, Lough Feeagh (mean depth 14.5 m) had a similar decline to Lough Doolough (mean depth 3.4 m) (Figure 5.3). Lough Feeagh was exceptional in that no seasonal variation was evident in 1996, whereas in 1997 it showed a typical pattern (Figure 5.3). This cannot be explained by an increased supply of colour in the summer of 1996 because flushing was the same as in 1997 (flushing between March and July inclusive was 0.18 in both 1996 and 1997). There were also no obvious changes in the catchment in 1996 that may have increased the loading of humic substances (Pers. Comm. P. McGinnity, Marine Institute).

5.4.3 Variation in colour between years

In the study lakes, colour increased earlier in 1997 and reached a higher maximum than in 1996. The earlier increase is easily explained by the higher summer precipitation transporting humic substances to the lakes. The higher maxima recorded may be explained by the timing of the higher rainfall - in early summer. High summer rainfall may release

more colour because it comes shortly after the period of colour production and there has been less time for colour adsorption within the catchment soils. In addition, the summer rainfall in 1997 may have acted to rewet the catchment soils prior to autumn precipitation. Colour release has been found to increase logarithmically with peat rewetting (moisture increase) (Mitchell & McDonald, 1992).

In Lough Pollaphuca, linear regression suggested that high precipitation resulted in a higher average colour and also a higher export of DOC between 1988 and 1999 (Figure 5.17). However, it may be difficult to partition the influence of low precipitation from adsorption to mineral soils. Most precipitation occurs in winter and therefore a low annual precipitation is likely to be caused by periods of low winter precipitation. Thus a low annual precipitation represents a reduced physical mechanism of export of colour but also a period where infiltration to mineral soils and adsorption would have been favoured during the winter. Further analysis may be worthwhile and could use information on both soil moisture and rainfall to produce a time-series model of colour as done by Naden and McDonald (1989).

In Lough Pollaphuca the export of DOC between 1988 and 1999 ranged from 55 to 102 kg ha^{-1} yr^{-1} (Figure 5.17). This means that predictive models for a series of lakes should take factors responsible for between year variation into account such as rainfall. Alternatively, predictions may be restricted to similar climatic conditions.

It was anticipated that the drought conditions observed in 1995 (Mac Cárthaigh, 1996) would have increased the production of humic substances in the catchment and resulted in a higher colour in late 1995 and early 1996 following rewetting. However, no such phenomenon was observed in the 31 lakes or in the time series for Lough Pollaphuca: Figure 5.17 demonstrates that inter-annual variation in mean colour and export was primarily dependent on rainfall. In contrast, Naden & McDonald (1989) found that drought increased the amount of colour released. However, under experimental conditions a substantial colour increase was only observed after 81 days drought but not after 30 days (Mitchell & McDonald, 1992). The drought that occurred in Ireland in 1995 lasted a maximum of 77 days in Birr in the midlands and a minimum of 27 days in Glencolumbkille in the north-west (Mac Cárthaigh, 1996). It was likely that peatland

catchments in this study may have only experienced a minor drought because these areas receive higher rainfall concomitant with peatland development. This may indicate that only periods of severe drought, not often observed in Ireland, may result in elevated colour release.

5.4.4 Variation in colour among lakes

The positive relationship found between the ratio of peat soils (ha) to lake area (Figure 5.18) may have several explanations. Firstly, a large area of peatland releases substantially more colour than other land classes (Urban *et al.*, 1989). Secondly, small lakes draining large areas of peatland will generally have a short retention time which leads to a fast replacement of lake volume with water of a higher colour derived from the drainage area. In addition, a smaller lake area means less dilution of colour by rainfall falling directly onto the lake, which is important at low catchment to lake ratios (Schindler, 1971; Engstrom, 1987). The proportion of catchment flowing into upstream lakes and amount of precipitation had a negative relationship with colour when included in a multiple regression with the ratio of peat soils (ha) to lake area (Table 5.3). Lakes with a large proportion of the catchment flowing into upstream lakes would be expected to have lower colour because of loss processes such as photolysis in the upstream lakes. The negative influence of precipitation may be because of dilution of the store of humic substances in the drainage area, although its significance in the multiple regression was highly dependent on four lakes.

Previous work in other countries supports these findings. Kortelainen (1993) found that the peatland to lake area ratio explained 63% of the variation in TOC in 970 Finnish lakes. Rasmussen *et al.* (1989) found that coloured lakes were likely to have short retention times and be located in catchments with low slopes or peat soils. Rasmussen *et al.* (1989) also found the proportion of indirect drainage to be a significant negative factor in explaining colour.

This study found poor relationships between either peat soils or the proportion of unexploited bogs alone (Figure 5.19, Figure 5.20). This was indicative of the importance of other variables such as residence time, upstream lakes and precipitation in explaining

colour in Irish lakes. In contrast, Kortelainen (1993) found that the proportion of peatland alone explained 49% of the variation in TOC in 183 lakes in northern Finland.

The calculation of the export of DOC was done by estimating DOC from colour (mg l^{-1} PtCo). This was necessary as colour is an absorbance measurement, not a concentration and therefore could not be used to calculate a load (Cuthbert & Giorgio, 1992). The calculation of DOC or TOC from colour using linear regression will be only approximate as such relationships have considerable scatter and actual concentrations may be mostly dependent on algae exudates during summer (Meili, 1992; Tipping *et al.*, 1988). In addition, calculating export from mean colour will produce only very approximate results because of the large amount of seasonal variation.

Although there are problems in estimating export of DOC from colour, such estimates are likely to give insights into the general differences in export of humic substances. Moreover, if direct measurements of DOC were used, the effects of autochthonous carbon in elevating DOC may have obscured relationships between humic substances and catchment characteristics in lake samples.

It is clear that lakes with high proportions of peat soils in their catchments tended to export more humic substances than those with other soil types (median of 74 and 28 kg DOC ha^{-1} yr^{-1} respectively). Lakes with catchments that received more than 1340 mm net rainfall had lower colour yet exported similar amounts of coloured substances as catchments with other peatland types (Figure 5.19, Figure 5.22). As the amounts exported were similar the explanation for the lower colour is likely to be the dilution of the coloured substances by the higher precipitation. The importance of high rainfall in leading to a lower colour in lakes is also visible in the graph of colour versus rainfall for the 187 lakes (Figure 5.25) where lakes tend to have lower colour if rainfall is greater than 1600 mm.

It is also likely that the peatland type played a role in determining the amount of colour released. As noted in Chapter 2 the peatland type 'moors and heathland' tended to occur where precipitation was highest and may release less coloured substances than other peatland types and be an additional factor lowering colour in these lakes. Some evidence that the moors and heathland category releases less coloured substances is the failure of the

land class to export more than other peatland types despite receiving substantially higher rainfall (Figure 5.23).

The seasonal release of colour and the dilution mechanism proposed to explain the low colour in lakes in catchments with high rainfall indicates that there is a finite amount of colour available for export. This supports the concept of a 'store' of colour in the catchment proposed by Naden and McDonald (1989). The concept of a finite store may seem counter-intuitive because peatlands cover a large area to a depth of 2 – 8 m (Schouten, 1984) and therefore represent a massive carbon store (Hope *et al.*, 1997). However, it is likely that it is mainly the aerobic surface layer of peatlands that contribute to colour release (Mitchell & McDonald, 1992). This is supported by dating of lake DOC which suggests that it is derived from recently (post 1950s) fixed carbon (Schiff *et al.*, 1990).

Peat catchments clearly exported more colour, but as peatland extent increased export of colour did not. The lack of a linear trend of increasing export with increasing proportion of peat soils is puzzling (Figure 5.22). Such a finding is in conflict with Dillon & Molot (1997) who did find a linear trend between peatland extent and export of DOC and colour ($r^2 = 0.78$ and 0.76). Hope *et al.* (1997) found that linear regression of soil carbon storage on DOC export explained 91% of the variation in 17 rivers. Perhaps if information on soil carbon storage was available it may have explained more variation in this study. However, as the production of colour mainly occurs on the aerobic surface layer of peatlands an argument may be made for using aerial extent rather than depth of peatlands (Mitchell & McDonald, 1992)

The findings from the lakes that were sampled once (n = 187) appear to support the conclusions drawn from the seasonally sampled lakes (n = 31). The importance of retention time and peatlands is evident in the correlation found with the ratio of peatland area to lake area. The reason why the correlation is weak may be owing to other factors such as the influence of precipitation and a varying release of colour from different peatland types. Previous studies have reported positive relationships between colour and flushing (e.g. Rasmussen *et al.*, 1989; Townsend *et al.*, 1996; Tipping *et al.*, 1988); the present study supports this but adds that high precipitation can lead to lower colour

indicating that a finite amount of colour may be released from upland soils. Perhaps this relationship has not been found previously because of a small range in rainfall in other studies. Dillon & Molot (1997) found that differences in export of DOC and colour could not be explained by precipitation in 20 catchments and this was attributed to the small range in precipitation among the catchments.

It is clear that some decline in colour takes place from north to south in response to increasing irradiation. The decline in colour from north to south may be explained by increased photolysis in both the catchment and the lake. The significance of the north-south increase in irradiation in this data-set may primarily be owing to the summer sampling strategy as this is when the effects of photolysis will be the most pronounced. Ireland may also have unique conditions that allow this to be observed. The geographic variation in precipitation that determines peatland development is mainly from west to east rather than north to south (Rohan, 1986); thus the peatland strip along the west coast that runs north to south provided good conditions in which the effect of irradiation could be observed. In contrast, the reverse is found in Finland, where colour increases rather than decreases from north to south. This has been attributed to reduced microbial activity at lower temperatures in the north (Kortelainen, 1993). Given the small temperature gradient in Ireland (Rohan, 1986) it is not surprising that this trend is not found.

5.4.5 Transparency and oxygen

The decrease in Secchi depth with colour is caused by the absorption of light by humic substances. Multiple regression using colour (mg l^{-1} PtCo) and chlorophyll *a* (µg l^{-1}) explained 82% of the variation in Secchi depth. The remaining variation (18%) may be attributed to non-algal particles and operator error in Secchi depth determination. However, one indicator of re-suspension of particles - mean depth divided by the square root of lake area did not explain additional variation in Secchi depth. Variation may also be caused by differences in phytoplankton size - a population of large algae such as *Anabaena flos-aquae* will scatter less light than a population of smaller algae with similar chlorophyll *a* (Edmondson, 1980). The importance of colour in determining the Secchi depth of Irish lakes has also been noted by Flanagan & Toner (1975) and in other countries by Lorenzen (1980) and Effler *et al.* (1985). Håkanson & Lindström (1997) used multiple regression to explain the variation in Secchi depth. Colour, total phosphorus and pH were

used to explain 74% of the variation. The influence of colour substantially reduces the usefulness of Secchi depth in estimating algal biomass. This necessitates that determinations of colour be made with Secchi depth.

The decline in oxygen in Lough Dan was clearly related to the substantial increase in colour (Figure 5.28). Crisman *et al.* (1998) found colour to be the most strongly correlated variable to oxygen in 55 lakes in Florida. Rasmussen & Kalff (1987) found colour to be a significant negative factor affecting zoobenthic biomass, although, trophic state was more important. A mechanism for such a decline in oxygen with an increase in colour has been proposed by Miles & Brezonik (1981). The mechanism is one where ferrous (Fe^{2+}) and ferrous-humic matter complexes are oxidised by oxygen to ferric (Fe^{3+}) and ferric-humic matter complexes. The ferric and ferric-humic matter complexes are then reduced by humic matter back to ferrous and ferrous-humic matter complexes completing the reaction cycle. This reduction proceeds more rapidly in the presence of light, as Miles & Brezonik (1981) found oxygen consumption to be 0.12 mg l^{-1} h^{-1} in daylight compared to 0.04 mg l^{-1} h^{-1} in darkness at 0.1 m depth. Lindell *et al.* (1995) noted that oxygen declined linearly with light exposure, but a considerable amount of oxygen remained after the longest light exposure. It is likely that oxygen declined through this process in other lakes (e.g. Feeagh) but the higher colour in Lough Dan led to a more noticeable decline as Miles & Brezonik (1981) noted a higher rate of oxygen decline in lakes that had higher colour.

The lower oxygen at depth in Lough Dan is interesting as one might expect oxygen to be lowest at the surface owing to light exposure. However, such a gradation may develop owing to diffusion of oxygen from the atmosphere at the lake surface. The lower oxygen at depth is unlikely to be due to an accumulation of humic substances with depth because Lough Dan was not thermally stratified between September and December 1997. Thus, concentrations of humic substances may be expected to be uniform with depth during this period (Tipping & Woof, 1983). The reduction in oxygen concentration in Lough Dan is small when compared to other humic lakes in Florida where surface oxygen may be as low as 1.1 to 5.8 mg l^{-1} (Miles & Brezonik, 1981). The magnitude of the decline in oxygen in Lough Dan may be an isolated case because 1997 had very high colour (Figure 5.28).

Other causes for the decline in oxygen may be less probable. Lough Dan is oligotrophic (Chapter 3) and was not thermally stratified during the period of lower oxygen concentrations. Therefore, decaying organic matter in the hypolimnion would not be a likely cause. Secondly, as the catchment is an upland one and TP was low during the period of oxygen decline (13 $\mu g\ l^{-1}$ in September 1997) it is unlikely that any gross pollution took place. Finally it is also unlikely that the oxygen decline was caused by bacterial respiration. The nutrient levels and poor substrate that recalcitrant humic substances provide would not sustain respiration sufficient to account for the decline in oxygen for a large volume of the lake over the winter months.

5.5 Conclusions

The main conclusions from this chapter are:

- A significant proportion of the 189 lakes sampled once during summer were highly coloured (32% ≥ 50 mg l^{-1} PtCo).
- The seasonal pattern was one of colour decline during spring and summer followed by an increase in late summer and autumn with increased flushing.
- Inter-annual variation in colour was mainly caused by the variation in the amount of precipitation.
- There was a higher export of coloured substances from catchments that had a high proportion of peat soils.
- It was found that peatland catchments that had a high precipitation tended to have a similar export but a lower colour than peatlands receiving lower precipitation. High precipitation may have led to dilution of the 'store' of colour in these catchments leading to lower colour.
- Peatlands are typically associated with high colour in freshwaters (Engstrom, 1987; Kortelainen, 1993; Mitchell & McDonald, 1995; Eckhardt & Moore, 1990). This study confirmed that peatlands are a dominant source of humic substances, but because catchments have a finite store of colour, high precipitation in some peatland catchments may result in lakes having a lower colour than in catchments with other soils.
- This study also found a decrease in colour with increasing sunshine hours from north to south. That colour declines linearly with irradiation is well known (Jefferson-Curtis & Schindler, 1997; Engstrom, 1987) but such a trend has not been identified in field data previously.
- It was also found that colour significantly reduced transparency and in certain cases may decrease the oxygen concentration.
- Irish lakes that have the highest colour tend to be small shallow lakes, located in large catchments with a high proportion of peat soils receiving medium precipitation (1500 mm or 1000 mm net precipitation).

6. THE VARIATION IN PHOSPHORUS AND ITS PREDICTION BY EMPIRICAL AND EXPORT COEFFICIENT MODELS.

6.1 Introduction

Phosphorus (P) has long been recognised as being of fundamental importance in the productivity of freshwaters. Log-linear relationships between total P and chlorophyll *a* have been presented as evidence of this (Sakamoto, 1966; Dillon & Rigler, 1974). However, many other factors can affect the TP - chlorophyll *a* relationship such as the variation in the chlorophyll *a* and P content between and within algal species, light limitation and zooplankton grazing (Foy & Withers, 1995).

The importance of P has been acknowledged by its inclusion in classification schemes (O.E.C.D., 1982) and national legislation (Department of the Environment and Local Government, 1998). However, it has been argued that there is some over-reliance on P as an indicator of freshwater quality (Moss *et al.*, 1996). Trophic boundaries based on P concentration do not adequately describe the many other factors that determine lake quality. The water framework directive (Council of the European Communities, 2000) addresses these past simplifications and in future, lakes will be assessed according to their ecological quality and will be compared with reference conditions. Comparison with reference conditions is important in that it provides a goal for rehabilitation of lakes (Moss *et al.*, 1996).

The aims of this chapter are to examine how catchment characteristics determine the concentration and export of P to Irish lakes by looking for empirical relationships. The applicability of an export coefficient approach to predicting annual export of P to lakes is assessed. In addition, the seasonal and inter-annual variation in phosphorus is examined, the latter by comparing TP concentrations in the 1980s with those found in 1996 and 1997 in four lakes.

6.1.1 Sources and behaviour of phosphorus in the drainage area

The major input of P in Ireland is from chemical fertiliser (62 kilo-tonnes) which is applied in a combined form with N or N and K; other inputs are smaller and include concentrates fed to cattle and sheep (9 kilo-tonnes) and pigs and poultry (6 kilo-tonnes) (Tunney, 1990; Murphy *et al.*, 1997). The inputs total 77 kilo-tonnes and exceed outputs of 31 kilo-tonnes thereby leading to an annual build-up of 46 kilo-tonnes of P in the soil (Tunney, 1990). The build-up of soil P implied by this budget has been confirmed by the increasing trend in measured soil P (Morgan's test) (Figure 6.1). As fertiliser application is still in excess of crop requirement, the soil P continues to increase despite fertiliser input being relatively stable since the 1970s. Soil P can accumulate (e.g. as calcium phosphate) and can now sustain grass production for over 30 years at some sites if manure is recycled (Tunney *et al.*, 1997). Soil P content is a crucial factor that determines P export to freshwater. Tunney *et al.* (2000) have shown an exponential relationship between soil P and the rate of P loss from Irish grasslands.

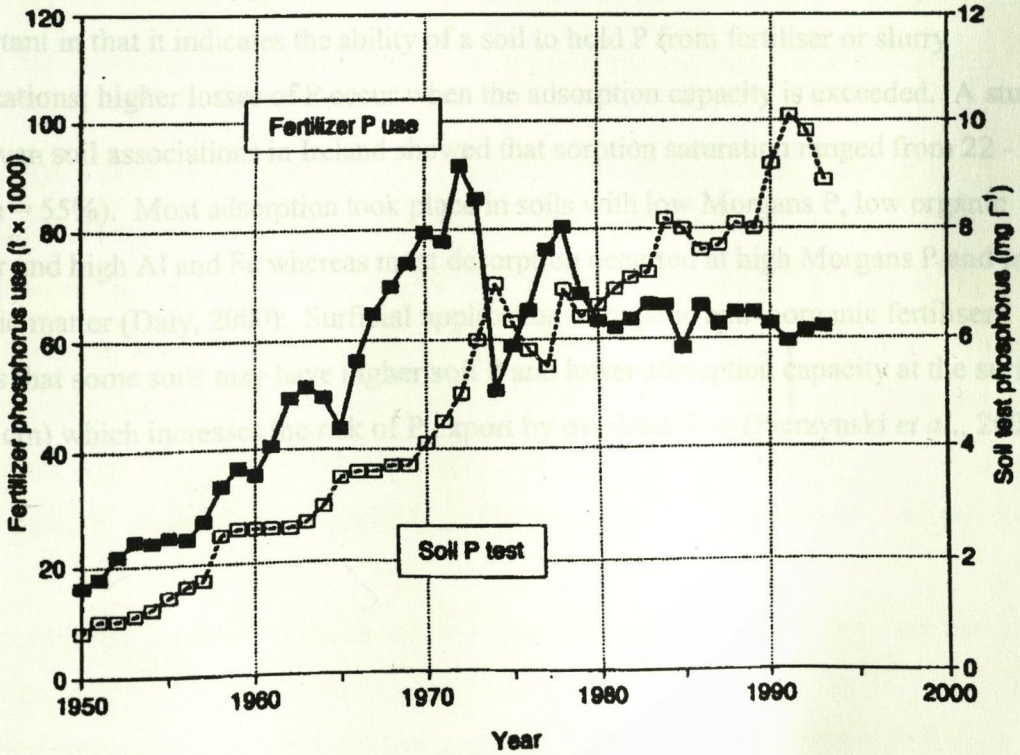


Figure 6.1 Trends in phosphorus fertiliser use and average soil-test phosphorus (Morgan) for samples from Irish farms over the past 45 years (from Tunney *et al.*, 1997).

Other sources of P include atmospheric deposition which has been measured as 0.19 and 0.22 kg ha^{-1} yr^{-1} in Northern Ireland (mean rainfall concentration of 19 and 15 $\mu g\ l^{-1}$) (Jordan, 1987; Gibson *et al.*, 1995b). Effluent from sewage treatment plants is also an important input to some freshwaters. In Ireland, sewage is the suspected cause of slight or moderate pollution in 18 - 20% of rivers routinely surveyed (Lucey *et al.*, 1999). Weathering from soil and rocks, although not strictly an additional input, will increase the pool of P available for plant growth (Pierzynski *et al.*, 2000). Geological sources can be important as shown by Close and Davies-Colley (1990).

Most P is present in soils as an insoluble precipitate of Ca, Fe, Al or in organic compounds (Pierzynski *et al.*, 2000). The major biological transformations of P are mineralisation of organic matter and immobilisation in organisms. The major inorganic transformations of P are fixation (adsorption and precipitation) and solubilization (desorption and mineral dissolution). Fixation is important in retaining P within the soil whereas solubilization increases the potential for plant uptake or export. Adsorption is the process whereby inorganic P is removed from solution by reaction with clays, oxides, hydroxides of Fe, Al and Ca carbonates and organic matter (Pierzynski *et al.*, 2000). Adsorption capacity is important in that it indicates the ability of a soil to hold P from fertiliser or slurry applications; higher losses of P occur when the adsorption capacity is exceeded. A study of eleven soil associations in Ireland showed that sorption saturation ranged from 22 - 79% (mean = 55%). Most adsorption took place in soils with low Morgans P, low organic matter and high Al and Fe whereas most desorption occurred at high Morgans P and low organic matter (Daly, 2000). Surficial application of organic and inorganic fertilisers means that some soils may have higher soil P and lower adsorption capacity at the surface (0 - 2 cm) which increases the risk of P export by overland flow (Pierzynski *et al.*, 2000).

6.1.2 Export of phosphorus to freshwater

There are many factors that affect P export to freshwater in addition to the adsorption or desorption capacity and soil P content already mentioned. One important factor in determining the amount and fraction exported is the type of pathway along which P is transported from soils to freshwater. Three pathways may be distinguished: overland flow, macropore or lateral flow and groundwater flow. Overland flow occurs when the infiltration capacity of the soils is exceeded and rainfall is transported over the surface of the soil. Overland flow from arable farmland contains mainly particulate phosphorus whereas grasslands contain mainly dissolved P because grasslands act as 'filters' for particulates (Pierzynski *et al.*, 2000; Power *et al.*, 1993; Tunney *et al.*, 2000). The P concentration in overland flow has been found to increase with soil P content (Tunney *et al.*, 1998).

In County Cork 20% of river-flow was derived from overland flow whereas 80% was attributed to subsurface flow (Kiely, 2000). Lateral flow occurs when P is transported in soil-water just below the surface. Kiely (2000) found that lateral flow occurred between 10 and 40 cm below the soil surface. Kurz (2000) found high P in zero tension samplers, which indicated that lateral flow through macropores was important in P transport.

The concentration of P in groundwater is generally lower than it is in overland or macropore flow because its deeper infiltration allows for greater adsorption. Of 189 groundwater stations analysed for PO_4^{3-}-P 87% had less than 40 μg l^{-1} (Lucey *et al.*, 1999). In comparison, concentrations in overland flow from a high soil P site (17 mg l^{-1} Morgan's P) were rarely below 300 μg l^{-1} PO_4^{3-}-P (Kurz, 2000). Groundwater may still represent a significant contribution of P to freshwaters in terms of eutrophication and this is being investigated in several Irish catchments by Garrett Kilroy (Department of Geology, TCD).

Where artificial drainage networks are installed these may also be an important pathway for P loss. Kurz (2000) found that export in artificial drainage of 0.56 kg TDP ha^{-1} (Nov - Mar) was intermediate between that in overland flow at two nearby sites of 0.39 (low soil P) and 1.71 kg TDP ha^{-1} (high soil P). In Ireland, the percentage of farmland drained by field drainage ranges from less than 2% to greater than 10% of farmland (Collins & Cummins, 1996). Soil hydrology is also important in P export: Daly *et al.* (2000) found

that rivers in catchments with wet soils had a higher P concentration than those with dry soils for a series of catchments that had a similar range in farming intensity (as indicated by high productivity grassland). Wet soils were defined as the soil types gleys, peaty gleys, peaty podzols and peats and dry soils as brown earths and podzolics.

Land management is also important in determining the export of P to freshwaters. Improper storage of slurry and silage effluent can result in farm-yards contributing up to 30% of total farm P losses (Morgan *et al.*, 2000). The increase in Ireland of winter housing of cattle with an associated increase in silage production, higher fertiliser use, slurry storage and disposal has been implicated in the increase of P loads to freshwaters (McGarrigle *et al.*, 1994). The type of farming is also important - arable land tends to export more P than grassland (Johnes *et al.*, 1994b). Stocking density is important as faeces production by animals increases the potential for P export, especially if followed by overland flow which can be promoted by poaching of land by cattle (Jordan & Smith, 1985). In addition, the hydrology is important as higher annual runoff results in higher export (Foy *et al.*, 1995; Foy & Bailey -Watts, 1998). The timing of fertiliser or slurry application is another factor because if it is followed by high rainfall then substantial export may take place (Kurz, 2000). Elevated summer precipitation can also lead to high export. For example, Kurz (2000) found that 41% of DRP export for 16 months occurred between the 3rd and the 10th August 1997 when 150 mm of rain fell in four days. Occasional high summer rainfall is a feature of Irish weather but the high rainfall experienced in August 1997 has been estimated to occur less than once in 30 years (Kiely, 2000; Tunney *et al.*, 2000).

Other factors that may influence the export of P to freshwaters include slope (Johnes *et al.*, 1994b), proximity of agricultural land to freshwater (Johnes, 1996) and the presence and composition of riparian zones (Peterjohn & Correll, 1984).

6.1.3 Behaviour of P in freshwater

During transport in streams numerous alterations in both the concentration and fraction of P can take place. These include sedimentation or entrainment of particulate P, uptake or release by stream macrophytes or algae and sorption or desorption reactions (Sharpley *et al.*, 1995; Smith & Jordan, 1985). Upon reaching the lake, P may undergo several complex

chemical and biochemical alterations. These include biological uptake, recycling or sedimentation and also coprecipitation with $CaCO_3$ (Horne & Goldman, 1994; Otsuki & Wetzel, 1972). Although the seasonal pattern of TP varies greatly between lakes, a generalised seasonal cycle of TP in lakes may be one where there is a winter maximum followed by a summer minimum: such a cycle is usually caused by uptake into algal cells and their subsequent sedimentation. This pattern is not always found, for example enriched lakes may deviate from this pattern by having a high summer TP because of internal loading from sediments (Gibson *et al.*, 1996). The difference in concentration between the lake and its inflowing rivers is mainly a function of residence time. The longer the residence time the lower the lake concentration relative to that of the inflow. Foy (1992) produced an empirical model that predicted mean lake TP concentration using mean input concentration and retention time for a series of Irish lakes:

$$P_{lk} = \frac{1.118 \cdot P_{in}}{(1+\sqrt{t_w})^{1.135}} \qquad \textbf{Equation 6.1}$$

where P_{lk} = mean annual lake TP, P_{in} = mean input TP and t_w = residence time in years.

6.1.4 Trends in Ireland

The increase in soil P concentration in Ireland has led to concerns about the potential impacts on freshwater quality from diffuse pollution (Tunney, 1990). Unfortunately, there are only a few time series in the UK and Ireland that allow assessment of long-term changes in diffuse inputs of P (Foy & Bailey-Watts, 1998). Common barriers to using many data-sets to quantify changes in diffuse inputs were identified by Foy & Bailey-Watts (1998) as: contributions from sewage treatment works that mask increases in diffuse loads, only trends in concentration rather than loads available, inconsistent methodology over time and infrequent monitoring. For example, Johnes and Heathwaite (1997) only had information on runoff-weighted PO_4^{3-} concentration for four years between 1970 and 1986. While changes in runoff-weighted PO_4^{3-} may be detected over this period the sampling frequency may be too poor to reliably quantify long-term changes in diffuse

loads. Foy & Bailey-Watts (1998) have shown that annual load in the Ballinderry river (Northern Ireland) was dependent on flow. Residuals of this regression between flow and MRP increased over time indicating an increase in diffuse loadings (Figure 6.2). The increase in MRP corresponded to an annual increase in loading of 0.0191 kg ha^{-1} yr^{-1} between 1974 and 1994. In contrast, dissolved organic P (DOP) and particulate P (PP) did not show an increase over time when adjusted for variation in flow (Figure 6.2). This work and that of Tunney *et al.* (2000) indicates that MRP rather than PP is the most important fraction lost from grassland in Ireland. Zhou *et al.* (2000) found that the concentration of MRP had increased linearly since the 1970s in Lower Lough Erne and its major inflowing river. The increase in MRP in the inflow was estimated to be 0.89 μg l^{-1} yr^{-1}. Evidence for an increasing trend of P loss is also available at field scale: a comparison of MRP exported from a grassland field experiment in Northern Ireland revealed that median concentrations were 10 μg l^{-1} higher in 1990-91 than in 1981-2 (Smith *et al.*, 1995). These increases in diffuse loadings are high enough to reduce the benefits of P removal at sewage treatment plants in Northern Ireland (Foy *et al.*, 1995; Foy & Bailey-Watts, 1998).

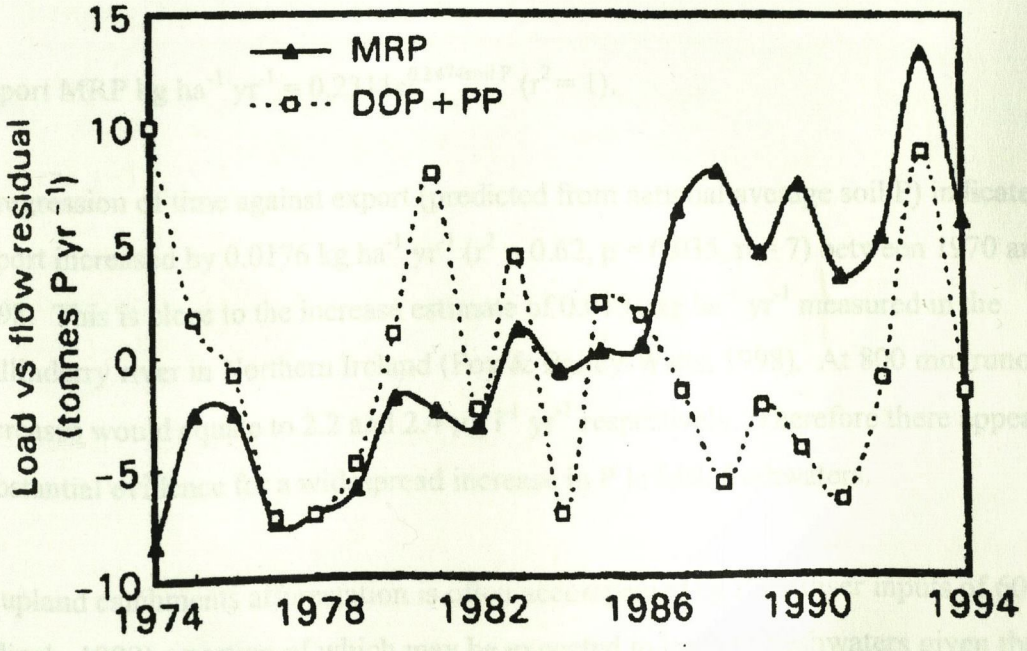


Figure 6.2 Residuals of a load versus flow regression for MRP and DOP + PP in the Ballinderry river (from Foy & Bailey-Watts (1998)). As the variation in flow has been accounted for the increasing trend in residuals indicates an increase in diffuse loadings.

In the Republic of Ireland long-term data sets on P loadings at a fine temporal resolution are not available, but recent repeat studies on Lough Conn, Derg and Ree have found evidence for increases since the 1970s and 1980s (Bowman, 1996; Bowman *et al.*, 1993; McGarrigle *et al.*, 1994). The most useful data-set for inferring water quality trends is the river quality assessments done routinely by the EPA since 1971. These assessments are mainly based on macroinvertebrate species assemblages. A survey of 2,900 km of river length since 1971 has revealed a dramatic decline in rivers classified as unpolluted and a concomitant increase in slightly and moderately polluted rivers (Figure 6.3) (Lucey *et al.*, 1999). It has been inferred that an increase in P from diffuse sources is responsible (Sherwood, 1997). McGarrigle (1998) provides evidence for this in demonstrating that rivers with lower biological quality tended to have higher P concentration (Table 6.1). Recent, more extensive (13, 200 km) river surveys support this trend (Lucey *et al.*, 1999). Another approach may be to use the relationship between soil P and MRP loss derived from Irish field experiments (Tunney *et al.*, 2000) to indicate trends in average export and concentration from past soil P data. National average soil P from 1970 to 1998 (Lehane, 1999) was used to predict changes in P export using the relationship between soil P and export observed in the field experiments of Tunney *et al.* (2000):

Export MRP kg ha^{-1} yr^{-1} = $0.2311e^{0.1474 soil\ P}$ ($r^2 = 1$).

A regression of time against export (predicted from national average soil P) indicated that export increased by 0.0176 kg ha^{-1} yr^{-1} ($r^2 = 0.62$, $p = 0.035$, $n = 7$) between 1970 and 1998. This is close to the increase estimate of 0.0191 kg ha^{-1} yr^{-1} measured in the Ballinderry river in Northern Ireland (Foy & Bailey-Watts, 1998). At 800 mm runoff these increases would equate to 2.2 and 2.4 µg l^{-1} yr^{-1} respectively. Therefore there appears to be substantial evidence for a widespread increase in P in Irish freshwaters.

In upland catchments afforestation is often accompanied by P fertiliser inputs of 60 kg ha^{-1} (Clinch, 1999) a portion of which may be expected to leach to freshwaters given the low adsorption capacity of organic soils (Daly, 2000). Gibson (1976) and Gibson *et al.* (1995a) have found higher TP concentrations in upland lakes with afforested catchments in Northern Ireland.

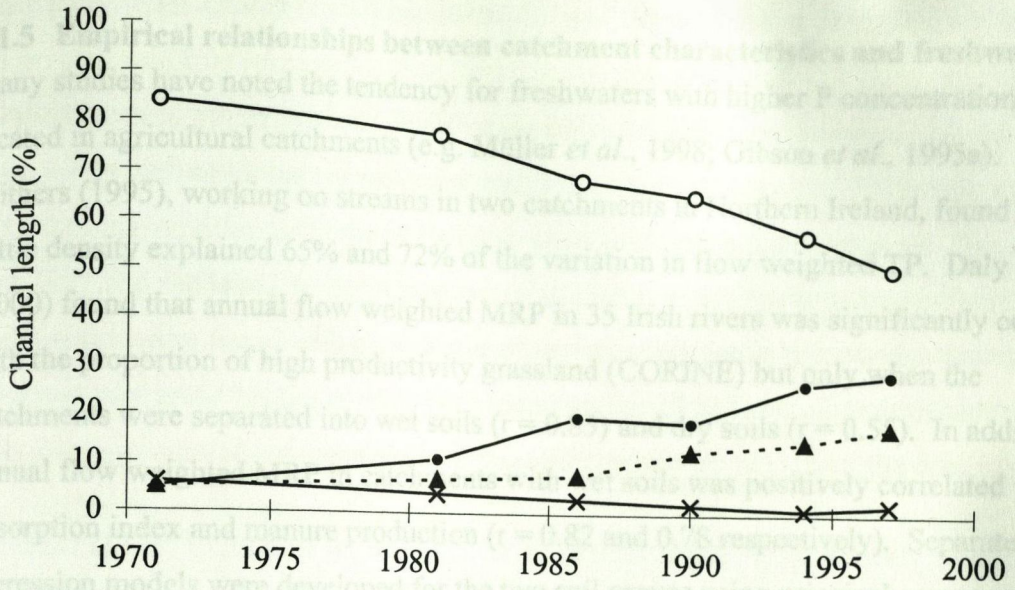


Figure 6.3 Change in the percentage of unpolluted (—O—), slightly polluted (—●—), moderately polluted (- - -▲- - -) and seriously polluted (—×—) channel length (2,900 km) between 1971 and 1997 (Lucey *et al.*, 1999).

Table 6.1 Relationship between river biological assessment categories (status, class and index) and median unfiltered molybdate reactive phosphorus (MRP) for the period 1991-4 (McGarrigle, 1998; Lucey *et al.*, 1999).

Status	Class	Index (Q)	Median MRP range (μg l^{-1})
Unpolluted	A	5, 4-5, 4	14 - 30
Slightly polluted	B	3-4	45
Moderately polluted	C	3, 2-3	70 - 123
Seriously polluted	D	2, 1-2, 1	87 - 215

6.1.5 Empirical relationships between catchment characteristics and freshwater P

Many studies have noted the tendency for freshwaters with higher P concentrations to be located in agricultural catchments (e.g. Müller *et al.*, 1998; Gibson *et al.*, 1995a). Foy and Withers (1995), working on streams in two catchments in Northern Ireland, found that cattle density explained 65% and 72% of the variation in flow weighted TP. Daly *et al.* (2000) found that annual flow weighted MRP in 35 Irish rivers was significantly correlated with the proportion of high productivity grassland (CORINE) but only when the catchments were separated into wet soils ($r = 0.83$) and dry soils ($r = 0.55$). In addition, annual flow weighted MRP in catchments with wet soils was positively correlated with a desorption index and manure production ($r = 0.82$ and 0.78 respectively). Separate regression models were developed for the two soil groups using principal component analysis. In the poorly drained catchments (wet soils), 68% of the variation in annual flow weighted MRP was explained using the parameters: high productivity grassland (CORINE), soil P desorption, soil P (Morgan's test) and the sum of peatland and semi-natural areas. A multiple regression model for the well-drained catchments (dry soils) explained 33% of the variation in annual flow weighted MRP and included the parameters: high productivity grassland, low productivity grassland and soil P (Morgan's test). Summer MRP was better predicted by these parameters ($r^2 = 0.62$). Agricultural areas may not always have the highest concentrations of P in water: Misztal *et al.* (1992) found higher concentrations in groundwater derived from peat bogs than from arable agriculture in Poland. However, P export per unit area was highest from arable land.

In non-agricultural catchments, other parameters may be useful in explaining the variation in freshwater TP. D'Arcy & Carignan (1997) found that 51% of the variation in TP in 30 Québec lakes with forested catchments was explained by retention time, catchment slope and drainage area. A second multiple regression model explained 53% of the variation using the ratio: lake perimeter to volume and catchment slope. Slope had a negative relationship with TP, catchments with lower slope were postulated to have saturated soils which would increase TP export by promoting overland flow during high rainfall events. In contrast, in agricultural catchments a high slope is generally associated with increased P export (Johnes *et al.*, 1994b). The importance of slope in promoting overland flow is likely to be dependent on the water saturation of the soil and rainfall intensity.

Close and Davies-Colley (1990) explained 55% of the variation in TP in 96 New Zealand rivers using multiple regression. Negative variables were altitude and the percentage of riverbed covered by periphyton. Positive variables were the percentage of volcanic rocks, loess, schist, soft sedimentary rocks and exotic forestry. Håkanson (1997) explained a total of 56% of the variation in TP in 67 Swedish lakes using multiple regression. The area of open land near the lake (%) had a positive relationship with TP whereas negative relationships were found with rock area near the lake (%), mean lake depth, drainage area relief and lake area. Müller *et al.* (1998) found higher TP at lower altitudes despite similar proportions of agriculture in upland and lowland catchments in Central Europe.

Schindler (1971) found that the variation in TP concentration was positively related to the ratio of catchment area to lake volume in forested catchments in Canada. Lakes with small volumes and large catchments tended to have higher TP concentrations, most likely owing to shorter retention times. The model was only useful in similar catchments that exported equal amounts of P per unit area. Kirchner (1975) also worked on lakes in forested catchments in Canada but found a positive relationship between drainage density and TP ($r = 0.94$, $n = 18$). It was postulated that the high drainage density led to less percolation through soils with less retention of rainfall P in the drainage area.

6.1.6 Export coefficient models of phosphorus loss to freshwater

Export coefficient models predict the total P load to a lake by firstly allocating an annual loss rate or coefficient in kg P ha^{-1} yr^{-1} to each of the different land classes in a catchment. The area (ha) of each land class is multiplied by its coefficient and all products are summed to estimate the total load to a lake. Coefficients may also be included for other P sources such as sewage. The success of a model is principally determined by the accuracy of the coefficients chosen. It is generally accepted that coefficients determined for land classes may only be of use in other catchments that are geographically close and have similar environmental characteristics such as geology, soils, hydrology and so on (Johnes *et al.*, 1994a,b; Clesceri *et al.*, 1986). This study will attempt to use two published export coefficient models to predict the P load to the 31 lakes examined. The models of Jordan *et al.* (2000) and Johnes *et al.* (1994a, b) were chosen because of their geographic proximity (Northern Ireland and England/Wales respectively).

The model of Jordan *et al.* (2000) may be well suited to predicting P export to the 31 lakes in this study. This is because the model was developed in a nearby area (Northern Ireland) and also because the coefficients were determined for land classes in the CORINE database which was also available for use in this study. Some of the coefficients were collated from the literature but some were also derived by regressing land class areas (ha) against TP load (kg yr^{-1}) (see McGuckin *et al.*, 1999). Coefficients were presented for 27 CORINE land classes and ranged from -6.57 kg ha^{-1} for freshwater to 4.90 kg ha^{-1} for non-irrigated arable land. The negative coefficient for freshwater indicates a net retention of P rather than export. The model was validated by regressing predicted load (tonnes) against independently observed load in 18 rivers. The model validation appeared successful ($r^2 = 0.89$, $p < 0.001$) although the success may have been overestimated by comparing loads rather than loads per unit area. The predicted loads may have matched the observed loads mainly by virtue of differences in catchment areas: very large catchments will export more TP than small catchments by virtue of their larger catchment area alone.

The model of Johnes *et al.* (1994a, b) has been published widely (e.g. Johnes *et al.*, 1996; Johnes, 1996; Johnes & Heathwaite, 1997; Johnes & Hodgkinson, 1998) and involves the application of export coefficients to livestock and humans as well as land classes. Livestock are important because they redistribute P from vegetation into faeces, which has the net effect of increasing P export. The procedure adopted by Johnes *et al.* (1994a, b) was to divide published coefficients into groups according to environmental characteristics. For each catchment an appropriate coefficient group is selected depending on agriculture practice, livestock, hydrology, geology, human population and sewage. The success of the coefficients in predicting observed P is then assessed and if found to differ by greater than ±5% the coefficients may be readjusted within published ranges. A validation step then follows where the ability of the model to predict previous years TP is assessed. If the model fails to predict previous years TP within ±10% then the coefficients may yet again be adjusted. Some external validation of the chosen coefficients has been achieved by Johnes *et al.* (1994a, b) as the same coefficients were successful in predicting TP in catchments with similar environmental characteristics. This approach to export coefficient modelling has been highly successful in predicting TP in 12 catchments ($r^2 =$ 0.98 between predicted and observed) (Johnes & Hodgkinson, 1998). Further refinement

to the model can be achieved by separately determining land use in riparian zones and allocating them higher export coefficients (Johnes, 1996; Johnes & Heathwaite, 1997).

The advantages of export coefficient models are that their data requirements are easily met, they are simple to construct and can be easily calibrated; they give catchment managers both insight into the sources of P and possible management options (Johnes *et al*, 1994a, b; Johnes & Heathwaite, 1997; Johnes, 1996). However, there are also several acknowledged limitations. These include the fact that the models do not give information on either the seasonal variation or the different fractions of P (Johnes *et al*, 1994a, b). The models also do not explain the complex processes controlling P loss to freshwater such as desorption and sorption saturation (Johnes *et al*, 1994a, b; Daly, 2000). In addition, although the location of land classes relative to surface drainage is important in P loss, many models do not take this into account (Johnes *et al.*, 1996). The choice of coefficients may also be difficult and although it is clear that environmental factors (e.g. slope) should guide the choice there is a lack of studies that give detailed guidelines (Young *et al.*, 1996). One substantial barrier to prediction using coefficients is the high dependence of annual export on flow. In a multiple regression of flow and time on MRP load, Foy and Bailey-Watts (1998) found that flow accounted for 44% of the variation in the river Ballinderry (Northern Ireland) between 1974 and 1994. Hindcasting of TP concentration using static coefficients (Johnes *et al.*, 1994a, b) may also be problematic as Tunney *et al.* (2000) have shown that export of P increases in a exponential way with soil P. The decline in water quality in Ireland over the last 20 years has occurred when P fertiliser application and cattle density has been relatively static (Murphy *et al.*, 1997; Department of Agriculture, Food and Forestry, 1997). This points to the linear increase in soil P as the cause and therefore constant coefficients for land and livestock export as used by Johnes *et al.* (1994a, b) will not be accurate in hindcasting exercises. Other factors that may need to be taken into account when hindcasting are changes in farming practices, such as an increase in winter housing and increased animal productivity as separate from stocking density.

6.1.7 Specific aims

The main aims of this chapter are:

- To examine the seasonal variation in TP.
- To determine whether the high export of TP that followed high summer rainfall in 1997 observed in the field experiments of Kurz (2000) had an effect at catchment scale that was observable in lake TP concentration.
- To test whether TP concentrations in four Clare lakes have increased in line with national trends since the 1980s.
- To estimate export of TP to the 31 lakes.
- To examine how catchment characteristics determine the concentration and export of P to Irish lakes by looking for empirical relationships.
- To determine if the soil drainage characteristics inherent in different soil types influence TP export as found by Daly *et al.* (2000) for flow-weighted river concentrations.
- To use two published export coefficient models (Jordan *et al.* (2000) and Johnes *et al.* (1994a, b)) to predict the P load to the 31 lakes examined.
- To produce an approximate estimate of TP export to a selection of lakes in the 1950s based on soil P.

6.2 Materials and Methods

The location of lakes and calculation of catchment characteristics was described in Chapter 2. Sampling frequency, methods of collection and storage of samples was described in Chapter 3.

Total phosphorus was determined in duplicate according to Eisenreich *et al.* (1975). Samples and standards (50 ml) were digested in polypropylene bottles. Water lost through evaporation was replaced with de-ionised water. Five ml of sample was then pipetted into test-tubes. After addition of reagents, absorbance was measured at 882 nm in a 40 mm cell. During 1996 a Shimadzu UV-120-02 spectrophotometer was used, a Shimadzu UV-1601 was used during 1997. High concentrations of total phosphorus were determined on a PYE Unicam SP6-350 spectrophotometer with a 10 mm pathlength cell and auto-sipper. All determinations of total phosphorus followed calibration with five standards in duplicate.

Some contamination of TP was found in digested blanks. This was eventually attributed to leaching of P from the polypropylene digestion bottles used. However, duplicate digestions in glass and polypropylene revealed a zero median difference in estimated concentration. Therefore, the contamination did not have a serious influence on the results, probably because standards were also digested and P leaching from the bottles may have been relatively consistent. Fuller discussion and quality control information are presented in Appendix 9.

The criterion of detection was 4 $\mu g\ l^{-1}$ and the limit of detection was 7 $\mu g\ l^{-1}$ TP (Caulcutt & Boddy, 1983).

To calculate loading to the lakes it was necessary to predict annual mean inflow concentration. This was estimated by rearranging the equation from Foy (1992) which predicted mean lake TP concentration for a series of Irish lakes using mean input concentration and retention time as below:

$$P_{lk} = \frac{1.118 \cdot P_{in}}{(1+\sqrt{t_w})^{1.135}}$$ **Equation 6.1**

Rearranged to:

$$P_{in} = \frac{P_{lk}(1+\sqrt{t_w})^{1.135}}{1.118}$$ **Equation 6.2**

where P_{lk} = mean annual lake TP, P_{in} = mean input TP and t_w = residence time in years.

The annual mean input concentration was then used to calculate export (kg) from the catchment (including the lake area) for 1997 as below. It was necessary to include the lake area as Foy's model included rainfall to the lake surface in P input estimates.

Load from catchment (kg yr^{-1}) = flushing · volume (m^3) · mean input concentration (kg m^3) **Equation 6.3**

The load of P from atmospheric deposition onto the lake surface was then calculated:

Load to lake surface (kg yr^{-1}) = Precipitation (m) · lake area (m^2) · rainfall P concentration (Jordan, 1987) (1.9 x 10^{-5} kg m^3) **Equation 6.4**

This was then subtracted from the load to the catchment (Equation 6.3 - Equation 6.4) to give the load from the drainage area. This load was then divided by the drainage area (ha) to give export for 1997 in kg TP ha^{-1} yr^{-1}.

e.g. Ballyquirke:

(1) Load from catchment (kg) = 31.47 · 1.99 x 10^6 (m^3) · 2.17 x 10^{-5} (kg P m^3)

= 1354.92

(2) Load to lake surface (kg yr^{-1}) = 1.36 (m) · 792400 (m^2) · 1.9 x 10^{-5} (kg P m^3)

= 20.49

Export - lake deposition (kg yr^{-1}) = 1354.92 – 20.49

= 1334.43

Export per unit drainage area (kg ha^{-1} yr^{-1}) = 1334.43 (kg yr^{-1}) / 7239.53 (ha)

= 0.184

The model of Foy (1992) was selected to predict inflow TP concentration as this model was developed using lakes in Northern Ireland and would therefore be more suitable than models from other countries. Using two other models cited in Foy (1992) (Vollenweider (1976) and the OECD (1982) general equation) would lead to an average difference between observed and predicted mean lake TP concentration of 9% and 30% using Foy's (1992) data. The magnitude of the differences between models used to calculate mean lake TP concentration are perhaps indicative of the level of confidence that should be placed in results produced by Foy's (1992) model for lakes in this study.

An index of desorption potential of the soils was calculated according to Daly *et al.* (2000). This involved partitioning the catchment soils (National Soil Survey, 1980) into one of four soil desorption groups. These groups were then expressed as a proportion of drainage area and a weighting factor was then applied according to Daly *et al.* (2000). High values indicate a higher desorption potential.

For the application of the export coefficient model of Johnes *et al.* (1994a, b) it was necessary to determine the mass of P excreted by cattle and sheep annually. This was estimated to be on average 10.02 kg P yr^{-1} for cattle by using data on P content of cattle slurries, annual manure production (Carton & Harnett, 1990) and size distribution of the national herd in 1995 (Department of Agriculture, Food and Forestry, 1997). Assuming that the P content of sheep excreta is close to that of cattle then the same procedure estimates annual P voided by sheep to be 0.91 kg P yr^{-1}. These are comparable to the range of values cited by Johnes *et al.* (1996) of 7.65-17.60 kg P yr^{-1} for cattle and 1.47-1.80 kg P yr^{-1} for sheep. The P content of rainfall was taken to be 19 μg l^{-1} (Jordan, 1987) as used by Foy (1992). The statistical procedures used are documented in Chapter 5.

6.3 Results

6.3.1 Seasonal variation in total phosphorus

The seasonal pattern of TP was quite variable although examining 1997 when sampling intensity was highest for eleven lakes reveals that minimum TP occurred most frequently in spring and summer (8 lakes out of 11) whereas the maximum occurred most frequently in autumn and winter (7 lakes of 11) (Table 6.2). August 1997 was notable because high maxima were observed in Lough Inchiquin and Ramor. Lough Ramor differed by having an erratic seasonal pattern - no consistent summer decline was visible which may indicate internal loading of P or fluctuating inputs in inflowing rivers.

6.3.2 Inter-annual variation in total phosphorus

Table 6.2 shows the average total phosphorus concentration in 1996 and 1997 for eleven lakes that were sampled at approximately monthly intervals. There does not appear to be a large difference in averages between years although concentrations in 1997 tended to be slightly higher than in 1996. In comparison with 1996, concentrations were clearly higher after August 1997 in Lough Gowna, Inchiquin and Ramor. The reason for this was most likely a combination of the higher precipitation in August 1997 and agricultural practices as detailed below.

Previous studies have indicated that there has been an increase in diffuse inputs of P since the 1970s in both Northern Ireland (Foy *et al.*, 1995; Foy & Bailey-Watts, 1998) and in the Republic of Ireland (McGarrigle *et al.*, 1994; Lucey *et al.*, 1999). Estimates of increases have been of the order 1.5 $\mu g\ l^{-1}\ yr^{-1}$ (Foy & Withers, 1995) to 2.1 $\mu g\ l^{-1}\ yr^{-1}$ (McGarrigle *et al.*, 1994). A comparison with previous work done on lakes in this study would be useful in providing further evidence of long-term changes in Ireland.

Four of the lakes in County Clare (Lough Inchiquin, Dromore, Cullaun and Ballycullinan) were studied previously in 1981 and 1982 by Allott (1990). Lough Inchiquin and Dromore were also sampled by Allott (1990) in 1985. It is apparent that there has been no substantial increase in TP concentration in Lough Inchiquin, Dromore or Cullaun (Figure 6.4 to Figure 6.6 and Table 6.3). Figure 6.4 and Figure 6.5 show that the seasonal decline of TP in Lough Inchiquin and Dromore almost coincided up to the beginning of June (Julian day 150) over the five years (1981, 1982, 1985, 1996 and 1997). After June,

concentrations were more variable between years but were not substantially different, and certainly an increase of 1.5 - 2.1 $\mu g\ l^{-1}\ yr^{-1}$ did not occur over this 16-year period. The variation after June may be ascribed to the timing of substantial summer or autumn precipitation. This is clearly evident in Lough Inchiquin (Figure 6.8) where summer precipitation caused TP to increase in August 1997 but not until October in 1996. Lough Cullaun displayed very little seasonal or inter-annual variation over the 16 years (Figure 6.6). To test if there was a statistical difference between years a two-way ANOVA with year and month as independent variables was performed (results are presented in full in Appendix 8). No evidence for a difference between years was found in Lough Inchiquin ($p = 0.209$) and Dromore ($p = 0.357$). Lough Cullaun was found to have a significant difference which a Scheffe post hoc test revealed was attributable to TP being lower in both 1996 ($p = 0.026$) and 1997 ($p = 0.011$) than in 1981.

In contrast, in Lough Ballycullinan, a Scheffe post hoc test revealed that TP was significantly higher in 1996 than in 1981 ($p = 0.039$) but was not higher than in 1982 ($p = 0.108$) (Figure 6.7). However, concentrations in 1997 were not significantly different than in 1981 ($p = 0.815$) or 1982 ($p = 0.982$). It is noteworthy that in 1996 the concentration of TP had a maximum in summer in contrast to the typical pattern of summer minima (Figure 6.7, Table 6.2). This and the lower TP in 1997 in comparison with 1996 may be indicative of a point source input.

Table 6.2 Total phosphorus $\mu g\ l^{-1}$ recorded for eleven lakes sampled approximately monthly between March 1996 and December 1997.

Lake	Jan	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Dec	Average Jan - Dec
Ballyquirke 96			19	18	21	24	18	16	20		**19**
Ballyquirke 97	17	21	14	20	16	23	22	25	23	21	**20**
Dan 96		15	10	9	< 7	< 7	8	7	14		**9**
Dan 97	9	12	10	13	15	15	11	13	14	24	**14**
Doolough 96		16	16	15	16	12	12	10	13		**14**
Doolough 97	17	19	15	17	13	13	15	19	21	26	**17**
Feeagh 96		16	14	12	9	12	11	10	10		**12**
Feeagh 97	13	12	11	10	< 7	8	10	13	8	12	**10**
Gowna 96		43	33	37	29	30	34	32	62		**37**
Gowna 97	39	37	31	42	36	38	55	65	75	54	**47**
Inchiquin 96			31	17	10	5	11	10	28		**16**
Inchiquin 97	33	28	23	12	6	12	41	32	36	39	**26**
Lene 96		11	9	12	9	8	17	15	5		**11**
Lene 97	8	11	13	20	20	14	11	11	5	12	**13**
Lickeen 96		22	20	18	14	10	12	11	14		**15**
Lickeen 97	25	23	22	18	10	13	14	13	15	20	**17**
Moher 96		16	14	8	8	< 7	8	< 7	10		**9**
Moher 97	13	16	12	13	11	5	12	14	15	17	**13**
Owel 96		9	13	7	13	7	10	7	5		**9**
Owel 97	8	10	14	16	15	10	8	11	6	10	**11**
Ramor 96		52	70	60	93	88	114	108	88		**84**
Ramor 97	62	62	60	93	72	59	205	105	111	81	**91**
No. of min. occurrences	**1**	**1**	**2**	**1**	**6**	**7**	**1**	**2**	**1**	**0**	
No. of max. occurrences	**2**	**4**	**2**	**1**	**2**	**1**	**4**	**1**	**2**	**3**	

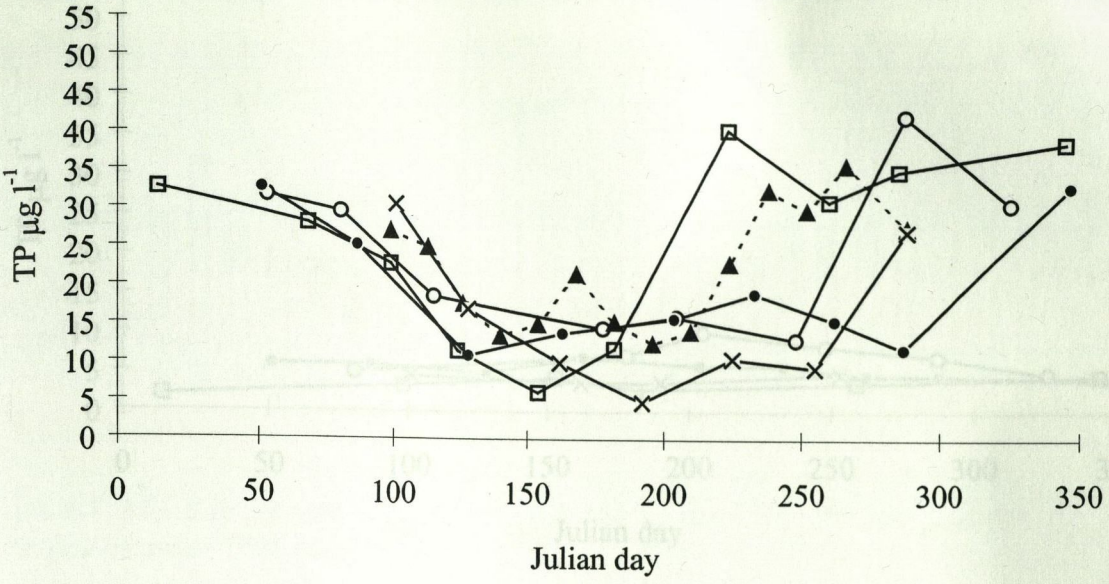


Figure 6.4 Total phosphorus in Lough Inchiquin in 1981 (—○—), 1982 (—●—), 1985 (···▲···), 1996 (—×—) and 1997 (—⊟—). Total phosphorus concentrations for 1981, 1982 and 1985 are from Allott (1990).

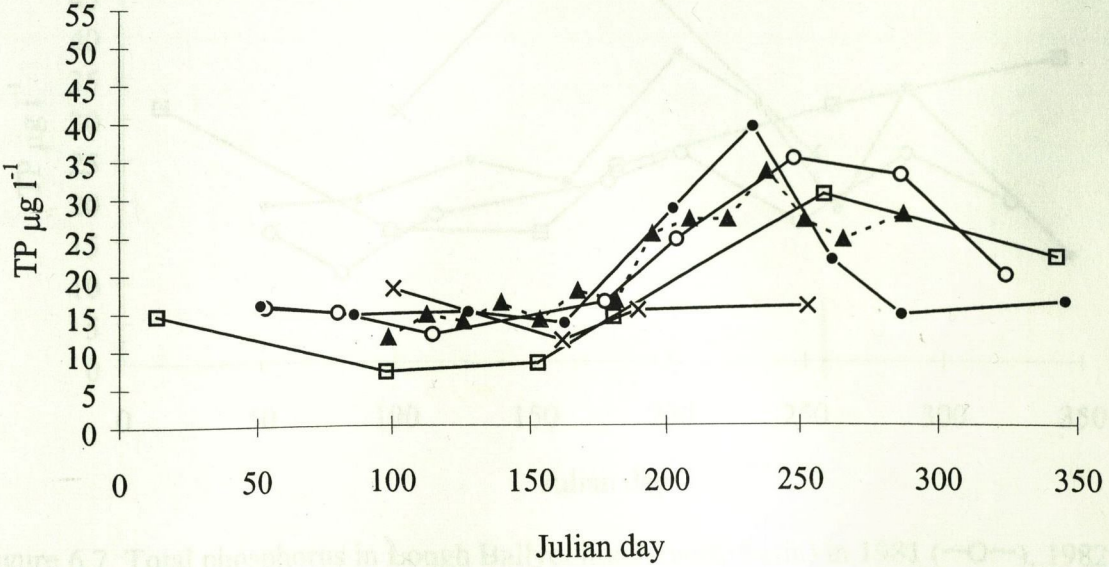


Figure 6.5 Total phosphorus in Lough Dromore in 1981 (—○—), 1982 (—●—), 1985 (···▲···), 1996 (—×—) and 1997 (—⊟—). Total phosphorus concentrations for 1981, 1982 and 1985 are from Allott (1990).

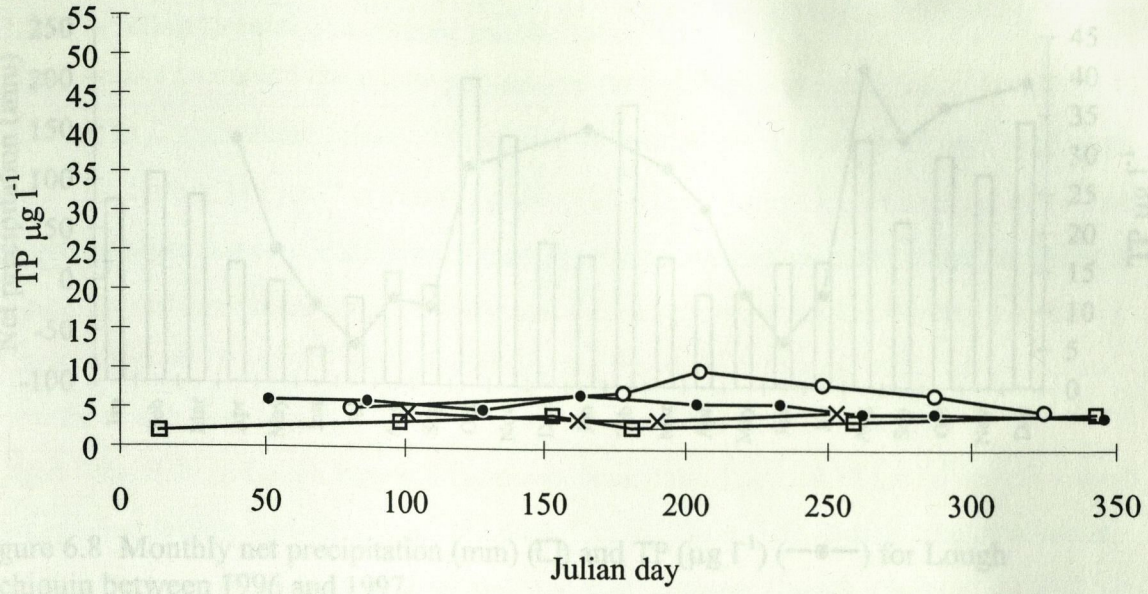


Figure 6.6 Total phosphorus in Lough Cullaun in 1981 (—O—), 1982 (—●—), 1996 (—×—) and 1997 (—⊟—). Total phosphorus concentrations for 1981 and 1982 are from Allott (1990).

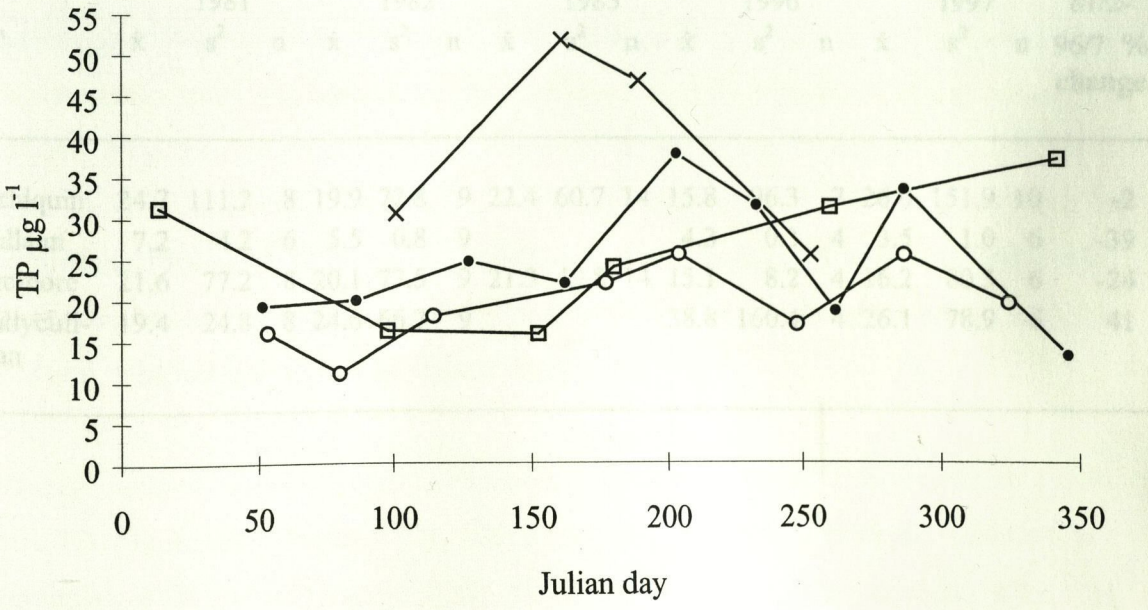


Figure 6.7 Total phosphorus in Lough Ballycullinan (north basin) in 1981 (—O—), 1982 (—●—), 1996 (—×—) and 1997 (—⊟—). Total phosphorus concentrations for 1981 and 1982 are from Allott (1990).

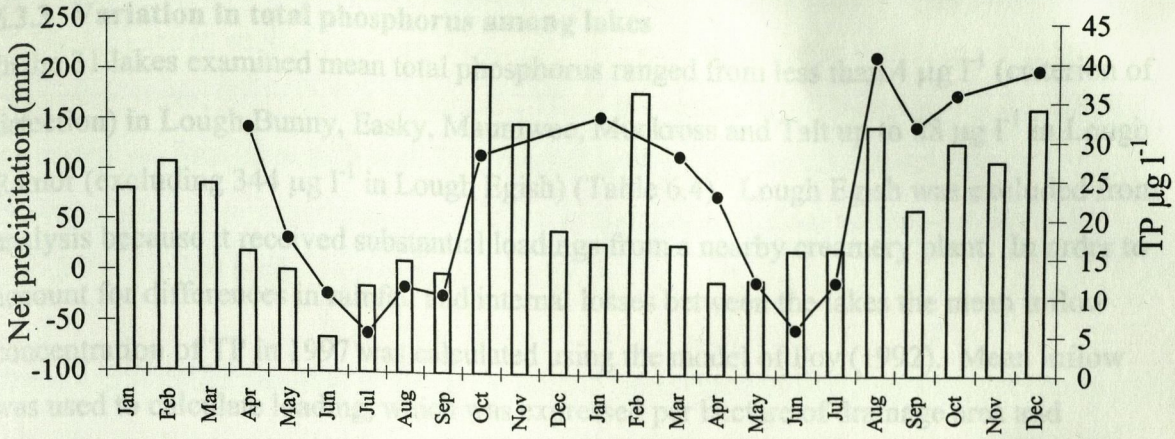


Figure 6.8 Monthly net precipitation (mm) (□) and TP (µg l^{-1}) (—●—) for Lough Inchiquin between 1996 and 1997.

Table 6.3 Mean TP (µg l^{-1}), variance and frequency of sampling for four Clare lakes between 1981 and 1997.

	1981			1982			1985			1996			1997			81/2-96/7 %
TP	$\bar{x}$	s^2	n	$\bar{x}$	s^2	n	$\bar{x}$	s^2	n	$\bar{x}$	s^2	n	$\bar{x}$	s^2	n	change
Inchiquin	24.7	111.2	8	19.9	72.8	9	22.4	60.7	14	15.8	96.3	7	26.0	151.9	10	-2
Cullaun	7.2	4.2	6	5.5	0.8	9				4.3	0.3	4	3.5	1.0	6	-39
Dromore	21.6	77.2	8	20.1	77.5	9	21.3	49.8	14	15.1	8.2	4	16.2	80.3	6	-24
Ballycull-inan	19.4	24.8	8	24.6	66.7	9				38.8	160.4	4	26.1	78.9	6	41

6.3.3 Variation in total phosphorus among lakes

In the 31 lakes examined mean total phosphorus ranged from less than 4 $\mu g\ l^{-1}$ (criterion of detection) in Lough Bunny, Easky, Maumwee, Muckross and Talt up to 88 $\mu g\ l^{-1}$ in Lough Ramor (excluding 344 $\mu g\ l^{-1}$ in Lough Egish) (Table 6.4). Lough Egish was excluded from analysis because it received substantial loadings from a nearby creamery plant. In order to account for differences in rainfall and internal losses between the lakes the mean inflow concentration of TP in 1997 was calculated using the model of Foy (1992). Mean inflow was used to calculate loading, which was expressed per hectare of drainage area and ranged from 0.00 in Lough Bunny, Maumwee, Easky and Talt to 0.76 kg $ha^{-1}\ yr^{-1}$ in Lough Mullagh (excluding 3.34 kg $ha^{-1}\ yr^{-1}$ in Lough Egish) (Table 6.4). Seven lakes had mean TP below the criterion of detection (4 $\mu g\ l^{-1}$) in 1997 (Bunny, Caragh, Cullaun, Easky, Maumwee, Muckross and Talt); nonetheless their mean concentrations were used to calculate export while acknowledging the lack of accuracy at these low levels.

Table 6.5 lists significant ($p \leq 0.05$) Spearman rank correlation coefficients (r_S) between catchment characteristics and TP exported to the lakes in 1997 (kg $ha^{-1}\ yr^{-1}$). Catchment characteristics relating to agriculture were the most strongly correlated. A regression between the proportion of the drainage area used for silage and TP export explained 64% of the variation, although the regression was highly dependent on four catchments that had greater than 17% silage (Figure 6.9). In addition, regressions of TP export against cattle density and the proportion of agricultural land (CORINE) explained 58% and 32% of the variation, respectively (Figure 6.10 and Figure 6.11).

Drainage areas with more than 52% wet soils as defined by Daly (2000) tended to export more TP (Figure 6.9 to Figure 6.11). The parameter 'wet soils' was a summation of the proportion of the soil types: gleys, peaty gleys, peaty podzols, peats and rocks in the drainage area. Wet soils may export more P owing to saturation of the surface of the soil, which is often P rich whereas free-draining soils would allow more opportunity for adsorption of P. Furthermore, lakes in catchments with free-draining soils also had a high alkalinity and may therefore have lower P owing to co-precipitation of P with $CaCO_3$ (the r_S between wet soils and alkalinity was -0.72 ($p \leq 0.0001$, $n = 31$)).

The negative correlations found between TP export and various estimates of precipitation (Table 6.5) are most likely because of co-linearity with agricultural variables. The soil desorption index (Daly, 2000) explained 28% of the variation in TP export but was highly dependent on four lakes with high TP export (Figure 6.12). No other catchment characteristics were significant ($p \leq 0.05$) in explaining additional variation in multiple regression models with silage or cattle density.

There was notable variation in TP export among lakes that had less than 4% agriculture in their catchments (Figure 6.11, $n = 7$). Within this group, catchment characteristics were unsuccessful in explaining the variation in TP export using linear regression ($p \leq 0.05$).

Table 6.6 shows significant ($p \leq 0.05$) Spearman rank (r_S) correlations between catchment characteristics and the transformed (Log x+3) TP concentration for 189 lakes that were sampled in summer. Transformation was necessary to improve the distribution of the data. Prior to log transformation 3 $\mu g\ l^{-1}$ TP was added to the data because three of the 189 lakes had slightly negative TP concentrations (maximum of -1 $\mu g\ l^{-1}$ TP) as estimated by the calibration curve. As with the 31 lakes, catchment characteristics that described agriculture were the most strongly correlated. In contrast to the 31 lakes, the proportion of agriculture in the catchment was more highly correlated than cattle density or the proportion of silage (Table 6.6, Figure 6.13).

When the 189 lakes were separated into geographic clusters as detailed in Chapter 2 only two groups: Monaghan - Cavan and Kerry - Cork had significant relationships ($p < 0.05$) between transformed TP concentration and the proportion of agriculture in the catchment (Table 6.7).

Table 6.4 Summary statistics for TP ($\mu g\ l^{-1}$) between March 1996 and December 1997 and export of TP to the lakes for 1997. Criterion of detection = 4 $\mu g\ l^{-1}$ and limit of detection = 7 $\mu g\ l^{-1}$ (Caulcutt & Boddy, 1983).

Lake	Mean TP	95% CI	n	Max.	Min.	Export (Tonnes yr^{-1})	Export (kg ha^{-1} yr^{-1})
Ballycullinan	31	7	10	52	16	0.04	0.26
Ballyquirke	20	2	17	25	14	1.33	0.18
Bray	9	2	10	16	4	0.03	0.28
Bunny	< 7	1	10	5	< 7	0.00	0.00
Caragh	4	2	10	10	< 7	1.17	0.08
Cullaun	4	1	10	5	< 7	0.24	0.03
Dan	11	2	18	24	4	1.48	0.24
Doolough	16	2	18	26	10	0.45	0.22
Dromore	16	4	10	31	7	0.07	0.25
Easky	< 7	1	10	6	< 7	0.00	0.00
Egish	344	46	9	429	226	2.21	3.33
Feeagh	11	1	18	16	< 7	1.64	0.17
Gara South	29	8	9	48	11	4.09	0.22
Gowna	43	6	18	75	29	5.81	0.50
Graney	16	4	10	30	8	1.57	0.15
Inchiquin	22	6	17	41	5	4.18	0.28
Leane	11	4	9	20	< 7	11.41	0.21
Lene	12	2	18	20	5	0.16	0.21
Lettercraffroe	10	2	10	16	6	0.03	0.11
Lickeen	16	2	18	25	10	0.15	0.20
Maumwee	< 7	1	10	5	< 7	0.00	0.00
Moher	11	2	18	17	<7	0.13	0.15
Muckno	33	7	10	57	23	4.06	0.26
Muckross	< 7	2	9	12	< 7	0.24	0.04
Mullagh	55	9	10	80	29	0.06	0.76
Oughter	72	14	11	114	46	67.91	0.46
Owel	10	1	18	16	5	0.53	0.15
Pollaphuca	8	3	10	19	< 7	3.49	0.12
Ramor	88	16	18	205	52	15.81	0.65
Rea	6	2	10	12	< 7	0.03	0.03
Talt	< 7	2	10	6	< 7	0.00	0.00

Table 6.5 Spearman rank correlation coefficients for TP export (kg ha^{-1} yr^{-1}) versus catchment characteristics. Only $r_S > 0.36$ ($p < 0.05$) are presented, n = 30 (Lough Egish excluded). An asterisk indicates climatic data were predicted using the model of Goodale *et al.* (1998).

Agricultural	r_S	Climatic	r_S
Silage (pr.)	0.509	September precipitation (mm)*	-0.480
Cattle (ha^{-1})	0.502	November precipitation (mm)*	-0.479
Total agriculture (pr.) (CORINE)	0.495	October precipitation (mm)*	-0.476
Total pasture (pr.) (CORINE)	0.489	July precipitation (mm)*	-0.468
Humans (ha^{-1})	0.484	August precipitation (mm)*	-0.465
Sum of rotation under 5 years (pr.)	0.448	Annual precipitation (mm)*	-0.461
Permanent meadow (pr)	0.442	December precipitation (mm)*	-0.457
Easting (km)	0.409	January precipitation (mm)*	-0.455
Rough grazing (pr.)	-0.394	Net rain 1997 (mm)	-0.437
Total area farmed (pr.)	0.394	March precipitation (mm)*	-0.435
Pasture low prod. (pr.) (CORINE)	0.381	April precipitation (mm)*	-0.433
Pasture mix (pr.) (CORINE)	0.365	February precipitation (mm)*	-0.432
		Mean net rain (mm) 1960-1990	-0.431
		May precipitation (mm)*	-0.431
		June precipitation (mm)*	-0.423
		Net rain 1996 (mm)	-0.374

Land class / soil	r_S	Morphometric	r_S
Soil desorption index	0.494	Mean depth/ max. depth	0.403
Rendzinas / brown earths (pr.)	0.461		
Total peatlands (CORINE) (pr)	-0.387		
Peat bogs (unexploited) (pr.) (CORINE)	-0.378		

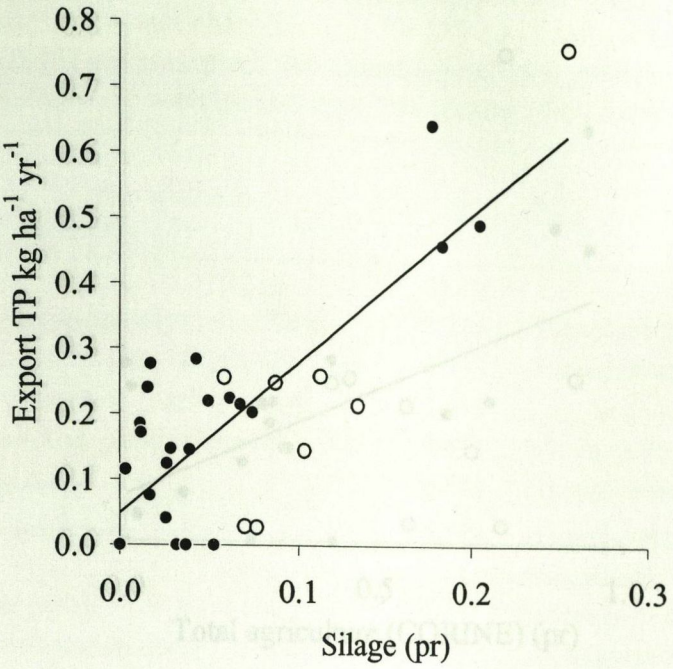


Figure 6.9 Relationship between the export of TP (kg ha^{-1} yr^{-1}) and the proportion of drainage area used for silage. Equation: $y = 2.3007x + 0.0486$ ($r^2 = 0.64$, $p \leq 0.0001$, $n = 30$, Lough Egish excluded). ● = > 52% of drainage area comprised of wet soils, O = < 33% wet soils.

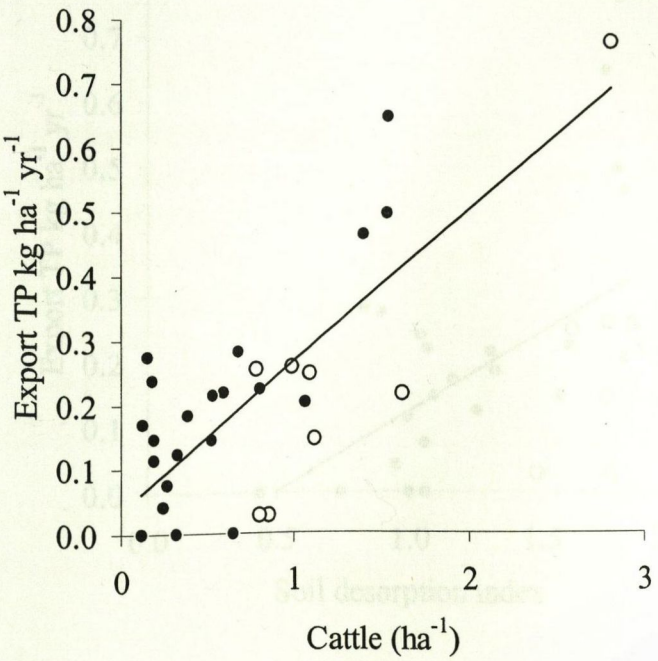


Figure 6.10 Relationship between the export of TP (kg ha^{-1} yr^{-1}) and cattle density in the drainage area. Equation: $y = 0.2299x + 0.0367$ ($r^2 = 0.58$, $p \leq 0.0001$, $n = 30$, Lough Egish excluded). ● = > 52% of drainage area comprised of wet soils, O = < 33% wet soils.

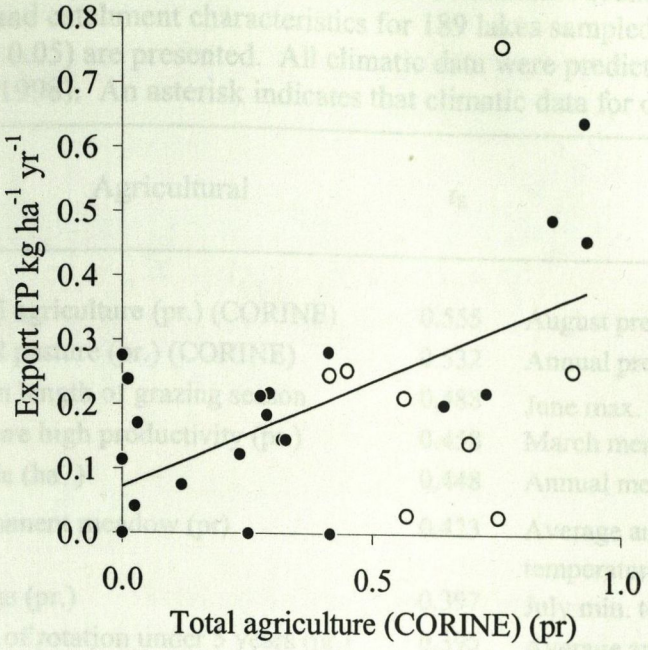


Figure 6.11 Relationship between the export of TP (kg ha^{-1} yr^{-1}) and the proportion of agriculture (CORINE) in the catchment. Equation: $y = 0.3336x + 0.0717$ ($r^2 = 0.32$, $p = 0.001$). ● = > 52% of drainage area comprised of wet soils, O = < 33% wet soils.

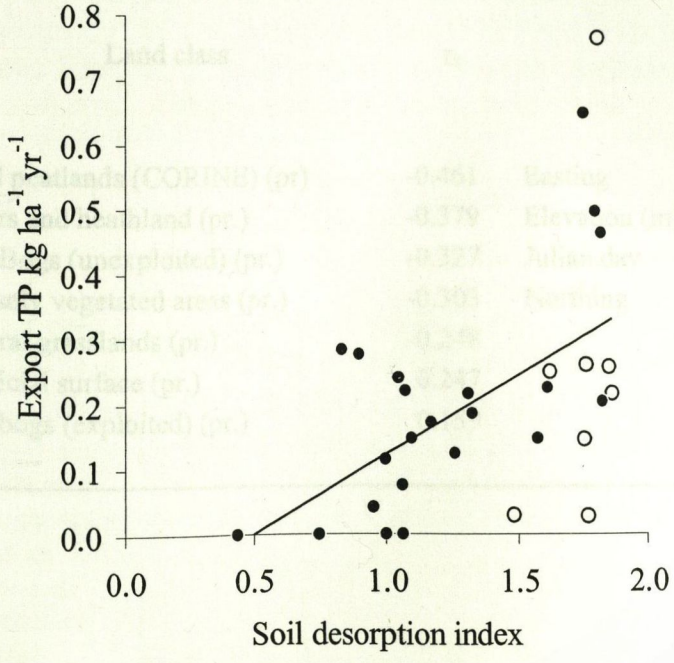


Figure 6.12 Relationship between the export of TP (kg ha^{-1} yr^{-1}) and the soil desorption index (Daly, 2000). Equation: $y = 0.2407x - 0.1195$ ($r^2 = 0.28$, $p = 0.002$). ● = > 52% of drainage area comprised of wet soils, O = < 33% wet soils.

Table 6.6 Spearman rank correlation coefficients found between transformed (Log x + 3) TP and catchment characteristics for 189 lakes sampled once in summer. Only $r_S > 0.143$ ($p < 0.05$) are presented. All climatic data were predicted using the model of Goodale *et al.* (1998). An asterisk indicates that climatic data for other months was also significant.

Agricultural	r_S	Climatic	r_S
Total agriculture (pr.) (CORINE)	0.555	August precipitation (mm)*	-0.533
Total pasture (pr.) (CORINE)	0.532	Annual precipitation (mm)	-0.517
Mean length of grazing season	0.488	June max. temperature °C*	0.465
Pasture high productivity (pr.)	0.458	March mean sunshine hours day^{-1}*	-0.435
Cattle (ha^{-1})	0.448	Annual mean sunshine hours day^{-1}	-0.326
Permanent meadow (pr)	0.423	Average annual maximum daily temperature °C	0.302
Silage (pr.)	0.397	July min. temperature °C*	0.236
Sum of rotation under 5 years (pr.)	0.395	Average annual daily temperature °C	0.210
Pasture mix (pr.)	0.383		
Rough grazing (pr.)	-0.380		
Pasture low prod (pr.)	0.304		
Sheep (ha^{-1})	-0.260		
Total area farmed (pr)	0.255		

Land class	r_S	Other	r_S
Total peatlands (CORINE) (pr)	-0.461	Easting	0.360
Moors and heathland (pr.)	-0.379	Elevation (m)	-0.302
Peat Bogs (unexploited) (pr.)	-0.327	Julian day	0.292
Sparsely vegetated areas (pr.)	-0.303	Northing	0.271
Natural grasslands (pr.)	-0.248		
Artificial surface (pr.)	0.247		
Peat bogs (exploited) (pr.)	0.159		

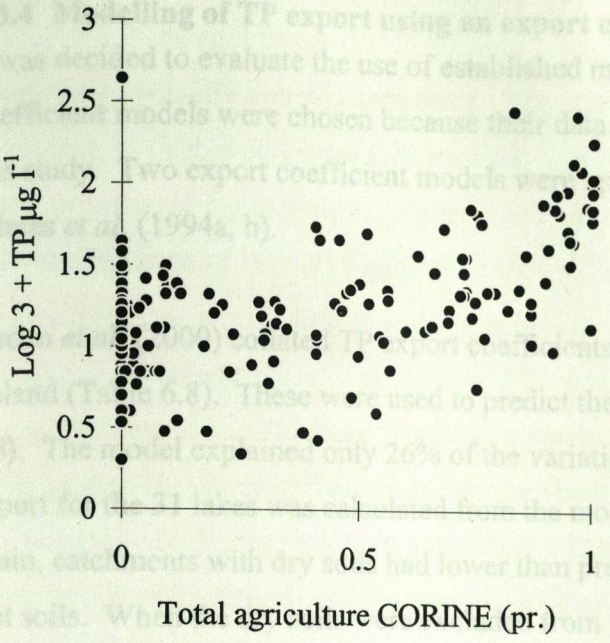


Figure 6.13 Relationship between the transformed (Log x + 3) concentration of TP ($\mu g\ l^{-1}$) and the proportion of agriculture (CORINE) in the catchment, n = 189.

Table 6.7 Results of regressions between the proportion of agriculture (CORINE) and the transformed (Log x + 3) concentration of TP ($\mu g\ l^{-1}$) for the 189 lakes by region (see Chapter 2 for map). Spearman rank correlation coefficients (r_S) are also presented. Standard error of slopes and constants are in brackets.

Group	n	r^2	Constant	Slope	p	r_S	p
Kerry, Cork	47	0.62	0.816 (0.045)	0.883 (0.104)	≤ 0.0001	0.648	≤0.0001
Clare, Galway	18	0.04	1.243 (0.152)	-0.215 (0.277)	0.450	-0.194	0.441
Mayo, Galway	48	0.04	1.087 (0.065)	0.397 (0.294)	0.184	0.139	0.346
Donegal, Sligo, Leitrim, Roscommon	36	0.07	1.102 (0.070)	0.264 (0.171)	0.132	0.315	0.061
Monaghan, Cavan, Longford, Leitrim, Westmeath, Roscommon	30	0.27	0.504 (0.374)	1.141 (0.440)	0.003	0.590	0.001
Wicklow	10	0.13	0.838 (0.102)	0.539 (0.497)	0.310	0.402	0.249

6.3.4 Modelling of TP export using an export coefficient approach

It was decided to evaluate the use of established models in predicting TP export. Export coefficient models were chosen because their data requirements were within the scope of this study. Two export coefficient models were applied, those of Jordan *et al.* (2000) and Johnes *et al.* (1994a, b).

Jordan *et al.* (2000) collated TP export coefficients for CORINE land classes in Northern Ireland (Table 6.8). These were used to predict the TP exported to the 31 lakes (Table 6.8). The model explained only 26% of the variation in the 'observed' export (observed export for the 31 lakes was calculated from the model of Foy (1992)) (Figure 6.14). Once again, catchments with dry soils had lower than predicted export compared to those with wet soils. When the dry soils were excluded from the regression, the model explained 56% of the variation in export. Even so, the model of Jordan *et al.* (2000) tended to substantially overestimate the amount exported (Figure 6.14). An attempt was made to determine whether further adjustments could be made to coefficients to account for other catchment characteristics that may affect TP export (e.g. slope, rainfall). To achieve this a correlation analysis was performed between the catchment characteristics and the residuals of the observed versus predicted regression (Figure 6.14) (dry soils excluded). Only the number of people (ha^{-1}) had a significant relationship with the residuals in regression (r^2 = 0.20, p = 0.0397, n = 22, equation: y = -0.0784 + 0.518x), indicating that diffuse losses from septic tanks may be an important source of P in addition to those accounted for by the CORINE coefficients.

The approach used by Johnes *et al.* (1994a, b) was to apply export coefficients from published literature according to catchment attributes such as the intensity of agriculture (upland or lowland), slope, runoff and rock type. For each catchment, coefficients were adjusted and then validated by assessing if previous years exports were predicted successfully. Table 6.9 shows the export coefficients used by Johnes *et al.* (1994a, b) and Johnes (1996). Three groups are discernible: firstly, lowland catchments with low runoff that typically had intensive agriculture to which high export coefficients were applied; secondly, upland catchments to which lower coefficients were applied and thirdly, limestone catchments (Meon, Windrush) to which low coefficients were also applied (Table 6.9). The 30 lakes (Egish excluded) were partitioned into three comparable

categories: firstly, those with predominantly limestone catchments, secondly, those with greater than 64% agriculture (CORINE), and finally those with less than 33% agriculture which were typically upland catchments. The comparable coefficients used by Johnes *et al.* (1994a, b) (Table 6.9) were then applied. The application of the model resulted in 63% of the variation being explained (Figure 6.15) but in most cases the predicted values were an overestimation of export. Figure 6.15 shows that there was no linear trend between predicted and 'observed' export within the limestone ($r^2 = 0.13$, $p = 0.7701$, $n = 9$) and upland catchment groups ($r^2 = 0.13$, $p = 0.181$, $n = 15$). It therefore follows that adjusting the coefficients applied to these groups as a whole would not improve the predictive ability of the model. In contrast, there was a strong linear trend ($r^2 = 0.93$, $p = 0.002$) in the six catchments with greater than 64% agriculture (Egish excluded) (Figure 6.15). This suggests that the approach of Johnes *et al.* (1994a, b) would give accurate predictions of lowland TP export if lower coefficients were used.

Table 6.8 Export coefficients for CORINE land classes from Jordan *et al.* (2000) and 'observed' and predicted export obtained from the model.

CORINE land class	TP export coefficient kg ha^{-1} yr^{-1}	Lake	'Observed' TP export kg ha^{-1} yr^{-1}	Predicted TP export kg ha^{-1} yr^{-1}
Arable	4.90	Ballycullinan	0.26	0.37
Artificial Surface	0.18	Ballyquirke	0.18	0.24
Bare Rocks	0.00	Bray	0.28	0.25
Beach Dunes Sands	0.00	Bunny	0.00	0.18
Broadleaf Forest	0.23	Caragh	0.08	0.11
Complex Cultivation	2.32	Cullaun	0.03	0.38
Coniferous Forest	0.39	Dan	0.24	0.32
Inland Marshes	0.23	Doolough	0.22	0.21
Intertidal flats	0.00	Dromore	0.25	0.15
Mixed Forest	0.23	Easky	0.00	0.23
Moors and heathland	0.10	Egish	3.33	0.62
Natural grasslands	0.64	Feeagh	0.17	0.15
Pasture high prod	0.84	Gara South	0.22	0.68
Pasture low prod	0.64	Gowna	0.50	0.75
Pasture mix	0.75	Graney	0.15	0.42
Peat Bogs exploited	0.23	Inchiquin	0.28	0.49
Peat Bogs unexploited	0.23	Leane	0.21	0.24
Peat Bogs	0.23	Lene	0.21	0.85
Principally Agriculture	0.49	Lettercraffroe	0.11	0.31
Salt marsh	0.00	Lickeen	0.20	0.39
Sparsely Vegetated Areas	0.00	Maumwee	0.00	0.21
Transitional woodland/scrub	0.23	Moher	0.15	0.32
Urban green	1.02	Muckno	0.26	0.69
Water	-6.57	Muckross	0.04	0.06
		Mullagh	0.76	0.75
		Oughter	0.46	0.58
		Owel	0.15	0.75
		Pollaphuca	0.12	0.53
		Ramor	0.65	0.71
		Rea	0.03	0.79
		Talt	0.00	0.26

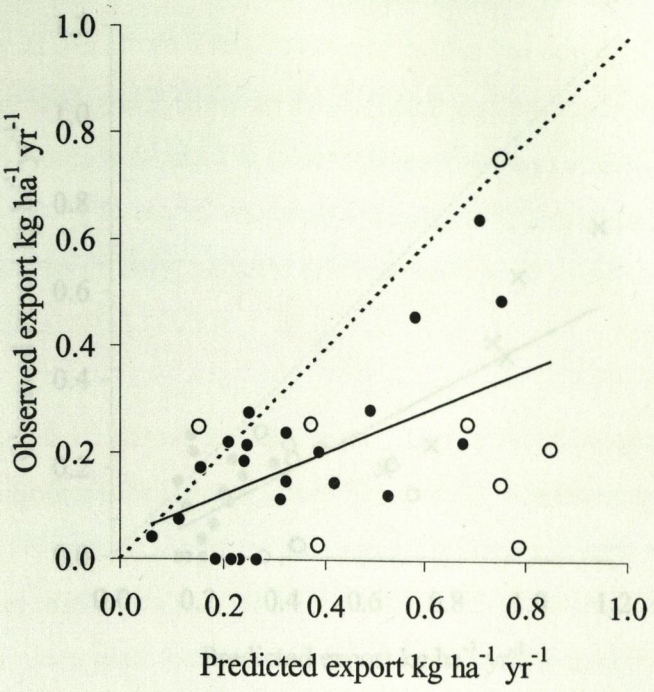


Figure 6.14 Relationship between 'observed' and predicted (model of Jordan *et al.*, 2000) TP export to 30 lakes, wet soils = ●, dry soils = O (Egish excluded). Solid line has equation: $y = 0.402x + 0.041$, $n = 30$, $r^2 = 0.26$, $p = 0.004$. Dashed line = 1:1 relationship. Equation for wet soils alone: $y = 0.6395x - 0.0286$, $n = 22$, $r^2 = 0.56$, $p \leq 0.0001$.

Table 6.9 Export coefficients (kg TP ha^{-1} yr^{-1} or %) applied to UK catchments (Johnes *et al.*, 1994a, b; Johnes, 1996). Coefficients applied are in boldface.

River	Catchment type	Rainfall mm	Runoff mm	Perm. grass	Temp. grass	Cereals	Rough Grazing	Cattle %	Sheep %	People	Rain %
Ant	Lowland	660	205	0.03	0.10	0.22	0.07	0.95	1.0	0.38	8.3
Meon	Lowland	920	339	**0.10**	0.30	**0.65**	**0.02**	**2.85**	**3.0**	**0.38**	**25.0**
Windrush	Lowland	810-680		0.10	0.30	0.65	0.02	2.85	3.0	0.38	36.7
Brook	Lowland	879	466	0.80	0.80	0.90	0.02	5.70	6.0	1.00	25.0
Waver	Lowland	960	478	0.10	0.30	0.60	0.02	2.55	3.0	0.38	25.0
Slapton	Lowland	1035	550	0.40	0.40	0.60	0.02	2.85	3.0	0.38	56.0
Cober	Lowland	1170	570	**0.40**	0.40	**0.60**	**0.02**	**2.85**	**3.0**	**0.38**	**25.0**
Erme	Lowland	1700	878	0.40	0.40	0.60	0.20	2.85	3.0	0.38	25.0
Cleddau	Lowland	1420	1030	0.80	0.80	0.90	0.02	5.70	6.0	1.00	25.0
Ryburn	Upland	1260	340	**0.30**	0.40	**0.60**	**0.02**	**1.28**	**1.5**	**0.38**	**25.0**
Erme	Upland	1700	878	0.30	0.40	0.60	0.02	1.28	1.5	0.38	25.0
Crake	Upland	1962	1422	0.30	0.40	0.60	0.02	1.28	1.5	0.38	25.0
Esk	Upland	2264	1789	0.30	0.40	0.60	0.02	1.28	1.5	0.38	25.0

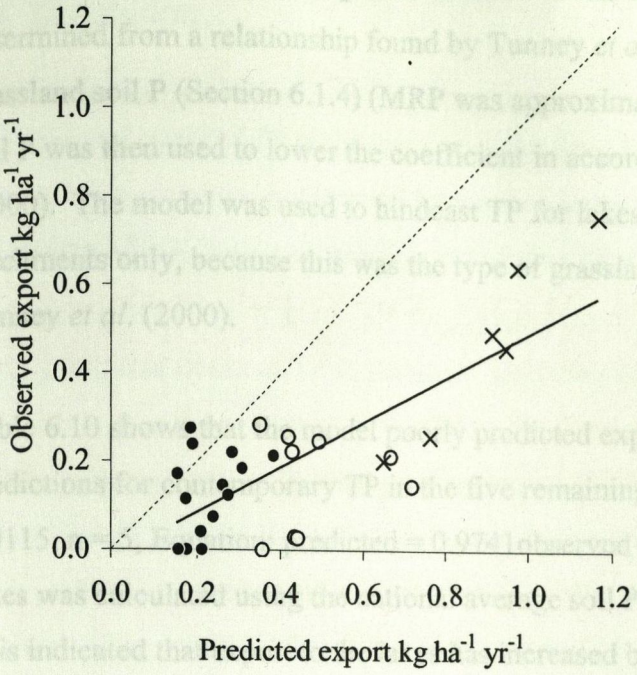


Figure 6.15 Relationship between 'observed' and predicted TP export to 30 lakes (after model of Johnes *et al.*, 1994a, b; Johnes, 1996), (● < 33% agriculture, O = limestone catchments, X > 64% agriculture), (Egish excluded). Equation: $y = 0.5158x - 0.0193$, $n = 30$, $r^2 = 0.63$, $p \leq 0.0001$. Dashed line = 1:1 relationship.

6.3.5 Hindcasting of TP

Previous attempts to hindcast P concentrations using an export coefficient approach have used constant coefficients with past export being estimated by changes in the area of agricultural land and stocking density (Johnes *et al.*, 1994a, b). Current research (Tunney *et al.*, 2000) indicates that the amount of P exported from an area is mainly dependent on soil P. As mentioned previously, soil P has increased in Ireland (Figure 6.1) therefore export coefficients are unlikely to remain constant over time. It is likely that P export from grassland has increased over the last 50 years as soil P increased. A model should therefore attempt to use lower coefficients, based on historical soil P data, to estimate past P export. Other factors such as changes in area farmed, stocking density and farm practices will play an auxiliary role.

It was decided to modify the model developed by Johnes *et al.* (1994a, b) by replacing the coefficients for grassland, cattle, sheep and rainfall (Table 6.9) with a single coefficient

derived from information on grassland soil P levels in the catchment. This coefficient was determined from a relationship found by Tunney *et al.* (2000) between MRP loss and Irish grassland soil P (Section 6.1.4) (MRP was approximately 70% of TP). Information on past soil P was then used to lower the coefficient in accordance with the model of Tunney *et al.* (2000). The model was used to hindcast TP for lakes in non-calcareous lowland catchments only, because this was the type of grassland used in the study carried out by Tunney *et al.* (2000).

Table 6.10 shows that the model poorly predicted export to Lough Muckno in 1997. The predictions for contemporary TP in the five remaining lakes were better ($r^2 = 0.91$, $p = 0.0115$, $n = 5$, Equation: predicted = 0.9741observed + 0.1055). Hindcasted export to the lakes was calculated using the national average soil P in 1950 (0.8 mg l^{-1} Morgan's P). This indicated that export to the lakes has increased by 51 to 150% since 1950 (Table 6.10).

Table 6.10 Morgan's Soil P (mg l^{-1}) (Tunney, 1997), 'observed' and predicted export (kg TP ha^{-1} yr^{-1}) for 1997 and 1950 (soil P of 0.8 – Tunney, 1990) and percentage increase from 1950 to 1997.

Lake	Soil P (range)	Soil P (median)	'Observed' export (1997)	Predicted export (1997)	Predicted export (1950)	Predicted % increase from 1950 to 1997
Gowna	3-6	4.5	0.50	0.49	0.32	53
Lickeen	3-6	4.5	0.20	0.36	0.23	57
Oughter	3-6	4.5	0.46	0.53	0.35	51
Ramor	6-10	8	0.65	0.80	0.35	129
Muckno	6-10	8	0.26	0.75	0.30	150
Mullagh	6-10	8	0.79	0.89	0.45	98

6.4 Discussion

6.4.1 Seasonal variation in total phosphorus

The seasonal cycle of TP in the lakes was variable, although the majority displayed a autumn/winter maximum followed by a spring/summer minimum which is consistent with the uptake of PO_4^{3-} by algal cells in spring followed by sedimentation as is typical in temperate lakes (Gibson *et al.*, 1996). Lough Ramor deviated from this general pattern by having frequent peaks of TP in summer. This may be caused by internal loading which is more important in shallow eutrophic lakes like Ramor (Gibson *et al.*, 1996; Moss *et al.*, 1996). Alternatively, additional riverine inputs caused the increase in summer TP but this is less likely given the low volume of summer flows in Ireland (Foy *et al.*, 1995). In this study, mid-lake concentrations were used to predict mean TP input using the modified equation of Foy (1992). Therefore, in the case of Lough Ramor, internal loading will increase mean lake TP leading to an overestimation of the inflow concentration. Lower amounts of internal loading in other lakes may be accounted for owing to the empirical nature of Foy's equation: inflow concentration was estimated from mean mid-lake concentration which would be influenced by internal loading.

6.4.2 Inter-annual variation in total phosphorus

Of the eleven lakes that were sampled monthly, three displayed a substantial increase in TP concentration in August 1997 (Inchiquin, Gowna and Ramor in Table 6.2). These increases coincided with high precipitation in that month (Figure 6.8). However, the increase was not widespread and was restricted to lakes with high mean TP. This may indicate that the increase was a result of both high summer rainfall and agricultural practices in the catchments (e.g. slurry spreading). If the increase were simply due to the normal input of nutrients with rainfall as occurs in autumn then the increase would have been widespread. It is interesting to note that a concurrent field experiment in Ireland in 1997 found that 150 mm of rainfall between the 3rd and 4th of August resulted in overland flow which accounted for 41% of the export of MRP over 16 months (Kurz, 2000). Tunney *et al.* (2000) suggested that such events may only occur less than once every 30 years. The consequences of a P increase in summer can be severe because the P input occurs when conditions are ideal for algal growth – high light levels, high temperatures

and a large algal inoculum. In Lough Ramor TP increased from 59 to 205 μg l^{-1} from July to August 1997 with a resulting increase in chlorophyll *a* from 30 to 185 μg l^{-1}.

Comparing the results of this study with previous work on four lakes in County Clare revealed that only Lough Ballycullinan had a higher TP concentration than in the 1980s. In Ballycullinan the seasonal behaviour of TP indicated that a point source was responsible: in the summer of 1996, contrary to the minimum usually observed, TP was at a maximum (Figure 6.7). This indicated that substantial loading from an external source must have occurred. Furthermore, concentrations were substantially lower in 1997, being similar to those of the 1980s. It is believed by Clare County Council officials that the high TP was caused by silage effluent transported from a nearby farmyard by the karstic drainage network.

The other Clare lakes (Cullaun, Inchiquin and Dromore) may be more suitable for assessing changes in diffuse P export since the early 1980s. The catchments of these lakes contain large proportions of agricultural land (41 - 57% CORINE) and may therefore be expected to show evidence of an increase in diffuse losses of P. However, it is clear from Figure 6.4 to Figure 6.6 that no increase in TP has taken place over the past 16 years; in fact comparing the means reveals that a decrease has taken place (Table 6.3). This conclusion contradicts a large amount of evidence indicating that inputs of P from diffuse sources have increased in Ireland (Foy *et al.*, 1995; Foy & Withers, 1995; Foy & Bailey-Watts, 1998; McGarrigle *et al.*, 1994; Lucey *et al.*, 1999).

There may be several reasons why an increase has not been observed in the three Clare lakes. Firstly, the increase in diffuse P export has been attributed to increasing soil P (Tunney, 1990; Tunney *et al.*, 2000), and it is possible that soil P in these catchments has not increased in line with the national trend. However, given the large increase in soil P nationally between 1981 and 1994 (6.8 to 9.0 mg l^{-1} Morgan's P, Tunney *et al.*, 1997, Figure 6.1) some increase in Clare would be expected. Another possibility is that soil P has not reached a 'breakpoint' where a linear increase in leaching with soil P is observed. Jordan *et al.* (2000) estimated that a linear increase in P export should occur once soil P reaches the 'breakpoint' of 22 mg l^{-1} Olsen (equivalent to 5.6 mg l^{-1} Morgan's - Tunney *et al.*, 1997). Although coarse, the national soil P map (Tunney, 1997) indicates that two of the catchments have soil P levels where a linear increase in export with increasing soil P

would be expected (Inchiquin and Dromore, 6-10 mg l^{-1} Morgan's P). The Cullaun catchment has soil P ranging from 3-6 mg l^{-1} Morgan's P which is below the 'breakpoint'. Therefore some increase in soil P with a corresponding increase in export would be expected in at least two of the lakes.

Secondly, it is often difficult to determine if a trend has occurred from a limited time series (Foy *et al.*, 1995), but this may not be a serious obstacle as two continuous years data was available in both the 1980s and 1990s. Thirdly, there is a possibility the inflowing concentrations were higher but this was not detected in mid-lake samples. McGarrigle *et al.* (1994) found that the inflowing concentration of TP to Lough Conn increased from 44.9 μg l^{-1} TP in 1981 to 65.6 μg l^{-1} TP in 1991 (two years with similar runoff). However, no significant increase in TP or chlorophyll *a* was detected in mid-lake samples. Loss processes within the lake and increased shoreline algal growths were postulated as reasons why no increase was observed in mid-lake TP. The situation in the Clare lakes may be different to Lough Conn. Loss processes may be expected to be lower because three of the four Clare lakes had very short residence times (means values in years for 1996-7 were: Inchiquin = 0.11, Cullaun = 0.08, Ballycullinan = 0.20 and Dromore = 1.79) in comparison with Lough Conn (0.8). Winter concentrations in the Clare lakes may therefore be similar to inputs (Lough Inchiquin was flushed 2.6 times in October 1996). The situation in Lough Conn may also be contrasted with Lough Ree where increases in both inflow and mid-lake TP were found to have occurred since the 1980s, probably as a result of the shorter residence time (0.2 year) (Bowman, 1996).

Fourthly, an increase may be masked in these lakes because of co-precipitation of PO_4^{3-} with carbonates (Otsuki & Wetzel, 1972). These lakes are known to precipitate marl (Findlay, 1996) and the decline in Ca^{2+} concentration by 7.2 mg l^{-1} in summer in Inchiquin may be evidence of this (Chapter 4, Figure 4.18). However, substantial precipitation of PO_4^{3-} only occurs when the pH is above 8.5 (Otsuki & Wetzel, 1972), which was only once recorded in Lough Dromore and Inchiquin in summer (maximum = pH 8.56). Phosphate loss by precipitation may, therefore, be mainly a summer phenomenon. If P had increased over the last 16 years then the increase should have been apparent in winter.

Finally, the lack of an expected increase may be because of higher P retention in the soils. As the soil parent material in the catchments is limestone then precipitation and adsorption with Ca would be expected (Pierzynski *et al.*, 2000). However, Daly (2000) examined the adsorption capacity of Irish agricultural soils and found that the total P sorption capacity was strongly correlated ($p = 0.001$) with Al and Fe concentrations but not with Ca. This supported Power *et al.* (1993) who found that acid brown earth soils derived from Clare shales had higher adsorption capacities than calcareous soils in Clare and Galway. However, the hydraulic properties of the soils may also be important. If rainfall drains to a greater depth in a soil this would substantially increase the potential for adsorption. The soils in the four Clare catchments are predominantly well drained, with only 13 to 25% being classed as poorly drained wet soils using the criterion of Daly (2000). Therefore, even though the total sorption capacity in Clare soils may be lower than or similar to other soils, the fact that they are well drained may bestow a greater adsorption potential. In support of this, Tunney *et al.* (2000), despite finding that limestone soils did not have a greater total sorption capacity than other soil types, suggested that higher P application on limestone soils may be compatible with good water quality. The determination of sorption capacity experimentally on a per weight basis will not account for the greater adsorption potential a well-drained soil has. In conclusion, several processes mentioned above may be combining to mitigate against increased P concentrations in freshwaters in Co. Clare. Further study should focus on obtaining information on farm management and soil P over the last 20 years. A field experiment on calcareous soils under Irish climatic conditions would also be beneficial.

6.4.3 Variation in total phosphorus among lakes

The 31 lakes examined had a very wide range in TP concentration (1 - 344 $\mu g\ l^{-1}$) (Table 6.4). This contrasts with Northern Ireland where a survey of 604 lakes found only four had a TP concentration less than 10 $\mu g\ l^{-1}$. This situation is similar to that of England whereas in Scotland 73% of lakes had a TP of less than 10 $\mu g\ l^{-1}$ (Foy & Bailey-Watts, 1998).

Catchment characteristics that described agriculture (mainly pasture) were the most strongly correlated with TP export and concentration in both the 31 and 189 lake data-sets. It was initially thought to be important that silage explained the most variation in TP export ($r^2 = 0.64$) (Figure 6.9). The proportion of grassland used for silage has increased in

Ireland since the 1960s and may be associated with increased nutrient export. This is because silage production is associated with the highest rate of fertiliser application to grassland, winter housing of cattle and disposal of slurry, all of which can lead to increased P export (McGarrigle *et al.*, 1994; Murphy *et al.*, 1997; Allott *et al.*, 1998; Morgan *et al.*, 2000; Kurz, 2000). However, the high r^2 with silage was highly influenced by four lakes that had a high proportion of silage and P export (Figure 6.9). There was only a small difference between the non-parametric r_S values for silage and other agricultural variables such as cattle (ha^{-1}) (Table 6.5). In addition, TP concentration in the 189 lakes was more strongly correlated with the proportion of agriculture (CORINE) than silage. However, the effects of management practices in areas used for silage are less likely to be detected in lake samples than in samples from streams draining such areas. Further work could indicate the importance of different farm management practices by measuring annual TP export from streams draining different areas of an agricultural catchment. In any case, the significant relationships found all point to agriculture as the major determinant of TP export and lake TP concentration in Ireland. Previous work in Northern Ireland supports this: Foy & Withers (1995) found significant empirical relationships between cattle density and flow-weighted TP in streams.

It was clear that agricultural catchments with a higher proportion of wet soils exported the most TP (Figure 6.9 to Figure 6.12). Wet soils have impaired drainage which may increase TP export by promoting overland flow and also by reducing infiltration and subsequent adsorption. This finding supports the conclusion of Daly *et al.* (2000) who found river MRP concentrations were higher in Irish catchments with wet soils. An additional factor that is likely to contribute to the higher export of TP from catchments with wet soils is their lower potential for chemical precipitation when compared to waters draining dry soils (brown earths and brown podzolics). Catchments with greater than 52% wet soils had a median alkalinity of only 20 mg l^{-1} $CaCO_3$ compared with 97 mg l^{-1} $CaCO_3$ in catchments with less than 33% wet soils. Higher losses of PO_4^{3-} by co-precipitation with carbonates (Otsuki & Wetzel, 1972) during transport to and within lakes may therefore occur in catchments with dry soils and such losses have been considered important in reducing P loading in Irish freshwaters (Bowman, 1996).

When the 189 lakes were separated into regional groups, only two groups (Monaghan - Cavan and Kerry - Cork) had significant relationships ($p < 0.05$) between TP concentration

and the proportion of agriculture in the catchment (Table 6.7). It was thought that as samples were collected in summer internal loss processes might obscure relationships with agriculture. However, Gibson *et al.* (1996) in an examination of the TP cycle found that the minimum was significantly correlated with the maximum ($r^2 = 0.57$, $p \leq 0.001$, $n = 27$) so some response to increased TP inputs from agriculture should be apparent. This is especially so since a similar relationship was found in this study - the minimum in the 30 lakes (Egish removed) increased linearly with both the mean ($r^2 = 0.97$, $p \leq 0.0001$) and maximum ($r^2 = 0.90$, $p \leq 0.0001$).

One reason for the lack of a relationship in some regions may be because of differences in farming intensity. The Cavan - Monaghan and Cork - Kerry areas have a higher quality of farming land than the other regions (Department of Agriculture and Food, 1989). Other areas may have a lower farming intensity which could explain why no increase in lake TP with agriculture was observed. This would be consistent with the concept of a 'breakpoint' where an increase in freshwater P is only observed after soil P reaches a certain level (Jordan *et al.*, 2000). In addition, other environmental factors specific to some regions may mitigate against TP loss. It was argued above that three Clare lakes, contrary to the national trend, displayed no increase in TP over 16 years because of the high adsorption potential of their well-drained soils. That TP did not show a trend with the proportion of agriculture in Clare - Galway supports this. Finally, care must be taken in drawing conclusions about these geographic groups as only one sample in summer was taken and the sample size was small compared to the total population of over 5500 lakes in Ireland (Irvine *et al.*, 2001).

6.4.4 Modelling of TP export using an export coefficient approach

The application of two published export coefficient models to the 30 lakes in this study explained 63% (Johnes *et al.*, 1994a, b) and 26% (Jordan *et al.*, 2000) of the variation in 'observed' export (observed export was actually calculated using mid-lake concentrations and estimated runoff). Exclusion of catchments with dry soils improved the r^2 to 0.56 in the model of Jordan *et al.* (2000). In six lowland catchments with intensive agriculture the predictions of the model of Johnes *et al.* (1994a, b) were strongly correlated with observed export ($r^2 = 0.93$, $p = 0.002$). The model substantially overestimated export but because of the high correlation between predicted and observed it may be possible to down-scale the

coefficients to accurately predict TP export to lowland lakes. In contrast, no significant correlation was found between observed and predicted export in the limestone or upland catchments. Prediction of TP loads may be difficult in limestone catchments because of the complex drainage, inaccuracies in catchment delineation and possible superior adsorption capacities of some of the soil profiles. The poor prediction by the model of Johnes *et al.* (1994a, b) for upland catchments indicates that the approach of assigning a single export coefficient of 0.02 to non-agriculture upland areas may be too simple and more detailed studies may be necessary to develop suitable coefficients for uplands. Atmospheric P deposition is a major input to these catchments but no information on the geographic variation of deposition is available (Jordan, 1997).

There may be other possible explanations for the differences between 'observed' and predicted export. The fact that human population density was significantly correlated with the residuals of the model of Jordan *et al.* (2000) indicated that P export from septic tanks might have been a significant source. Other factors that may explain further variation include the proximity of land classes to freshwaters and soil P concentrations. Johnes and Heathwaite (1997) determined land classes in a 50 m riparian zone and allocated them higher P export coefficients in order to achieve an improved model. In addition, it must be stated that errors will be present in the calculation of the observed export because it was calculated using mid-lake concentration using the formula of Foy (1992). Export may be overestimated because of elevated mid-lake TP caused by the release of P from sediments in shallow lakes and also underestimated owing to co-precipitation with $CaCO_3$ in calcareous lakes.

Both the models of Johnes *et al.* (1994a, b) and Jordan *et al.* (2000) tended to overestimate the export of TP to the lakes. This may be indicative of the lower lake TP concentrations found in the Republic of Ireland in comparison with where the models were developed – Northern Ireland (Jordan *et al.*, 2000) and England and Wales (Johnes *et al.*, 1994a, b) (Foy & Bailey-Watts, 1998). The higher export in the catchments used by Johnes *et al.* (1994a, b) may be because of higher soil P rather than direct fertiliser losses as current fertiliser additions are similar (mean = 12 kg P ha^{-1} yr^{-1} in Johnes *et al.* (1994a, b) compared with a mean of = 13 kg P ha^{-1} yr^{-1} in Murphy *et al.* (1997)).

It was surprising that the model of Jordan *et al.* (2000) did not explain more variation in TP export to the 30 lakes. Better results were expected because data from the CORINE database used by Jordan *et al.* (2000) was also used in this study. In addition, as Northern Ireland is geographically close it was expected that the coefficients would be more suitable as Clesceri *et al.* (1986) found that coefficients are often region specific. One reason for the poor results may be that many of the coefficients were derived by multiple regression of land class areas (ha) on total loads (kg yr^{-1}). This approach may not be as valid as the application of coefficients derived from field studies and may produce counter-intuitive results (Young *et al.*, 1996). For example, McGuckin *et al.* (1999) used the multiple regression approach and implausibly recorded a negative export in the moor and heath CORINE category. Some of the coefficients used by Jordan *et al.* (2000) were from McGuckin *et al.* (1999) but when counter-intuitive coefficients were produced other published sources were used. Furthermore, validation of the model by Jordan *et al.* (2000) was based on a regression of observed with predicted loads (tonnes). The validation appeared successful ($r^2 = 0.89$) but may have been highly influenced by not dividing the loads by catchment area prior to validation. Very large catchments will export more TP than small catchments by virtue of their larger catchment area alone. Another factor that may account for the model's poor performance is that the CORINE information was gathered at low resolution. The minimum size of land class resolved was 25 ha (O'Sullivan, 1992) and seven of the catchments in this study were less than 500 ha.

The application of the model of Johnes *et al.* (1994a, b) involved splitting the 31 lakes into three groups according to catchment characteristics and applying a different suite of export coefficients for each group. This followed the original approach of Johnes *et al.* (1994a, b) where export coefficients were applied from published literature according to catchment attributes such as the intensity of agriculture (upland or lowland), slope, runoff and rock type. In contrast, Irvine *et al.* (2000) applied a single suite of export coefficients to these lakes in order to indicate the general applicability of the coefficients. One of the benefits of grouping the lakes is that it allows differences in export from different catchment types to be taken into account. For example, higher coefficients were applied to cattle and permanent grassland in lowland catchments than upland catchments. This may reflect higher export in lowland catchments owing to higher soil P levels.

6.4.5 Hindcasting of TP

Combining the models of Johnes *et al.* (1994a, b) and Tunney *et al.* (2000) produced hindcasted estimates of TP export in 1950. It was estimated that TP export to six lowland lakes in agricultural catchments has increased by between 51 and 150% since 1950 (Table 6.10). These estimates were within the range found in Northern Ireland by Anderson (1997) who found that diatom inferred changes in concentration from before 1940 to the 1990s varied widely from between -17 to 478% (Table 6.11).

This approach taken to hindcasting TP loads has several benefits. Firstly, varying the coefficients according to soil P is based on recent work that found a strong relationship between soil P and P export (Tunney *et al.*, 2000). Secondly, the method is relatively simple to use and less time consuming than using diatoms from sediment cores to infer TP. In addition, the lakes were mainly in the intensively farmed Cavan-Monaghan region where finding a lake in pristine condition to determine spatially based reference conditions would be very difficult.

The performance of the model may be improved if information on present and historical soil P was available at catchment level. The approach used assumed that the national average soil P in 1950 (0.8 mg l^{-1} Morgan's P) was an accurate estimate for all catchments, which is likely to be a gross simplification. In addition, the soil P measurements are only published from 1950, which means that the approach may not provide estimates of TP from an earlier period. Earlier estimates would be desirable if the method was to be used to define reference conditions for lakes as Anderson (1997) showed that increases occurred in TP between 1900 and 1940 in addition to larger increases after 1940 (Table 6.11). Despite these drawbacks the approach may be useful in lake management. The water framework directive (Council of the European Communities, 2000) requires EU states to define reference conditions by using either a spatial comparison of lakes or modelling or failing this by expert opinion. Perhaps, following further validation, the model could be used to hindcast export for 1950 with expert opinion being used to estimate export prior to 1950.

Table 6.11 Diatom-inferred TP μg l^{-1}, measured TP μg l^{-1} and percentage change in TP in four lakes in Northern Ireland (Anderson, 1997).

Lake	Diatom-inferred pre 1900 minimum TP	Diatom-inferred pre 1940 mean TP	Measured TP 1990s	Measured mean TP 1990s	Predicted % change Pre 1940 to 1990s
Ballywillin	36	67	310, 464	387	478
Brantry	33	66	23, 50, 91	55	-17
Corbet	58	89	285	285	220
Heron	25	51	121	121	137

6.5 Conclusions

- The seasonal cycle of TP in the lakes was variable, although the majority of lakes displayed an autumn/winter maximum followed by a spring/summer minimum.
- High summer rainfall led to increased TP in lakes with agricultural catchments in August 1997. This finding, coupled with similar observations from contemporaneous field experiments (Tunney *et al.*, 2000) indicates that short rainfall events in agricultural catchments in summer can result in substantial P loss with serious implications for lake quality.
- In contrast to national trends, no increase in TP concentration was found in three lakes in County Clare since 1981. It is possible that this was mainly because of a greater adsorption potential of the soils owing to their higher infiltration capacity.
- Most empirical relationships found were between TP and descriptors of agriculture in catchments but these relationships typically explained less than 60% of the variation in TP. This was probably a result of the complex behaviour of P in catchments.
- An examination of the 30 lakes (Lough Egish excluded) indicated that catchments with well-drained soils tended to export less P.
- The export estimates produced by the export coefficient model of Johnes *et al.* (1994a, b) were strongly correlated to 'observed' export in six lowland catchments with intensive agriculture. The model was not successful in predicting export in upland and limestone catchments.
- Combining the models of Johnes *et al.* (1994a, b) and Tunney *et al.* (2000) produced hindcasted estimates of TP export in 1950. It was estimated that TP export to six lowland lakes in agricultural catchments has increased by between 51 and 150% since 1950.

7. THE VARIATION IN THE CONCENTRATION AND FRACTIONS OF NITROGEN WITH CATCHMENT CHARACTERISTICS

7.1 Introduction

7.1.1 Nitrogen in the environment

Nitrogen is the most abundant gas in the Earth's atmosphere comprising 78% N_2 by volume (Manahan, 1994). It is important biologically as it is an essential component of proteins and therefore plays a role in the nutrient economy of freshwaters. It is generally thought to be a more frequent limiting nutrient in marine waters than freshwaters (Barnes & Hughes, 1988). Nitrogen exists in a variety of forms in the environment. Gaseous fractions include the stable dinitrogen molecule (N_2), nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3), ammonium (NH_4^+) and organic nitrogen. Freshwater contains the fractions present in the atmosphere and also nitrite (NO_2^-), nitrate (NO_3^-), NH_4^+, urea ($CO[NH_2]_2$) and organic nitrogen (Sprent, 1987; Horne & Goldman, 1994).

Nitrite is perceived as being mainly a transient fraction in oxygenated freshwaters. Of the biologically available fractions, NH_4^+ is the most readily assimilated whereas NO_3^- is the most abundant (Stewart, 1980; Smith *et al.*, 1995). Dissolved organic nitrogen consists of complex molecules of biological origin that are derived from either allochthonous or autochthonous sources (e.g. algal exudates). Particulate organic nitrogen in lakes is mainly of biological origin (mostly algae and zooplankton).

The aims of this chapter are to determine the principle factors controlling total nitrogen (TN) concentration and its constituent fractions in Irish lakes. The objective is to produce a regression model capable of predicting total nitrogen concentrations. Ideally the model should have the ability to project future trends and hindcast past concentrations. Other aims are the examination of the seasonal variation in nitrogen fractions and comparison with past (1980s) concentrations. Factors that influence N are now introduced separately as inputs, outputs and other controlling factors. This is followed by a literature review of previous work that has related catchment characteristics to nitrogen in freshwaters.

7.1.2 Sources and regulation of nitrogen in the drainage area

The inputs, outputs and cycling of nitrogen in grassland are presented schematically in Figure 7.1. These flows of nitrogen are discussed below in terms of inputs, outputs and processes controlling these flows.

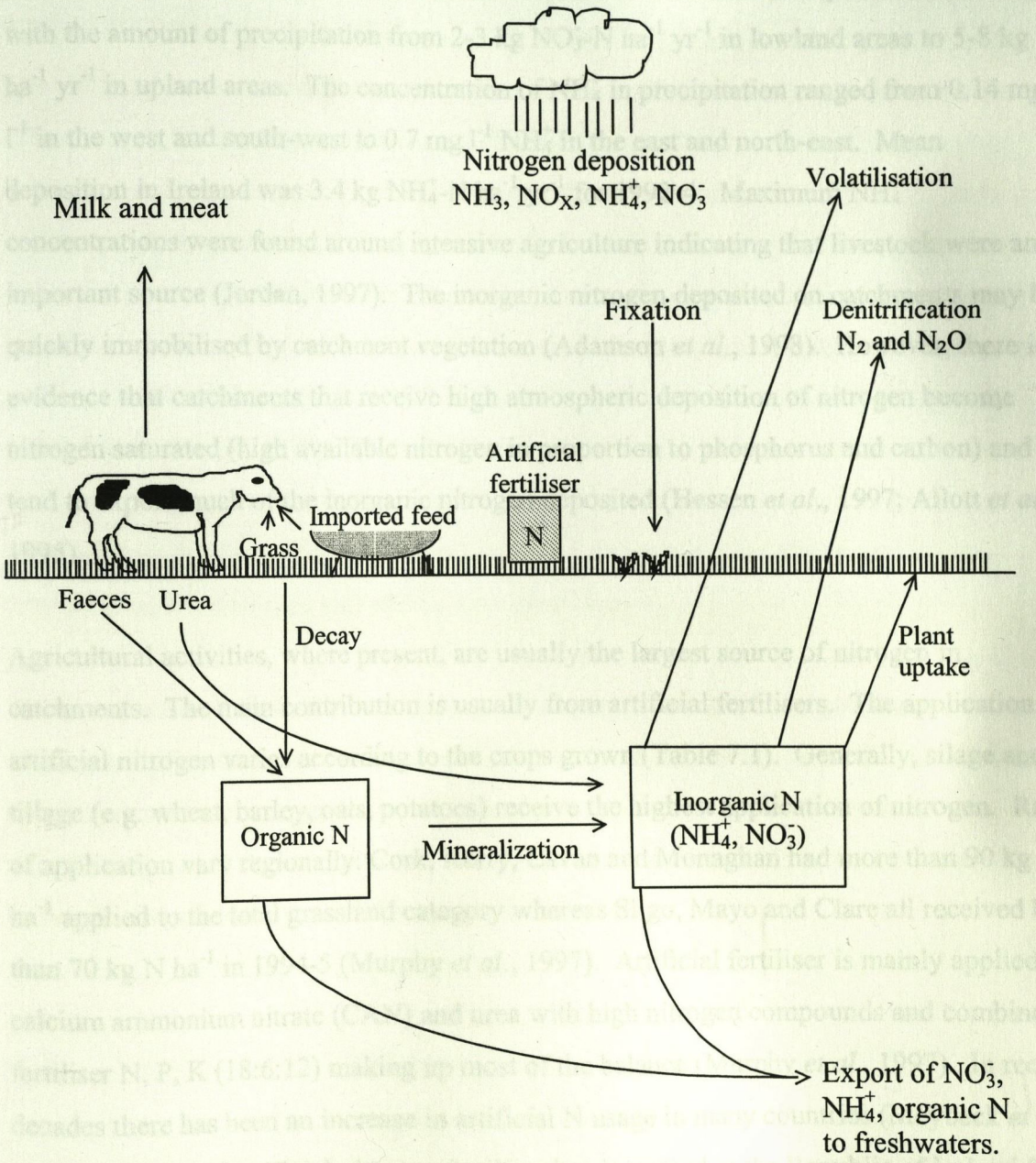


Figure 7.1 Flow diagram of nitrogen transformations in grassland (Smith *et al.*, 1995).

Nitrogen is introduced into the terrestrial ecosystem in precipitation and dry deposition. The principal fractions are NO_3^- and NH_4^+; organic nitrogen is less frequently measured but concentrations can be important (Gibson *et al.*, 1995b; Adamson *et al.*, 1998). Jordan (1997) found that concentrations of NO_3^- in Irish precipitation ranged from 0.14 mg l^{-1} in the west to over 0.56 mg l^{-1} in the east and south-east. Total annual deposition increased with the amount of precipitation from 2-3 kg NO_3^--N ha^{-1} yr^{-1} in lowland areas to 5-8 kg ha^{-1} yr^{-1} in upland areas. The concentration of NH_4^+ in precipitation ranged from 0.14 mg l^{-1} in the west and south-west to 0.7 mg l^{-1} NH_4^+ in the east and north-east. Mean deposition in Ireland was 3.4 kg NH_4^+-N ha^{-1} yr^{-1} for 1992-4. Maximum NH_4^+ concentrations were found around intensive agriculture indicating that livestock were an important source (Jordan, 1997). The inorganic nitrogen deposited on catchments may be quickly immobilised by catchment vegetation (Adamson *et al.*, 1998). However, there is evidence that catchments that receive high atmospheric deposition of nitrogen become nitrogen saturated (high available nitrogen in proportion to phosphorus and carbon) and tend to export much of the inorganic nitrogen deposited (Hessen *et al.*, 1997; Allott *et al.*, 1995).

Agricultural activities, where present, are usually the largest source of nitrogen in catchments. The main contribution is usually from artificial fertilisers. The application of artificial nitrogen varies according to the crops grown (Table 7.1). Generally, silage and tillage (e.g. wheat, barley, oats, potatoes) receive the highest application of nitrogen. Rates of application vary regionally: Cork, Kerry, Cavan and Monaghan had more than 90 kg N ha^{-1} applied to the total grassland category whereas Sligo, Mayo and Clare all received less than 70 kg N ha^{-1} in 1994-5 (Murphy *et al.*, 1997). Artificial fertiliser is mainly applied as calcium ammonium nitrate (CAN) and urea with high nitrogen compounds and combined fertiliser N, P, K (18:6:12) making up most of the balance (Murphy *et al.*, 1997). In recent decades there has been an increase in artificial N usage in many countries (Meybeck *et al.*, 1989). The use of artificial nitrogen fertiliser has increased in the Republic of Ireland from 87,100 tonnes in 1970-71 to 416,918 tonnes in 1995-96 (Figure 7.2). In Northern Ireland, fertiliser usage has increased from approximately 40 kg N ha^{-1} yr^{-1} to 120 kg N ha^{-1} yr^{-1} between 1970 and 1991 (Smith *et al.*, 1995).

The increased use of artificial fertilisers has led to an increase in freshwater NO_3^- concentrations (Meybeck *et al.*, 1989). In the Ondava-Stropkov catchment in Slovakia NO_3^- increased with fertiliser application (0.7 mg l^{-1} NO_3^- with 6 kg N ha^{-1} yr^{-1} in 1950 to 11.7 mg l^{-1} NO_3^- with 168 kg N ha^{-1} yr^{-1} in 1986/87) and after a sharp decline in fertiliser use in 1988 there was a corresponding decline in river nitrate (Pekárová & Pekár, 1996). Increased fertiliser use in the Slapy reservoir catchment (Czech Republic) between 1959 and 1990 led to an increase in the mass ratio of TN to TP because P was retained more effectively in the catchment soils than N (Kopáček *et al.*, 1995). Such patterns within individual catchments provide strong evidence that the use of artificial fertiliser leads to higher nitrate in freshwaters. Examination of a long time-series within a single catchment rather than on a regional basis removes variation associated with additional catchment parameters (e.g. soils, slope). It is widely accepted that leaching of nitrogen directly from artificial fertiliser is not the principal method of export to freshwaters (e.g. Addiscott, 1988; Vagstad *et al.*, 1997). Tracing of nitrogen to determine its source has shown that artificial nitrogen is usually cycled within the soil before being exported to freshwater (Addiscott & Powlson, 1992). Factors that affect this cycling include temperature, precipitation and soil type and will be discussed later.

Slurry and manure applied to land supply substantial amounts of nitrogen. However, as slurry most often originates from consumption of grass, hay or silage produced within the catchment it does not represent an additional source. It does however represent a significant process whereby nitrogen is cycled in the catchment. Imported feed for livestock also represents an additional source of nitrogen.

Table 7.1 Fertiliser used on different land use categories in selected counties of Ireland for 1994 and 1995 (Murphy *et al.*, 1997). The all crops category is an average of different crop types for each county. Total grassland refers to N usage for silage, grazing and hay. Rough grazing was not included in the survey.

Counties	Silage kg N ha^{-1}	Grazing kg N ha^{-1}	Hay kg N ha^{-1}	Total grassland kg N ha^{-1}	All crops kg N ha^{-1}
Cavan	78	78	44	90	67
Clare	88	49	36	57	98
Cork	156	164	75	173	116
Donegal	115	63	79	83	116
Galway	101	62	47	80	90
Kerry	109	90	48	102	167
Leitrim	49	19	31	21	191
Longford	81	50	34	59	33
Mayo	105	50	60	66	70
Monaghan	107	97	43	111	61
Roscommon	53	36	24	38	89
Sligo	81	38	39	62	111
Westmeath	104	51	38	71	77
Wicklow	122	87	67	83	122
Average	**96**	**67**	**48**	**78**	**101**

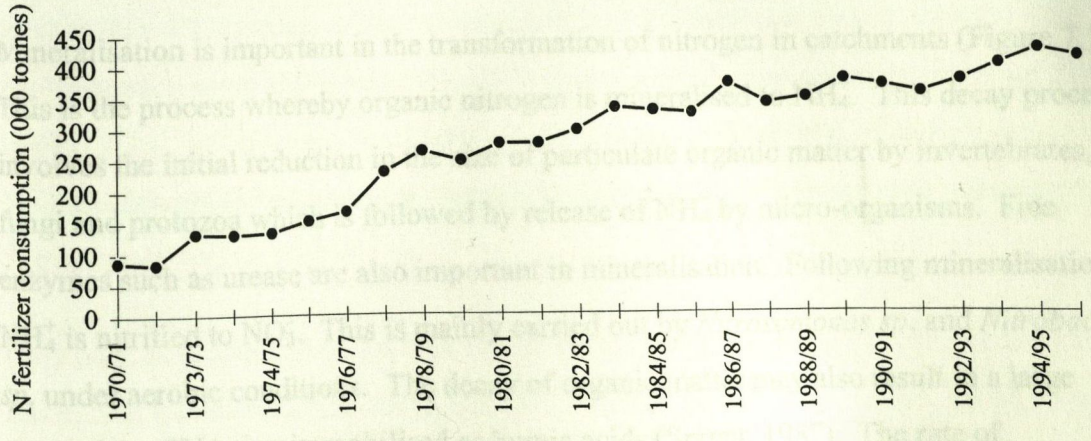


Figure 7.2 Annual sales of nitrogen fertiliser in the Republic of Ireland (Minister for Agriculture Food and Forestry, 1999†; Murphy *et al.*, 1997).

† http://www.irlgov.ie/daff/tabmenu.htm

Biological fixation is another source of nitrogen in catchments. Nitrogen fixing organisms include Cyanobacteria, other bacterial genera and bacteria located in the root nodules of legumes. Biological nitrogen fixation involves the reduction of dinitrogen gas to ammonia and molecular hydrogen and is catalysed by the enzyme complex nitrogenase. This process takes place in the absence of oxygen (Sprent, 1987). Nitrogen fixation in an experimental field (Co. Down, Northern Ireland) with a high percentage of clover (11 - 18%) was estimated to be 202 to 236 kg N ha^{-1} yr^{-1}. The leaching of NO_3^- from the clover plot was similar to grass plots receiving 300 kg N ha^{-1} yr^{-1} (Garrett *et al.*, 1992). However, clover coverage is generally much smaller than this and Smith *et al.* (1995) estimated biological fixation of nitrogen to be 10 kg N ha^{-1} yr^{-1} in Northern Ireland.

Another source of nitrogen in catchments may be from the release of nitrogen stored in bedrock. Holloway *et al.* (1998) found high concentrations of TN in several rocks including slate (997 ± 377 mg N kg^{-1}) and biotite schist (717 ± 145 mg N kg^{-1}). Nitrogen mainly occurred in inorganic form although slate also contained organic nitrogen. The inorganic nitrogen was assumed to be NH_4^+ incorporated into muscovite and sericite. Intrusive igneous rocks such as granite had a much lower concentration of less than 50 mg N kg^{-1}. Holloway *et al.* (1998) attributed differences in stream NO_3^- to rock type in catchments that were otherwise similar.

Mineralisation is important in the transformation of nitrogen in catchments (Figure 7.1). This is the process whereby organic nitrogen is mineralised to NH_4^+. This decay process involves the initial reduction in the size of particulate organic matter by invertebrates, fungi and protozoa which is followed by release of NH_4^+ by micro-organisms. Free enzymes such as urease are also important in mineralisation. Following mineralisation, NH_4^+ is nitrified to NO_3^-. This is mainly carried out by *Nitrosomonas sp.* and *Nitrobacter sp.* under aerobic conditions. The decay of organic matter may also result in a large proportion of N being immobilised as humic acids (Sprent, 1987). The rate of mineralisation increases at higher temperatures. Ferrier *et al.* (1995) have predicted that climate change in Scotland will increase temperature and affect seasonal rainfall patterns thereby decreasing soil moisture status. The resultant changes in mineralisation, river flow and denitrification were predicted to lead to a net increase in river NO_3^- of 121% (approximately 2 mg l^{-1} NO_3^--N) by the years 2050-2060.

Processes whereby nitrogen is removed from the drainage area include volatilisation, denitrification, export of farm produce and export to aquatic systems (Figure 7.1). Volatilisation is the process whereby ammonia (NH_3) is lost to the atmosphere. Total NH_3 emissions from agriculture in Ireland have been estimated as 108.2 kilo tonnes yr^{-1} (Carton & Harnett, 1990). Grazing livestock, landspreading of manures and stored manure account for 48%, 40% and 12%, respectively, of agricultural NH_3 emissions (Carton & Harnett, 1990). The proportion volatised that is returned to the land is estimated as 75% (Johnston & Jenkinson, 1989 cited in Garrett *et al.*, 1992). However, local deposition is affected by site characteristics such as the type of vegetation and the concentration of NH_3 in the air at the site of deposition. In general non-agricultural areas located close to agriculture receive higher deposition (Sutton *et al.*, 1998). Given that Irish agriculture is mainly cattle-based with resulting high NH_3 emissions it is surprising that no work has quantified its effect on upland catchments and their freshwaters.

Denitrification by organisms (about 25 genera) occurs in most environments under anaerobic conditions. The process can involve a series of steps from NO_3^- to NO_2^- to NO to N_2O and N_2. Chemodenitrification leads to the production of NO and may be considerable in environments of low pH (Sprent, 1987). Conditions that promote denitrification include soil NO_3^- concentrations higher than 2 mg N kg^{-1}, high soil moisture and a soil temperature greater than 4°C (Jordan, 1989). Garrett *et al.* (1992) recorded mean (1989-92) denitrification rates of 9% and 11% of N input at grazed grassland sites receiving 100 and 200 kg N ha^{-1} yr^{-1} nitrogen fertiliser in County Down. About 40% of soil emissions of N_2O are thought to be induced by agricultural nitrogen input into catchments (Kroeze & Seitzinger, 1998).

Only a small proportion of the N in forage is retained by ruminants (15% in dairy cattle, 5% in beef cattle and 3% in sheep) (Blaxter cited in Garrett *et al.*, 1992). Garrett *et al.* (1992) found that the mean retention of N in cattle over 3 years on a plot receiving 100 kg N ha^{-1} yr^{-1} fertiliser was 17 kg N ha^{-1} yr^{-1}. Nitrogen retention in the cattle increased at higher N application but the efficiency decreased.

The export of nitrogen to freshwaters is dependent on many variables including season, land management practices, vegetation, soil type, nitrogen fraction and precipitation.

Export is generally higher in winter than in summer. Neill (1989) found higher NO_3^- concentrations in rivers in south-west Ireland during winter. This was attributed to increased leaching, lower plant uptake and nitrogen derived from decay of plants in the drainage area. Lower NO_3^- in summer was attributed to increased NO_3^- uptake by vegetation and less precipitation to export NO_3^-. However, a winter maximum in NO_3^- concentration is not always found; for example Hooda *et al.* (1997) found higher NO_3^- concentrations in some streams in Scotland during summer which they suggested may be because of a 'concentration effect' where the measured concentration of NO_3^- may be higher owing to a lower volume of rainfall passing through the soil and evaporative concentration of NO_3^-. Nitrate concentration tends to increase initially with precipitation in winter, after which a gradual decline takes place with late winter rainfall (Jordan & Smith, 1985). Arheimer *et al.* (1996) worked on Swedish and Finnish streams and noted that at high flows, streams with low annual NO_3^- concentrations tended to show a dilution of NO_3^-. Catchments that showed a dilution at high flows tended to have a low slope and a high proportion of organic soils.

The type of agricultural practice has an important influence on N loss from catchments. Ploughed fields may release considerably more nitrogen than grassland (Ryden *et al.*, 1984; Neill, 1989). Nitrate loss from grazed grassland can be more than five times higher than that of cut grassland. However, if cut grass is used as feed and organic waste is returned to the grassland then no substantial difference in NO_3^- loss should occur over the long term (Ryden *et al.*, 1984). The period of time livestock are allowed to graze the catchment is also likely to affect nitrogen in the catchment (Jordan & Smith, 1985). This is largely regulated by the growing season of grass which decreases from south to north in Ireland. Slurry collected from animal housing units is generally returned to the catchment by spreading in autumn or spring. The period in which slurry may be spread is restricted by disease control measures and by prevailing weather (Carton & Harnett, 1990). If the application of fertiliser is followed by heavy rainfall, substantial export to rivers may occur. However, the amount exported during such events may be lower than occurs following similar rainfall in winter because of the uptake of N by plants in summer (Garrett *et al.*, 1992). However, a high nutrient export in the summer may have a more significant impact on freshwater quality.

The application of artificial fertilisers also influences the export of nitrogen. Garrett *et al.* (1992), working on fertilised grazed plots in County Down, found that nitrate was the dominant fraction lost. The loss of NO_3^- and NH_4^+ increased with increasing fertiliser application but the loss of total Kjeldahl nitrogen (corresponding to the NH_4^+ and organic fractions) was independent of nitrogen input. Garrett *et al.* (1992) found that the amount of N leached following fertiliser application differed between countries. In several countries the amount of NO_3^- leached had a curvilinear response to fertiliser input. Nitrate leaching was initially minimal because nitrogen application did not exceed demand and this was followed by a break in the response curve where leaching was more linear with fertiliser application (Garrett *et al.*, 1992). In contrast, in Ireland the export of nitrogen with increasing fertiliser has been shown to be linear rather than curvilinear in both plot experiments (Garrett *et al.*, 1992) and long-term studies of catchments (Smith & Stewart, 1989). The reason for this linear relationship in Ireland, as proposed by Garrett *et al.* (1992), is that the supply of nitrogen from soil organic matter (and mineralisation of soil organic matter) decreases as the addition of artificial nitrogen increases. This leads to a more linear response of leaching to nitrogen application rather than the curvilinear response observed at drier sites with less soil organic matter.

Vegetation exerts substantial control on the export of nitrogen to freshwaters. As mentioned above this is evident in the seasonal pattern of nitrogen concentrations in rivers in temperate regions. Nitrogen in freshwater tends to be highest in winter and lowest in spring owing to uptake by vegetation in the catchment (e.g. Reynolds *et al.*, 1994). In catchments dominated by agriculture, poor crop growth or crop failure may lead to an increase in nitrogen exported to rivers providing rainfall is sufficient (Vagstad *et al.*, 1997). In addition, the presence of trees and shrubs close to rivers (riparian zone) can have the effect of decreasing the concentration of nitrogen exported (Peterjohn & Correll, 1984). Stream NO_3^- has been found to increase with conifer maturity (especially > 30 years) in Welsh upland catchments (Reynolds *et al.*, 1994). This was attributed to increased mineralisation in older stands. Storage of N in biomass represents a temporary removal of nitrogen from the reactions of the system. Freifelder *et al.* (1998) cites values of 50 kg N ha^{-1} yr^{-1} for temperate forests and 4 kg N ha^{-1} yr^{-1} for storage in soil organic matter in California.

The export of nitrogen from catchments is certainly dependent on sufficient precipitation to export the nitrogen. In Slovakia when the hydrologic year 1990-91 had approximately half the runoff of the long-term average, NO_3^- export from five catchments was only 35% to 66% of average levels (Pekárová & Pekár, 1996). Gasser (1980) collated data from three grassland sites in the UK and found that as precipitation increased NO_3^- concentrations in the drainage water decreased. However, the reverse was true for export where higher precipitation led to higher export. It is, therefore, important to consider precipitation when relating land use to nitrogen concentration in freshwaters.

Nitrate may be more readily exported than NH_4^+. This is because NH_4^+ is both adsorbed to soils and preferentially taken up by biota (Curtis *et al.*, 1998).

7.1.3 Nitrogen in freshwaters

The main input of N to lakes is usually through inflowing rivers but other sources may be important in summer when the NO_3^- load in inflowing rivers is low. Such inputs include nitrogen contained in precipitation falling directly onto the lake surface and nitrogen fixation by Cyanophytes. Nitrogen fixation may be at a maximum in late summer and autumn when Cyanophytes are present and the concentration of phosphate is high. Nitrogen fixation is suppressed when NH_4^+ and NO_3^- are present. In Lough Windermere, nitrogen fixation accounted for 0.2 to 0.5% of the annual nitrogen budget. In drier climates nitrogen fixation in eutrophic lakes can account for up to 80% of the annual nitrogen budget. Lake sediment may also release NH_4^+ and NO_3^- into the water column (Horne & Goldman, 1994).

Loss of N from lakes takes place by export through the lake outflow, denitrification and sedimentation of both algae and detritus. Loss of N by denitrification takes place mainly in the anoxic part of the sediment and usually exceeds nitrogen fixation rates (Horne & Goldman, 1994). Lakes are effective nitrogen traps. Arheimer & Brandt (1998) found that the N load in southern Sweden was greatly reduced by lakes - an average reduction of 45% which equates to a retention of 30-40 kg N per hectare of lake area annually. Stewart *et al.* (1976) found than total nitrogen in inflowing waters decreased from 8.47 mg l^{-1} to 3.10 mg l^{-1} after passing through two loughs in Scotland. This represented a decrease of 63% of inflow TN concentration.

Nitrate is the principal inorganic nitrogen fraction in lakes. For example, Allott (1990) found that NO_3^- comprised an average of 62% of TN in Lough Inchiquin (Co. Clare) whereas NH_3 comprised only an average of 1.3% (max. = 3.7%). Even in rivers that receive effluent from sewage treatment works NH_4^+ can be a small proportion of TN export (0.3 - 1.2%) (Russell *et al.*, 1998). Nitrite is generally a very small proportion of inorganic N in Irish waters (Smith *et al.*, 1995). The principal organic fractions of N in lakes can be divided into dissolved organic nitrogen and particulate organic nitrogen (mainly in algae and zooplankton). The proportions of the N fractions change within lakes seasonally. Nutrient uptake by algae will cause a seasonal decline in the major inorganic N fractions with a corresponding increase in particulate organic nitrogen. The seasonal decline in inorganic N will be more prominent in eutrophic lakes where other nutrients are not limiting (Horne & Goldman, 1994). The extent to which nitrogen inputs are altered by biological processes within a lake depends on residence time and the abundance of other nutrients such as phosphorus. Lakes with long residence times may have lower concentrations of inorganic nitrogen because of algal uptake over a longer period. The dissolved organic nitrogen fraction is generally perceived as unavailable in the short term. However, Bushaw *et al.* (1996) demonstrated biological availability and NH_4^+ release from dissolved organic matter following irradiation, especially at ultraviolet wavelengths. About half of the dissolved organic nitrogen was assumed to be available for photochemical conversion to NH_4^+.

7.1.4 Differences in freshwater nitrogen fractions between catchments

There is a tendency for freshwaters located in agricultural catchments to have a high proportion of nitrogen as NO_3^- whereas dissolved organic fractions tend to be more important in catchments with forestry or peatland. In County Antrim (Northern Ireland) mean export from grazed lowland watersheds of the river Main were 33 kg NO_3^--N ha^{-1} yr^{-1} and 38 kg TN ha^{-1} yr^{-1} (total Kjeldahl N + NO_3^-) which corresponds to 86% NO_3^- (Smith, 1976). In comparison, NO_3^- was only 9% of exported TN (total Kjeldahl N + NO_3^-) from the peat dominated Loughgarve catchment whereas dissolved organic N (soluble Kjeldahl N - NH_4^+) was 38% (Gibson *et al.*, 1995b). Misztal *et al.* (1992) found that NO_3^- was the principal N fraction exported from arable land but not from peat bogs and forestry in the Lake Piaseczno catchment in Poland (Table 7.2). Høyås *et al.* (1997) recorded that NO_3^- in

south eastern Norway comprised 90% of TN lost from agricultural land but only 50% of TN lost from forested catchments. Adamson *et al.* (1998) found organic nitrogen to be the dominant fraction in a stream draining a blanket peat catchment. Although the blanket peat had high concentrations of NH_4^+ in soil water at a depth of 50 cm, it was likely that most export took place from the upper 10 cm of bog where organic nitrogen was the dominant fraction in soil solution. However, some nitrification may have occurred in the soils adjacent to the stream or in the stream itself. An increase in NO_3^- and a decrease in organic nitrogen as stream size increased was taken to indicate that some mineralisation may have occurred within the stream. Kopáček *et al.* (1995) found that NO_3^- was greater than 71% of TN in alpine lakes whereas organic nitrogen was 91% in forest lakes. Alpine lakes had more NO_3^- because of thinner soils, less vegetation in catchments and interception of cloud droplets at higher altitudes which had a high concentration of inorganic nitrogen.

There is evidence that upland catchments that receive high atmospheric deposition of nitrogen become nitrogen saturated (high available nitrogen in proportion to phosphorus and carbon) and have a higher proportion of TN as NO_3^-. Hessen *et al.* (1997) studied a river draining a heathland in south-western Norway and found a median NO_3^--N concentration of 0.155 mg l^{-1} which was 67% of TN (0.232 mg l^{-1}). Only a few of the 13 upland catchments in the UK sampled by Harriman *et al.* (1998) had their largest proportion of nitrogen export as dissolved organic nitrogen.

Where agricultural intensification has led to an increase in TN over time, the main fraction to increase is usually NO_3^-. Høyås *et al.* (1997) compared the periods 1966-1974 with 1991-1996 and found that the NO_3^- fraction accounted for most of the increase in TN. Nitrate in the Slapy reservoir in Central Europe has increased between 1959 and 1993 while the concentration of organic nitrogen has remained the same (Kopáček *et al.*, 1995).

Table 7.2 Mean (1982-89) export of nitrogen to Lake Piaseczno (Misztal *et al.*, 1992). Export is in kg ha^{-1}, the percentage of TN (total Kjeldahl nitrogen + NO_3^--N) each fraction comprises is in brackets. Total Kjeldahl nitrogen measurements include dissolved NH_4^+ and organic N but not NO_3^-).

Export (Kg ha^{-1})	Peat bog	Arable land	Forest	Forest/recreation
Total Kjeldahl N + NO_3^--N	1.6 (100%)	9.0 (100%)	1.6 (100%)	1.6 (100%)
NO_3^--N	0.2 (13%)	5.3 (59%)	0.2 (13%)	0.1 (6%)
NH_4^+-N	0.5 (31%)	1.0 (11%)	0.2 (13%)	0.4 (25%)

7.1.5 Empirical relationships between catchment characteristics and nitrogen

Empirical relationships between nitrogen and catchment characteristics generally focus on the main inputs (atmospheric and agricultural) and on processes which control nitrogen cycling. Catchment characteristics are generally related to either nitrogen concentration or export.

Empirical relationships between atmospheric deposition and freshwater nitrogen are usually estimated for upland catchments where precipitation is the major nitrogen input. A proportion of the available N deposited would be expected to be retained by catchment vegetation. If exports of available N fractions are similar to inputs then this may indicate a saturation of nitrogen relative to the vegetation's requirements for other nutrients. Allott *et al.* (1995) found that surface water NO_3^- concentrations in upland catchments in England, Scotland and Wales reflected TN deposition. Arheimer *et al.* (1996) found that Swedish and Finnish forested river catchments, which had no significant difference in NO_3^- between growing and dormant seasons, had higher inorganic nitrogen deposition than other catchments. Such a muted seasonal pattern may be an initial sign of nitrogen saturation. Black *et al.* (1993) studied nitrate concentrations along 10 km of seven rivers in north-east Scotland. Nitrate concentrations were generally lower in the summer, but several rivers had substantial NO_3^- concentrations in the upper part of the catchment in summer where concentrations were similar to that in precipitation. This was attributed to possible nitrogen saturation in the peat soils, although stretches of river adjacent to waterlogged peat at the top of catchments had markedly lower NO_3^-, which was attributed to denitrification.

Harriman *et al.* (1998) did not find a significant relationship between N deposition and mean NO_3^- inflow and outflow in 13 upland lakes. Instead, it was postulated that NO_3^- leaching was related to soil carbon. Sites with high carbon relative to nitrogen may be able to assimilate more of the deposited nitrogen, thus reducing leaching. To test this, NO_3^- was plotted against the ratio of nitrogen deposition to DOC export. As the ratio increased (i.e. indicating more nitrogen deposited relative to carbon in soils) the NO_3^- in the inflow and outflows increased ($r = 0.90$, $p < 0.05$). This indicated that nitrogen deposition may lead to NO_3^- leaching if the carbon content of the soils is low in upland catchments. The lack of phosphorus relative to nitrogen and carbon may also lead to elevated freshwater nitrogen concentrations. Hessen *et al.* (1997) suggested that P limitation in the drainage area and stream may be the principal factor leading to elevated NO_3^- in a stream draining a heathland in south-west Norway. Curtis *et al.* (1998) working on the same 13 upland sites in the UK as Harriman *et al.* (1998) noted that significant leaching losses were only apparent when TN deposition was in excess of 10 kg ha^{-1} yr^{-1}.

Intensive agriculture involves the use of large amounts of N as fertiliser. This has meant that numerous studies have associated freshwater nitrogen with agricultural activities. Thornton & Dise (1998) sampled 55 streams in the English Lake District and found higher flow weighted NO_3^- concentrations in streams draining predominantly (63-100%) agricultural catchments with thick soils in comparison to those with upland or forested catchments. Pekárová & Pekár (1996) in a study of 15 Slovakian catchments found streams draining agricultural catchments had a higher NO_3^- concentration compared with streams in mountainous and forested catchments. Høyås *et al.* (1997) recorded annual TN concentrations 40 times higher in rivers draining agricultural catchments than natural forests in south eastern Norway. Clear cut forests had intermediate concentrations. Misztal *et al.* (1992) determined that groundwater inflow from an arable area contributed the majority of the nitrogen load to Lake Piaseczno in south-east Poland. Other catchment land classes such as forestry and peat bogs contributed much less (Table 7.2). Langan *et al.* (1997) recorded higher concentrations of total oxidised nitrogen in sub-catchments with intensive agriculture in the river Dee in north-east Scotland. Hooda *et al.* (1997) in a study of six Scottish catchments ranked land use according to increasing stream NO_3^- concentrations as woodland through grassland to arable. Nitrate concentrations were the

same or higher downstream of farms compared with upstream. Edwards *et al.* (1985) attributed high summer NO_3^- concentrations in a Scottish upland catchment partly to sheep grazing. Müller *et al.* (1998) found that TN in the epilimnion of 68 small central European lakes was higher at lower altitudes, where the proportion of agricultural land was greater despite these lakes having longer retention times. Lakes where concentrations of TN were less than in precipitation were mainly above 1000 m and had short residence times (mean = 26 days).

Numerous authors have produced predictive models relating nitrogen to agricultural activities. Neill (1989) studied seven catchments in south-west Ireland and found that the percentage of land ploughed was correlated to both maximum NO_3^- concentration ($r = 0.96$, $n = 7$) and NO_3^- export ($r = 0.99$, $n = 5$). However, nitrogen fertiliser application rates were also correlated to river NO_3^- and it was unclear whether the percentage of land ploughed or nitrogen fertiliser application rate was the main factor controlling NO_3^-. As the range in percentage of land ploughed (2.7-30.6%) was greater than the range of nitrogen applied (47.6 to 68.2 kg N ha^{-1} yr^{-1}), the ploughing of land was deemed to be the most important factor controlling NO_3^- in the catchments.

Extensive work has been done in Northern Ireland in predicting river NO_3^- from catchment characteristics. Most of this work has involved attempts to model a time series of NO_3^- for major rivers entering Lough Neagh whereas there have been few attempts to produce predictive models for lakes. Smith (1976) found a close correlation between fertiliser usage and mean NO_3^- concentration in the river Main between 1969 and 1973. Subsequently Smith (1977) found that the mean NO_3^- concentration in all the major rivers flowing into Lough Neagh was correlated to fertiliser usage.

Foy *et al.* (1982) found that an increase in milk production explained 57% of the variation in NO_3^- export for six major rivers entering Lough Neagh between 1971-1979. A multiple regression model that included milk production, flow and the percentage of rough land explained 80% of the variation in NO_3^- export. This indicated that the intensification of agriculture had led to increased NO_3^- export.

Smith & Stewart (1989) found that yearly fertiliser usage explained 42% of the variation in NO_3^- loading to Lough Neagh from six major rivers entering Lough Neagh between 1971

and 1987. A multiple regression model explained 95% of the variation and included the independent variables 'fertiliser usage', 'previous April-September rain', 'June to September air temperature' and 'river flow for December-May'. It was estimated that 9 - 16% of the fertiliser applied was lost to rivers and this amounted to 50% of the NO_3^- load in the rivers. Previous April-September rain had a negative effect on NO_3^- loading and was associated with higher NO_3^- loss following a long dry period. The negative effect of June to September air temperature on NO_3^- loading was attributed to either increased NO_3^- uptake by vegetation or increased denitrification. River flow for December-May had a positive effect on NO_3^- loading because of the importance of runoff in removal of NO_3^-.

However, this model failed to predict the next six years NO_3^- loading (Stronge *et al.*, 1997). This failure was attributed to using flow as an independent variable to predict load. As flow was used to calculate load it may not have been independent. Stronge *et al.* (1997) developed a new model using improved time series techniques. The model was based on NO_3^- concentration rather than load to ensure the independence of predictors. The model explained 74% of the variation. In this model fertiliser usage was replaced by a measure of the efficiency of fertiliser usage - the 'utilised metabolisable energy to fertiliser sales ratio'. Once again the model included climatic variables (previous May to September rainfall, sun hours for December to April and rainfall from January to June).

Johnson *et al.* (1997) explained 69% of the variation in summer TN in 62 sub-catchment streams in America. The multiple regression model included the percentage of row cultivation (positive relationship), slope and the diversity of land cover types per km^2 (negative relationships). A second model was also successful in explaining summer TN. The model included the percentage of row cultivation and other agricultural land and explained 62% of the variation. The TN concentrations in autumn were related to catchment area (positive relationship), percentage of shrubs or herbs, standard deviation of elevation and the percentage of dune and lacustrine sand (negative relationships) (r^2 = 0.34, $p = 0.0001$). The variation in TN was explained equally well by catchment characteristics as ecotone data (catchment characteristics for a region 100 m on each side of the river).

Herlihy *et al.* (1998) sampled 368 streams in the mid-Atlantic region of the United States and found that NO_3^- increased logarithmically as the percentage of agricultural land increased and the percentage of forestry decreased. Forestry and agriculture accounted for most catchment land use (average of 97%). A multiple regression model explained 34 to 39% of the variation in NO_3^-. Splitting the 368 streams into regions generally improved the r^2 except in regions that were dominated by either agriculture or forestry alone.

Most empirical relationships relate freshwater N to inputs from agriculture or precipitation. However, there are several studies have used other catchment characteristics to explain the concentration or export of N. Arheimer *et al.* (1996) found higher NO_3^- concentrations in catchments at lower altitudes with higher flows, higher temperatures and fine soils in the south of Sweden and Finland. Reynolds *et al.* (1994) found no relationship between NO_3^- and catchment area, or percentage deciduous forest cover in 136 streams in upland Wales. Instead, the concentration of NO_3^- declined significantly with increasing coverage of peat and stagnopodzols ($r = -0.47$ in summer, $r = -0.43$ in winter). Concentrations were higher with increasing percentage of conifers ($r = 0.28$ in summer, $p < 0.001$ and $r = 0.39$ in winter, $p < 0.01$). Nitrate also had a significant positive relationship with the area weighted age of conifers ($r = 0.45$ in summer, $p<0.001$ and $r = 0.54$ in winter, $p < 0.001$). Stream chloride was significantly related to NO_3^- ($r = 0.62$, $p = 0.001$), which may have indicated that atmospherically derived NO_3^- was important in determining stream NO_3^-. A positive correlation was also found between total hardness and NO_3^- which may be because of increased mineralisation in soils of higher base status.

Loss processes in upstream lakes may result in lower N concentrations in downstream lakes. Arheimer *et al.* (1996) found that catchments with the highest percentage of lakes showed the most pronounced decline in river NO_3^- during the growing season in Sweden and Finland. However, the loss of N in upstream lakes is likely to be dependent on lake productivity; Harriman *et al.* (1998) found than NO_3^- retention in 13 upland lakes in the United Kingdom was generally low (<5%).

Hooda *et al.* (1997) found that there was a tendency for rivers in the east of Scotland to have a higher nitrogen concentration and export than in the west (six catchments). This was despite the fact that nitrogen input to the western catchments was double that in the east and that atmospheric deposition was higher in the west. The lower concentrations in

the west were attributed to the longer growing season of up to 100 days and the higher precipitation leading to more denitrification. The NO_3^- concentration may also have been lower in the west owing to the poorly drained soils promoting overland flow which may have less nitrogen than soil through-flow. The higher NO_3^- concentrations observed in the east may have also been because of higher soil organic matter leading to more NO_3^- mineralised. Garrett *et al.* (1992) found a similar result for Northern Ireland. They found lower NO_3^- leaching in the west than east of Northern Ireland. As dilution had been accounted for, the regional difference was attributed to differences in nitrogen cycling such as more denitrification in the wetter more poorly drained soils of the west. In addition the higher soil moisture deficits in the east may have retarded plant NO_3^- uptake and availability.

Lepistö *et al.* (1995) used correlation and multiple regression to explain the concentration of NO_3^- and organic nitrogen in 20 forested catchments in Sweden and Finland. Nitrate concentrations had a negative correlation with discharge and altitude and a positive correlation with deposition. Organic nitrogen concentration was negatively correlated with altitude and positively correlated with percentage of fine soil, temperature and nitrogen deposition.

Close & Davies-Colley (1990) used multiple regression to explain 61% of the variation in NO_3^- in 101 New Zealand river sites. The variables included in the model that had a negative influence on NO_3^- were: catchment area, elevation, inverse specific mean annual seven day low flow, percentage of lake area in the catchment, mean annual flood divided by catchment area, percentage of area with slopes greater than 20°, mean annual water temperature and the percentage of the catchment in tussock and undeveloped grassland. Explanatory parameters with a positive influence on NO_3^- were: the percentage of alluvium, sand, peat and gravel and the percentage of hard sedimentary rocks.

It is clear from previous work that a wide variety of catchment characteristics can be employed to describe variation in nitrogen in freshwaters. This study is the first to attempt to define such relationships for a diverse series of catchments and lakes in Ireland.

7.1.6 Specific aims

The aims of this chapter are:

- To examine the seasonal variation in TN and its components: DON, NO_3^- and PON.
- To examine whether the concentration of TN has changed in four Clare lakes since the 1980s and which fractions have changed.
- To determine which catchment characteristics control the TN concentration in Irish lakes.
- To see whether the proportion of NO_3^- and DON is dependent on catchment characteristics.
- To build a multiple regression model to explain the variation in TN and to allow future and past concentrations of TN to be estimated.
- To determine, across a series of non-agricultural catchments, whether higher atmospheric N deposition in the east has resulted in higher lake TN concentrations.

7.2 Materials and Methods

The location of lakes and calculation of catchment characteristics was described in Chapter 2. Sampling frequency and methods of collection and storage of samples was described in Chapter 3.

Nitrate was measured on filtrate (Whatman GF/C - particle retention 1.2 μm) by chemically suppressed ion chromatography (Dionex system). Samples were initially analysed in duplicate but this was reduced to a single determination owing to the consistency of results. Determinations of nitrate followed calibration with five standards. There was no consistent quality control for nitrate. However, standards were run after every 10 samples on the ion chromatograph to detect if drift was taking place. Quality assurance information is provided in Appendix 10 and measured values were within 95% confidence limits of the certified mean.

Total nitrogen and total dissolved nitrogen (performed on filtrate) was determined by alkaline persulphate digestion on 50 ml samples (Koroleff, 1983b). Samples were digested in duplicate. Samples were diluted by a factor of 10 to a final volume of 3.5 ml and buffered with ammonium chloride. This was followed by flow injection analysis (Tecator 5020, 5032, 5007) which involved cadmium reduction followed by azo dye colourimetry. Calibration of the instrument used a five point standard curve. Recalibration took place at regular intervals throughout the analysis. A quality control solution for TN was prepared in March 1996. The quality control used an independent salt (KNO_3) to that used for preperation of standards and thus provides a degree of quality assurance. Eighteen litres of quality control of concentration 1 mg l^{-1} NO_3-N were made. Sub-samples of 250 ml volume were taken from the 18 l and frozen in polyethylene bottles until required. Two 50 ml aliquots of quality control were digested for each analysis. Three sub-samples from each quality control were prepared. Two quality controls were run after each calibration of the instrument. The quality control chart for TN is presented in Figure 7.3. The average concentration of the quality control was 1.02 mg l^{-1} and the standard deviation was 0.04 mg l^{-1}.

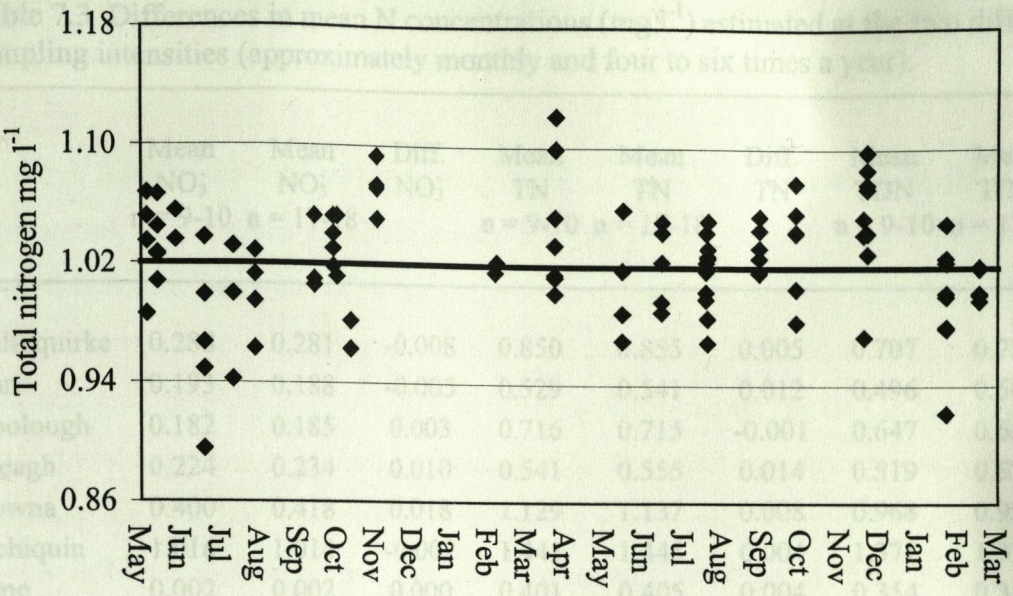


Figure 7.3 Quality control chart for TN (mg l^{-1}) between May 1996 and March 1998. Major gridline corresponds to average, minor gridlines represent 2 standard deviations.

The statistical procedures used are documented in Chapter 5. Analysis was mainly performed on arithmetic mean concentrations. The means were calculated for all lakes for both 1996 and 1997 to represent an annual average. As the lakes were sampled at different intensities: approximately monthly for eleven lakes and four to six times a year for the remaining 20 lakes, there is a question as to whether this was a valid approach. To test this, an assumption was made that the eleven lakes sampled 17 to 18 times during 1996 and 1997 represented annual means. The means for these eleven lakes were recalculated at the sampling intensity of the 20 lakes sampled four to six times a year (Table 7.3). Very little difference between means estimated at different sampling intensities was found.

Table 7.3 Differences in mean N concentrations (mg l^{-1}) estimated at the two different sampling intensities (approximately monthly and four to six times a year).

	Mean NO_3^- n = 9-10	Mean NO_3^- n = 17-18	Diff. NO_3^-	Mean TN n = 9-10	Mean TN n = 17-18	Diff. TN	Mean TDN n = 9-10	Mean TDN n = 17-18	Diff. TDN
Ballyquirke	0.288	0.281	-0.008	0.850	0.855	0.005	0.707	0.736	0.029
Dan	0.193	0.188	-0.005	0.529	0.541	0.012	0.496	0.500	0.004
Doolough	0.182	0.185	0.003	0.716	0.715	-0.001	0.647	0.650	0.003
Feeagh	0.224	0.234	0.010	0.541	0.555	0.014	0.519	0.537	0.018
Gowna	0.400	0.418	0.018	1.129	1.137	0.008	0.968	0.988	0.021
Inchiquin	1.016	1.014	-0.002	1.441	1.445	0.004	1.371	1.375	0.004
Lene	0.002	0.002	0.000	0.401	0.405	0.004	0.354	0.329	-0.025
Lickeen	0.131	0.150	0.019	0.850	0.838	-0.012	0.718	0.719	0.000
Moher	0.336	0.351	0.015	0.777	0.779	0.002	0.715	0.729	0.014
Owel	0.067	0.073	0.007	0.610	0.597	-0.013	0.519	0.522	0.004
Ramor	0.781	0.947	0.165	1.859	2.003	0.144	1.508	1.642	0.134

Nitrogen inputs to the catchments were estimated by summation of a number of sources. In order for the input of N from precipitation to be calculated the median concentrations of NH_4^+-N and NO_3^--N in precipitation (mg l^{-1}) were obtained from Jordan (1997). These concentrations were derived from maps based on 15 stations for 1992-1994. The concentration of N in precipitation was multiplied by the amount of precipitation (predicted using the model of Goodale *et al.*, 1998) to give deposition in kg ha^{-1} yr^{-1} as detailed below:

e.g. Median annual concentration of 0.21 mg l^{-1} NO_3^--N = 0.00021 kg NO_3^--N m^3

Precipitation of 800 mm yr^{-1} = 8000 m^3 ha^{-1} yr^{-1}

Concentration multiplied by precipitation = 0.00021 kg NO_3^--N m^3 · 8000 m^3 ha^{-1}

= 1.68 kg NO_3^--N ha^{-1} yr^{-1}

The deposition of N was multiplied by catchment area to give an estimate of precipitation input. An estimate of 10 kg N ha^{-1} yr^{-1} nitrogen fixation in pasture in the drainage area was used (Smith *et al.*, 1995). Nitrogen inputs to the catchment by human excreta were derived

by multiplication of the human population (from the 1991 census) by annual N excretion (9.1 g TN day^{-1} as estimated by Smith 1976).

Nitrogen input to the catchments from agriculture was estimated using CORINE land class information and fertiliser application rates for each county (Murphy *et al.*, 1997). Specifically, the areas (ha) of the CORINE land classes: pasture (high productivity), pasture (low productivity), pasture (mixed) and principally agriculture were summed. This area was multiplied by each counties fertiliser application rate (kg ha^{-1} yr^{-1}) to grassland (total grassland category) (Murphy *et al.*, 1997). The input to crops was calculated by summing the CORINE land classes arable and complex cultivation and multiplying by the county fertiliser application to crops (mean of several crop types) (Murphy *et al.*, 1997). The input to forestry was calculated by summing the CORINE land classes; broad leaf forestry, coniferous forestry and mixed forest and multiplying by 18.75 kg ha yr^{-1} (150 kg at 8 year intervals) (Clinch, 1999).

The estimation of nitrogen input to the catchments is likely to be very approximate. The main sources of error in estimating the N inputs may be the poor resolution of the CORINE data (25 ha), the lack of catchment specific estimates of N fixation, the assumption that all pasture will receive the average fertiliser application rate for that county and estimating an annual input to forestry that was derived from a national figure of N application at eight year intervals. Even though the estimation of N inputs is likely to be crude the errors are likely to be minor in comparison to the range of N inputs found among the 31 catchments. This is because of the diversity of catchment types, which ranged from small upland peat catchments to large lowland pasture catchments.

7.3 Results

7.3.1 Seasonal variation in nitrogen

Three fractions of nitrogen were measured: total nitrogen (TN), total dissolved nitrogen (TDN) and nitrate (NO_3^-). To examine the seasonal variation in N these results are reconstituted as three fractions (Figure 7.4). Firstly, nitrate nitrogen, which refers to the concentration of NO_3^--N alone (does not include NO_2^-). Secondly, the concentration of particulate organic nitrogen (PON) which was calculated by subtracting TDN from TN. This represents the nitrogen in particulate matter retained on GF/C filter papers (particles > 1.2 μm). Thirdly, an estimate of dissolved organic nitrogen (DON) was calculated by subtracting NO_3^--N from TDN. This fraction mainly represents dissolved organic nitrogen but may have included small amounts of NH_4^+, $CO[NH_2]_2$ and NO_2^-. The sum of all the above fractions is total nitrogen.

The total nitrogen concentration and the proportion of the different fractions varied seasonally (Figure 7.4 to Figure 7.9). Total nitrogen was generally lower in summer than in winter (Figure 7.4). The largest decline in TN from winter to summer occurred in the more nutrient rich lakes that had the highest TN (Figure 7.4 and Lough Ramor, Figure 7.9). Lakes that had relatively low nutrient concentrations had a much smaller decline in TN (e.g. Lough Doolough, Figure 7.6). Nitrate was the fraction that had the largest seasonal variation (Figure 7.4). Lakes with consistently low NO_3^- did not show a typical seasonal decline in TN (e.g. Lough Lene, Figure 7.8). The PON fraction showed an increase from winter to summer (Figure 7.4, Figure 7.5). Eutrophic lakes had the largest concentrations of PON (Figure 7.4, Figure 7.9). The DON fraction had the least seasonal variation but tended to be higher in summer than in winter (Figure 7.4).

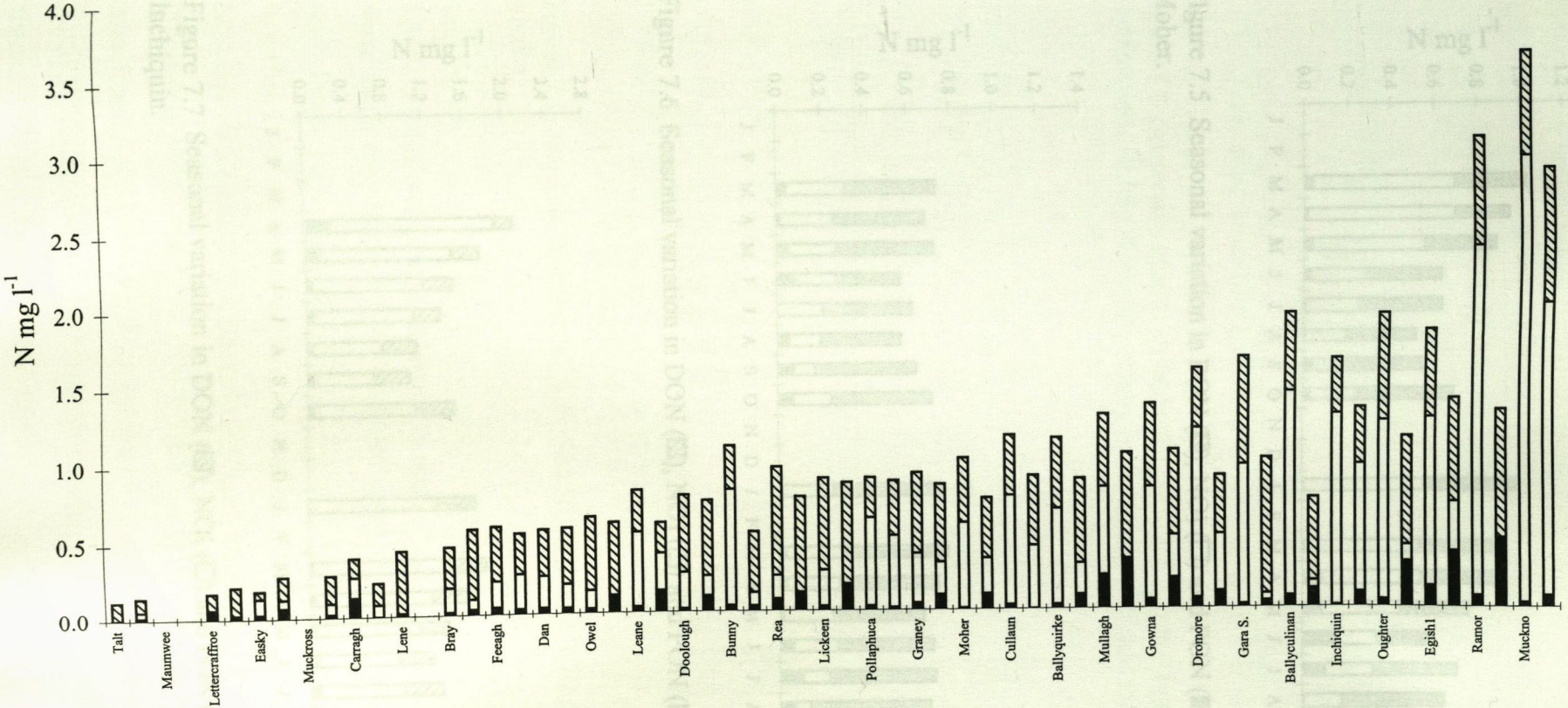


Figure 7.4 DON (▨), NO_3^- (□) and PON (■) (mg l^{-1}) in January (first column) and July (second column) in 1997. The estimates of the different fractions in Loughs Maumwee (January, July), Muckross (January) and Lene (July) did not tally by 0.010 to 0.021 mg l^{-1} N. The estimate of the different fractions Lough Cullaun (July) did not tally by 0.050 mg l^{-1} N and are not presented.

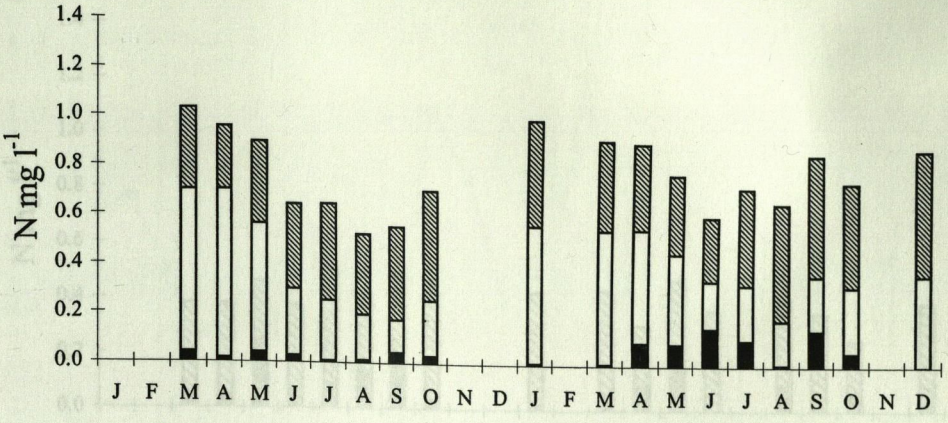


Figure 7.5 Seasonal variation in DON (▨), NO_3^- (□) and PON (■) (mg l^{-1}) in Lough Moher.

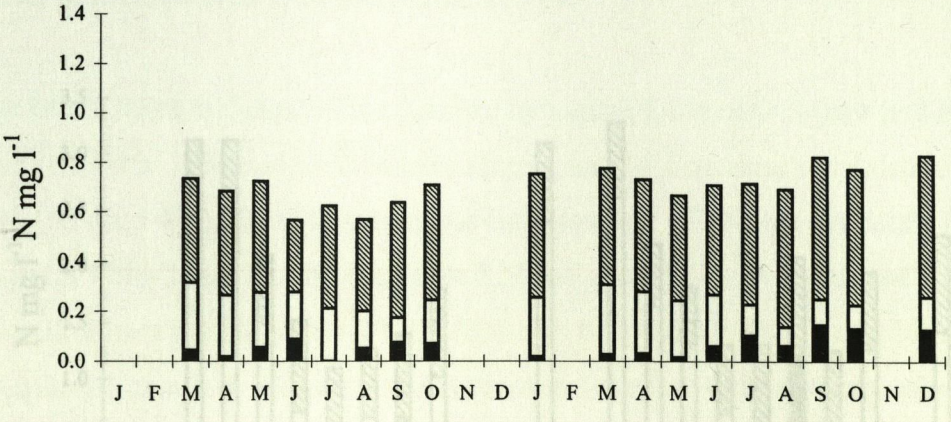


Figure 7.6 Seasonal variation in DON (▨), NO_3^- (□) and PON (■) (mg l^{-1}) in Doolough.

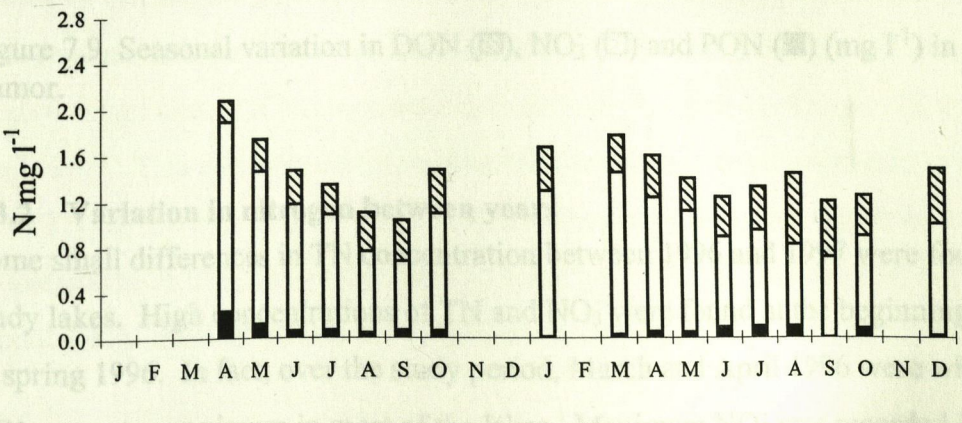


Figure 7.7 Seasonal variation in DON (▨), NO_3^- (□) and PON (■) (mg l^{-1}) in Lough Inchiquin.

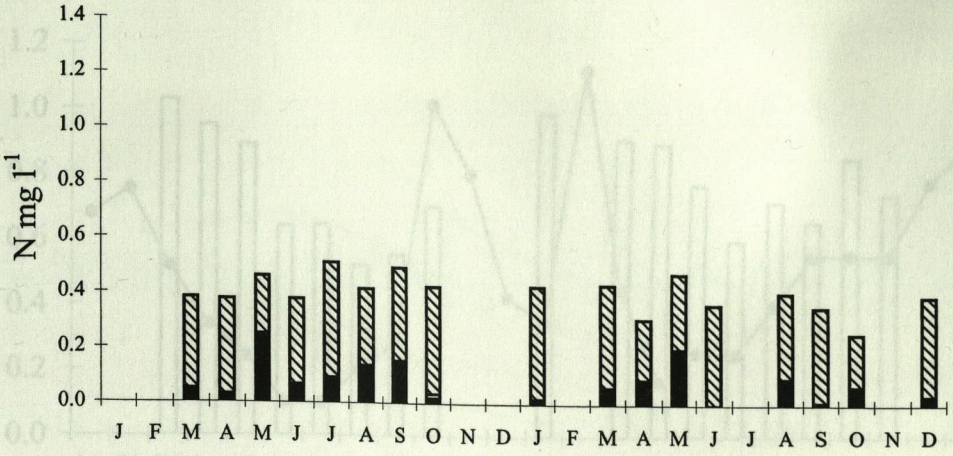


Figure 7.8 Seasonal variation in DON (▨), NO_3^- (□) and PON (■) (mg l^{-1}) in Lough Lene. The fractions in July 1997 did not tally by 0.010 mg l^{-1} N and are not presented.



Figure 7.9 Seasonal variation in DON (▨), NO_3^- (□) and PON (■) (mg l^{-1}) in Lough Ramor.

7.3.2 Variation in nitrogen between years

Some small differences in TN concentration between 1996 and 1997 were found in the study lakes. High concentrations of TN and NO_3^- were found at the beginning of the study in spring 1996. In fact, over the study period, March and April 1996 were when TN and NO_3^- were at a maximum in most of the lakes. Maximum NO_3^- was recorded in 22 out of 29 lakes in March and April 1996 and maximum TN was recorded in 16 out of 29 lakes in March and April 1996 (n = 29 as Egish and Gara South were not sampled in March and April 1996). In addition, high summer rainfall in 1997 resulted in an earlier increase in TN than in 1996 (e.g. Lough Moher Figure 7.10).

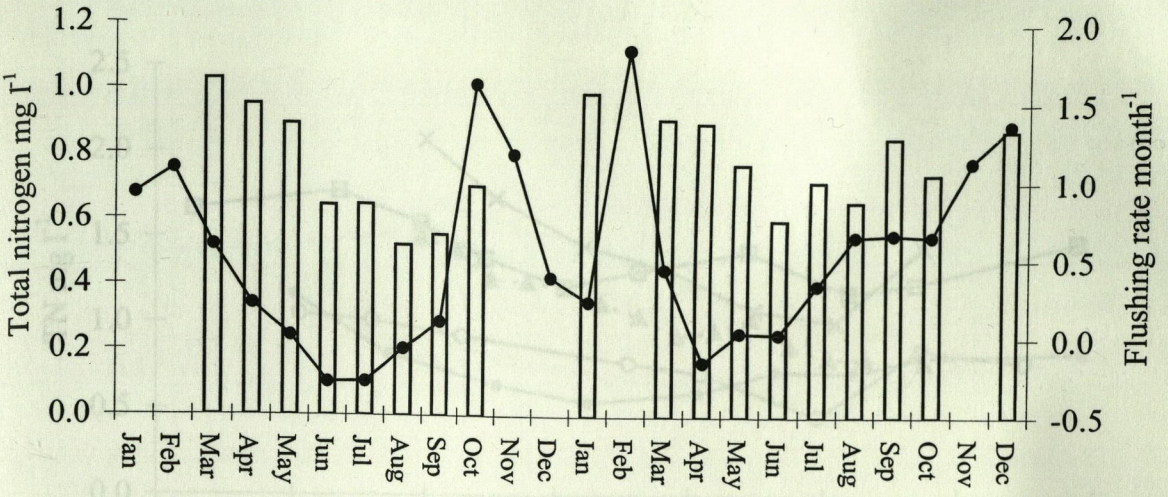


Figure 7.10 Seasonal variation of total nitrogen (□) and flushing rate (—•—) in Lough Moher between March 1996 and December 1997.

Four of the lakes in County Clare (Loughs Inchiquin, Dromore, Cullaun and Ballycullinan) were studied in 1981 and 1982 and two (Inchiquin and Dromore) were also sampled in 1985 (Allott, 1990). In all four lakes the concentration of TN was substantially higher in the years 1996-7 than in 1981-2 (Figure 7.11 to Figure 7.14). An intermediate concentration was observed in 1985, which may have been caused by the higher precipitation that year because concentrations in October 1985 appear to return to levels similar to 1981-2 (Figure 7.11 and Figure 7.12). To test if there was a statistical difference between years a two-way ANOVA with year and month as independent variables was performed (results are presented in full in Appendix 8). Evidence for a difference in concentration between years was found in all four lakes ($p \leq 0.0009$, $n = 25$ to 41). Table 7.4 shows that mean TN has increased in these lakes by between 81 and 105% from 1981-2 to 1996-7. This corresponds to a mean concentration increase ranging from 0.52 to 0.65 mg l^{-1} TN for the four lakes. Total dissolved nitrogen was measured in 1985 and a comparison with 1997 shows that most of the increase in TN has been in the NO_3^- fraction (Figure 7.15). Smaller increases were observed in the particulate organic N fraction.

One of the possible reasons for an increase in TN may have been the increase in application of artificial N fertiliser. Although the sampling frequency is too low to define a trend it can be noted that the increase in TN in Lough Inchiquin was at a similar rate to national N fertiliser usage (Figure 7.16).

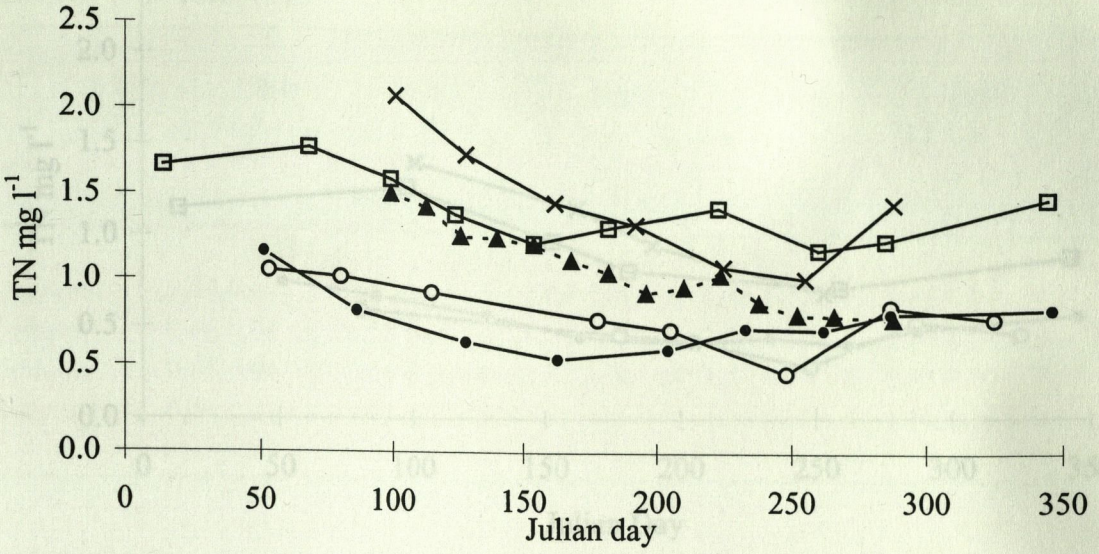


Figure 7.11 Total nitrogen in Lough Inchiquin in 1981 (—O—), 1982 (—●—), 1985 (· · ·▲· · ·), 1996 (—×—) and 1997 (—⊟—). Total nitrogen concentrations for 1981, 1982 and 1985 are from Allott (1990).

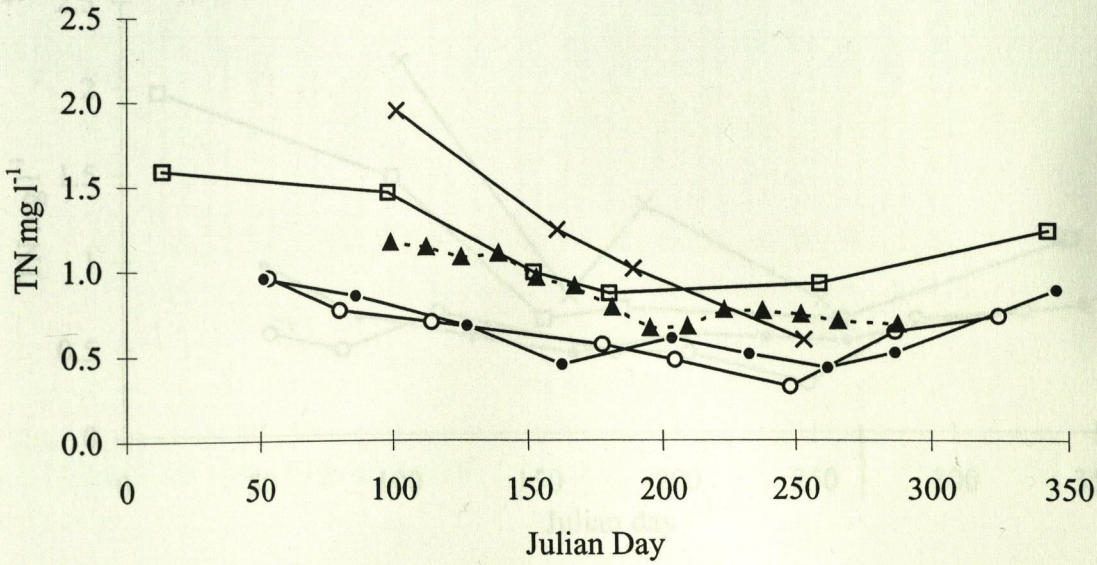


Figure 7.12 Total nitrogen in Lough Dromore in 1981 (—O—), 1982 (—●—), 1985 (· · ·▲· · ·), 1996 (—×—) and 1997 (—⊟—). Total nitrogen concentrations for 1981, 1982 and 1985 are from Allott (1990).

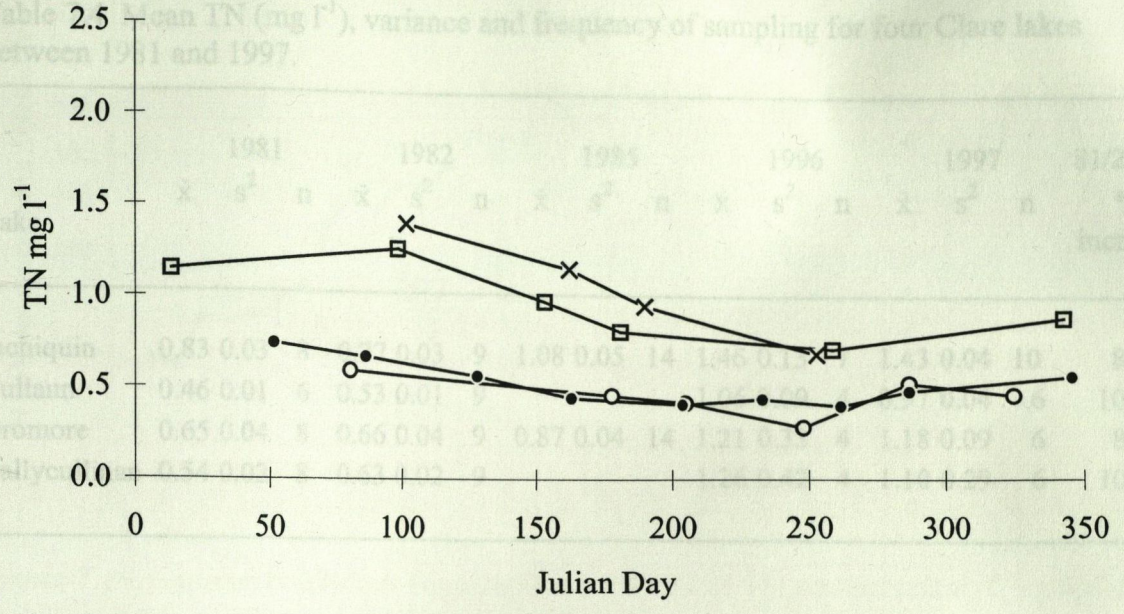


Figure 7.13 Total nitrogen in Lough Cullaun in 1981 (—O—), 1982 (—•—), 1996 (—×—) and 1997 (—⊟—). Total nitrogen concentrations for 1981 and 1982 are from Allott (1990).

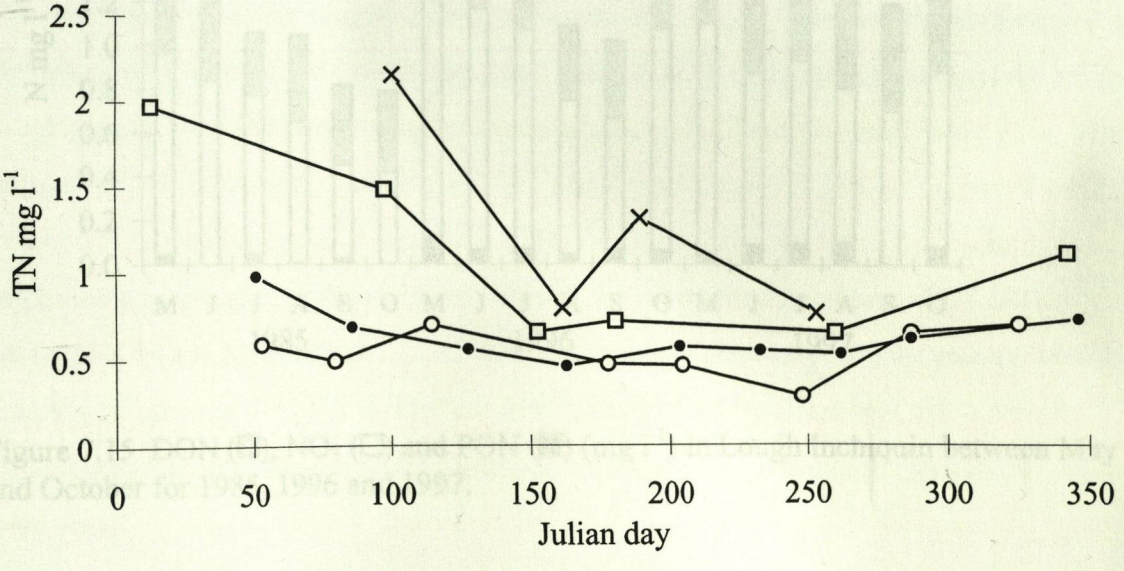


Figure 7.14 Total nitrogen in Lough Ballycullinan (north basin) in 1981 (—O—), 1982 (—•—), 1996 (—×—) and 1997 (—⊟—). Total nitrogen concentrations for 1981 and 1982 are from Allott (1990).

Table 7.4 Mean TN (mg l^{-1}), variance and frequency of sampling for four Clare lakes between 1981 and 1997.

Lake	1981			1982			1985			1996			1997			81/2-96/7
	$\bar{x}$	s^2	n	$\bar{x}$	s^2	n	$\bar{x}$	s^2	n	$\bar{x}$	s^2	n	$\bar{x}$	s^2	n	% increase
Inchiquin	0.83	0.03	8	0.77	0.03	9	1.08	0.05	14	1.46	0.13	7	1.43	0.04	10	81
Cullaun	0.46	0.01	6	0.53	0.01	9				1.06	0.09	4	0.97	0.04	6	105
Dromore	0.65	0.04	8	0.66	0.04	9	0.87	0.04	14	1.21	0.33	4	1.18	0.09	6	82
Ballycullinan	0.54	0.02	8	0.63	0.02	9				1.26	0.42	4	1.10	0.29	6	102

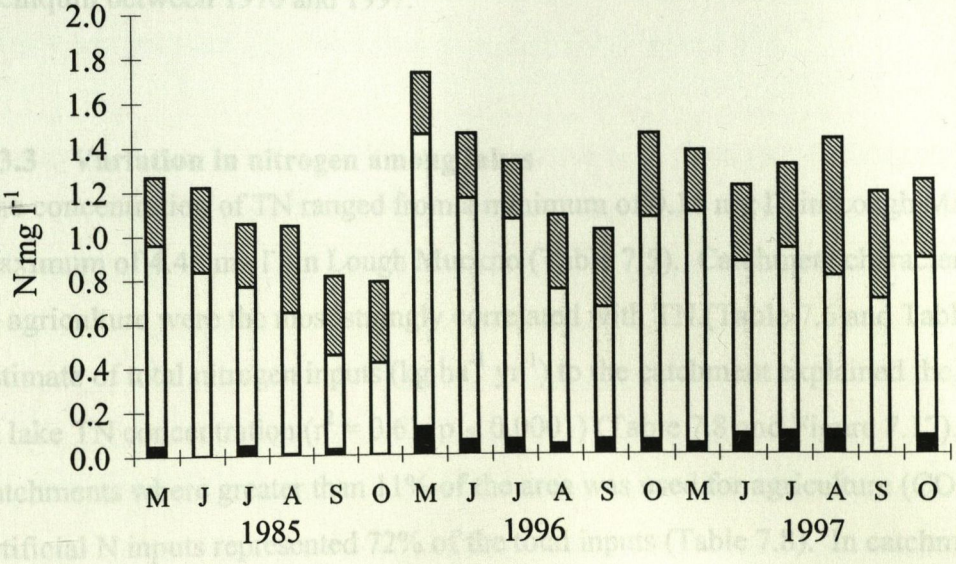


Figure 7.15 DON (▨), NO_3^- (□) and PON (■) (mg l^{-1}) in Lough Inchiquin between May and October for 1985, 1996 and 1997.

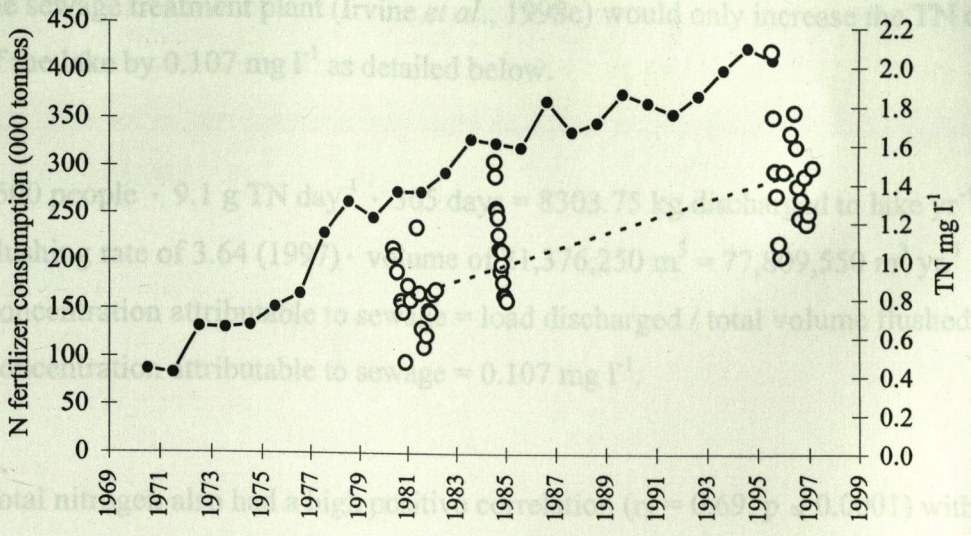


Figure 7.16 National N fertiliser consumption (—●—) and TN concentration (O) in Lough Inchiquin between 1970 and 1997.

7.3.3 Variation in nitrogen among lakes

The concentration of TN ranged from a minimum of 0.11 mg l^{-1} in Lough Maumwee to a maximum of 4.48 mg l^{-1} in Lough Muckno (Table 7.5). Catchment characteristics relating to agriculture were the most strongly correlated with TN (Table 7.6 and Table 7.7). The estimate of total nitrogen inputs (kg ha^{-1} yr^{-1}) to the catchment explained the most variation in lake TN concentration ($r^2 = 0.61$, $p \leq 0.0001$) (Table 7.8 and Figure 7.17). In catchments where greater than 11% of the area was used for agriculture (CORINE) artificial N inputs represented 72% of the total inputs (Table 7.8). In catchments with less than 4% of the area used for agriculture, precipitation and fertiliser applied to forestry (where present) were the dominant inputs of N (Table 7.8). Nitrogen inputs from humans were small.

The proportion of the catchment under agriculture (sum of the CORINE classes pasture high productivity, pasture low productivity, mixed pasture, principally agriculture, arable and complex cultivation) explained 53% of the variation in TN ($p \leq 0.0001$) (Figure 7.18). Lough Muckno had substantially higher TN which was initially thought to be owing to N inputs from the Castleblaney sewage treatment plant (Figure 7.18). However, it was estimated that less than 4% of the TN concentration in Lough Muckno was derived from inputs from this source. This figure was estimated by assuming a per capita contribution of 9.1 g TN (Smith, 1976) in which case, the sewage from the 2500 people connected to

the sewage treatment plant (Irvine *et al.*, 1998c) would only increase the TN concentration of the lake by 0.107 mg l^{-1} as detailed below.

2500 people · 9.1 g TN day^{-1} · 365 days = 8303.75 kg discharged to lake yr^{-1}
Flushing rate of 3.64 (1997) · volume of 21,376,250 m^3 = 77,809,550 m^3 yr^{-1} flushed
Concentration attributable to sewage = load discharged / total volume flushed
Concentration attributable to sewage = 0.107 mg l^{-1}.

Total nitrogen also had a high positive correlation ($r_S = 0.69$, $p \leq 0.0001$) with the density of cattle (Table 7.6 and Figure 7.19). However, linear regression between cattle and TN only explained 23% of the variation and Lough Mullagh which has the highest cattle density had substantially lower than expected TN (Figure 7.19).

Measured net precipitation (1997) had a negative r_S of -0.68 ($p < 0.0001$) with TN (Table 7.6). The relationship between mean (1996-97) net precipitation and TN was best described by a power trend-line (Figure 7.20) ($r^2 = 0.41$). The equation in Figure 7.20 predicts that mean lake TN concentration in catchments receiving 1200 mm net precipitation will be 0.46 mg l^{-1} but will be almost double (0.94 mg l^{-1} TN) in catchments receiving half this precipitation (600 mm). This superficially suggests that catchments receiving high precipitation had lower TN concentrations because of dilution of soil N. The form of the relationship in Figure 7.20 indicates that where precipitation decreases by half the concentration doubles. For this dilution relationship to be real, soil N concentration would need to be similar across catchments, which would be unlikely. Moreover, the quantification of causal relationships between TN and precipitation is difficult because precipitation was co-linear with many other environmental variables - including pasture and fertiliser application (Table 7.9 and Chapter 2). Therefore the relationship between precipitation and TN was significant partly because precipitation also describes differences in agriculture between catchments. However, the relationship between TN and precipitation indicates that dilution of soil N may play some role in determining TN concentration.

Several other parameters had a high r_S with TN such as the proportion of rendzinas and brown earth soils and catchment slope (Figure 7.21 and Figure 7.22). These parameters may also act as surrogates as they were co-linear with precipitation and agricultural variables (Table 7.9).

Table 7.5 Summary of total nitrogen concentrations (mg l^{-1}) recorded in the lakes studied between March 1996 and December 1997.

Lake	Average	95% C.I.	n	Max.	Min.
Talt	0.19	0.04	10	0.36	0.12
Maumwee	0.28	0.07	10	0.51	0.11
Muckross	0.28	0.06	9	0.47	0.18
Lettercraffroe	0.30	0.06	10	0.46	0.18
Caragh	0.30	0.05	10	0.40	0.14
Easky	0.33	0.07	10	0.50	0.19
Lene	0.40	0.03	18	0.51	0.26
Bray	0.42	0.04	10	0.57	0.35
Dan	0.54	0.02	18	0.67	0.43
Feeagh	0.55	0.03	18	0.66	0.39
Owel	0.60	0.04	18	0.71	0.38
Leane	0.71	0.07	9	0.86	0.59
Bunny	0.72	0.16	10	1.16	0.39
Doolough	0.72	0.04	18	0.84	0.57
Rea	0.74	0.10	10	0.95	0.46
Moher	0.78	0.07	18	1.03	0.52
Pollaphuca	0.83	0.06	10	0.95	0.67
Lickeen	0.84	0.05	18	1.01	0.61
Ballyquirke	0.86	0.08	17	1.12	0.63
Graney	0.86	0.09	10	1.23	0.66
Cullaun	1.00	0.15	10	1.40	0.70
Mullagh	1.08	0.16	10	1.76	0.81
Gowna	1.14	0.14	18	1.78	0.75
Ballycullinan	1.16	0.34	10	2.16	0.65
Dromore	1.19	0.25	10	1.96	0.60
Gara S.	1.37	0.34	9	2.17	0.77
Inchiquin	1.45	0.13	17	2.08	1.03
Egish	1.51	0.14	9	1.86	1.29
Oughter	1.53	0.21	11	2.05	1.09
Ramor	2.00	0.34	18	3.31	1.09
Muckno	3.02	0.52	10	4.48	1.72

Table 7.6 Spearman rank correlation table between TN (mg l^{-1}) and agricultural and climatic catchment characteristics (n = 31). Only $r_S \geq 0.36$ ($p < 0.05$) are presented. An asterisk indicates climatic data from other months was also significant.

Agricultural	r_S	Climatic	r_S
Total agriculture (pr.) (CORINE)	0.79	Net precipitation 1997 (mm)	-0.68
Total pasture (pr.) (CORINE)	0.74	Predicted annual precipitation (mm)	-0.66
Total N input kg ha^{-1} yr^{-1}	0.71	Net precipitation 1996 (mm)	-0.61
Cattle (ha^{-1})	0.69	July max. temperature °C*	0.56
Silage (pr.)	0.65	May mean sunshine hours day^{-1}*	-0.55
Pasture mix (pr.)	0.64	Mean annual maximum daily temperature °C	0.51
Pasture high productivity (pr.)	0.59	July minimum temperature °C	0.45
Sum of rotation under 5 years (pr.)	0.56	Easting	0.38
Permanent meadow (pr)	0.53		
Sheep (ha^{-1})	-0.48		
Total grassland (pr)	0.48		
Total area farmed (pr)	0.46		
Humans (ha^{-1})	0.36		
Pasture low productivity (pr.)	0.36		

Table 7.7 Spearman rank correlation table between TN (mg l^{-1}) and land class / soil and morphometric catchment characteristics (n = 31). Only $r_S \geq 0.36$ ($p < 0.05$) are presented.

Land class / soil	r_S	Morphometric	r_S
Rendzinas & brown earths (pr.)	0.73	Slope°	-0.69
Total peatlands (pr.) (CORINE)	-0.62	Mean catchment elevation (m)	-0.58
Peat Bogs unexploited (pr.)	-0.61	Catchment area m^2 / (mean catch. height - lake height m)	0.54
Peat (pr.)	-0.58	Catchment area (ha) / volume (m^3)	0.52
Podzols & gleys (pr.)	0.44	Mean catchment boundary height (m)	-0.52
Total lake area (pr.)	-0.41	Flow path	0.48
Sampled lake area (pr)	-0.41	Shoreline development · shoreline slope	0.45
		Shoreline development (D_L)	0.44
		Other lake area and sampled lake area (pr)	-0.43
		Unexploited peat (ha.) / total lake area (ha)	-0.43
		Max. height (m) of catchment boundary	-0.42
		Catchment area/ lake area	0.41
		Drainage density (km^2)	-0.40
		Compactness coefficient of catchment	0.38
		Ruggedness number	-0.37
		Maximum depth (m)	-0.37
		Crenulation of catchment perimeter	0.37
		Lake altitude -mean catchment perimeter altitude (m)	-0.36

Table 7.8 Nitrogen inputs (tonnes) into catchments. Agricultural inputs were derived using information on CORINE land cover in catchments and a fertiliser use survey (Murphy *et al.*, 1997). Catchments with less than 4% agriculture (CORINE) are marked with an asterisk.

Lake	Rain	Fixation	Grassland	Crops	Humans	All forestry	Total input (tonnes)	Total input kg ha^{-1} yr^{-1}
Ballycullinan	0.88	0.64	3.64	0.00	0.09	0.00	5.24	37
Ballyquirke	30.12	20.92	167.32	0.00	5.76	6.79	230.91	32
Bray*	1.64	0.00	0.00	0.00	0.08	0.00	1.72	12
Bunny	47.78	31.10	177.26	28.79	2.32	1.27	288.51	38
Caragh	64.62	18.39	187.53	0.00	3.23	13.13	286.90	18
Cullaun	51.88	47.61	271.37	37.35	3.02	0.01	411.24	49
Dan*	66.17	0.66	5.50	0.00	1.67	10.76	84.77	13
Doolough	17.01	6.40	36.47	0.00	0.83	2.34	63.05	29
Dromore	1.88	1.30	7.41	0.00	0.30	1.59	12.49	39
Easky*	6.86	0.00	0.00	0.00	0.26	0.00	7.12	6
Egish	4.41	6.53	72.43	0.00	1.03	0.00	84.41	108
Feeagh*	61.11	3.05	20.13	0.00	1.90	34.07	120.26	12
Gara South	73.15	135.39	514.49	0.00	7.78	0.50	731.30	40
Gowna	42.77	110.13	991.17	28.49	10.98	4.32	1187.86	93
Graney	73.23	35.07	199.89	0.00	2.54	53.11	363.84	33
Inchiquin	102.79	60.70	345.97	0.00	3.70	3.68	516.83	35
Leane	341.44	148.29	1512.52	273.82	60.12	75.96	2412.15	44
Lene	6.10	5.78	41.04	62.50	2.37	0.00	117.79	101
Lettercraffroe*	2.12	0.00	0.00	0.00	0.26	2.83	5.21	14
Lickeen	5.89	5.27	30.04	0.00	0.39	0.00	41.59	51
Maumwee*	2.33	0.00	0.00	0.00	0.04	0.00	2.37	6
Moher	5.07	3.02	19.91	0.00	0.20	1.22	29.41	31
Muckno	91.70	145.12	1610.85	0.00	9.54	9.39	1866.61	116
Muckross *	39.19	1.44	14.69	0.00	2.07	15.03	72.42	12
Mullagh	0.63	0.86	7.78	0.00	0.24	0.00	9.51	83
Oughter	501.71	1372.70	12354.27	74.67	142.23	29.66	14475.25	98
Owel	15.31	31.78	225.61	70.69	13.11	3.22	359.71	77
Pollaphuca	296.49	56.55	469.38	1647.40	18.59	74.05	2562.45	85
Ramor	136.92	230.33	2072.98	72.39	23.87	8.82	2545.30	101
Rea	5.19	10.12	80.97	9.72	1.08	0.11	107.20	79
Talt	2.61	1.20	7.46	0.00	0.11	0.00	11.38	24

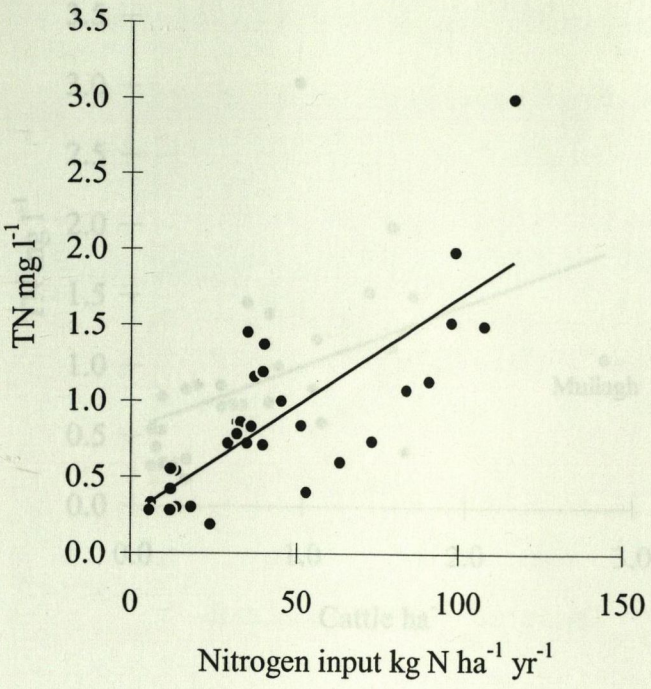


Figure 7.17 Relationship between mean lake TN concentration and total N input to catchments. Equation: $y = 0.0146x + 0.2472$, $r^2 = 0.61$, $p \leq 0.0001$, $n = 31$.

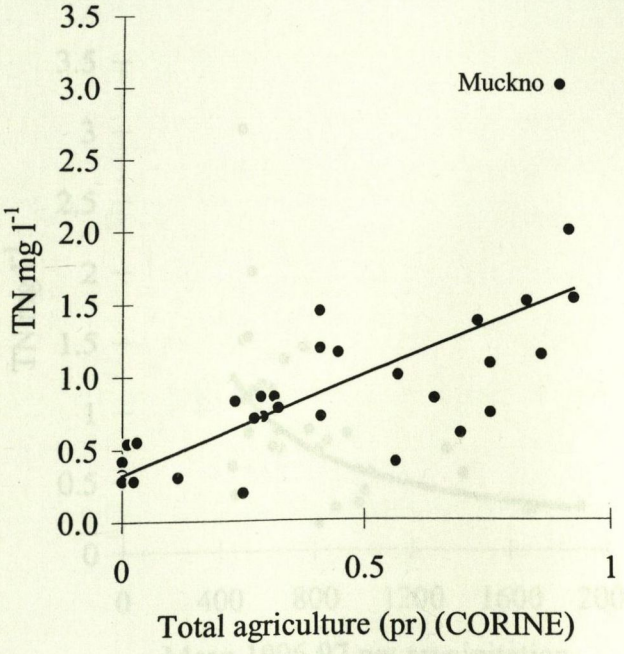


Figure 7.18 Relationship between mean lake TN concentration and the sum of the proportion of land in agricultural use (CORINE). Equation: $y = 1.3657x + 0.3217$, $r^2 = 0.53$, $p \leq 0.0001$, $n = 31$.

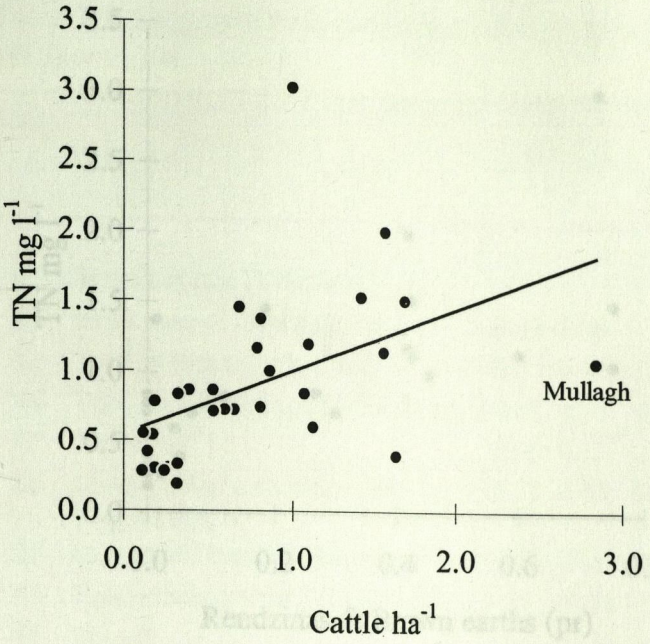


Figure 7.19 Relationship between TN concentration and cattle ha^{-1}. Equation: $y = 0.4561x + 0.5424$, $r^2 = 0.23$, $p = 0.0062$, $n = 31$.

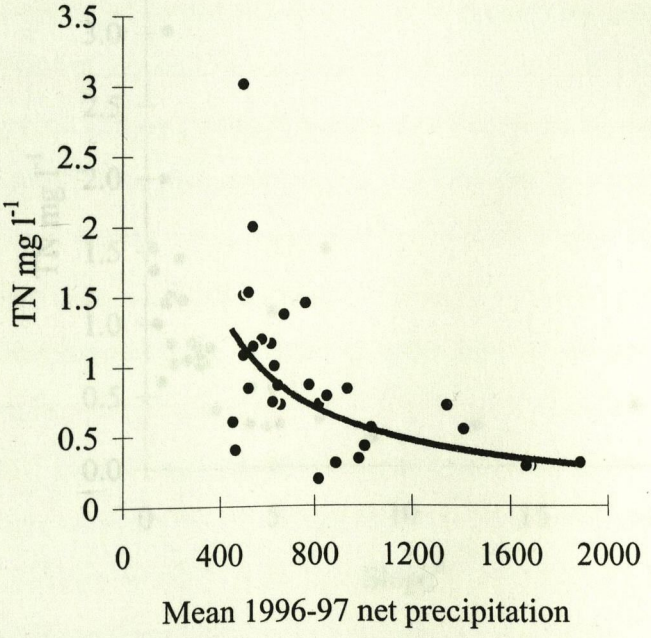


Figure 7.20 Relationship between TN concentration and mean (1996-97) net precipitation. Solid line is a best fit power trend-line with equation: $y = 671.58x^{-1.027}$, $r^2 = 0.41$, $n = 31$.

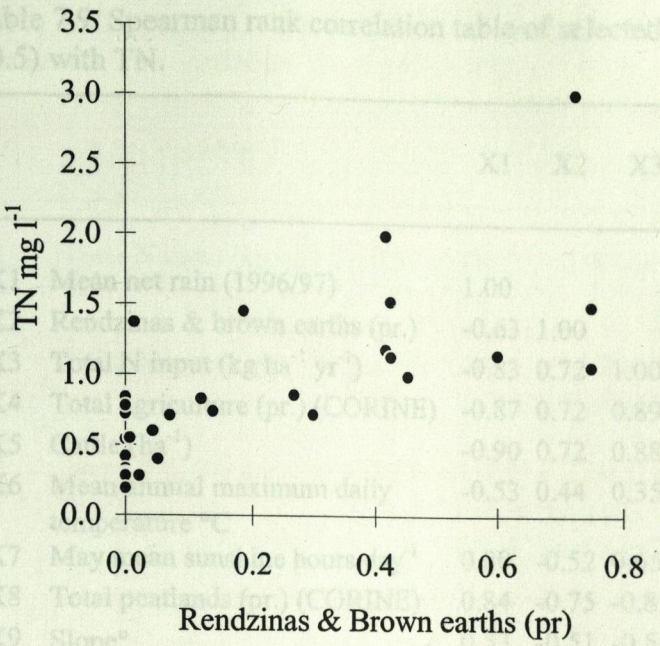


Figure 7.21 Relationship between TN concentration and Rendzinas and brown earth soils (n = 31).

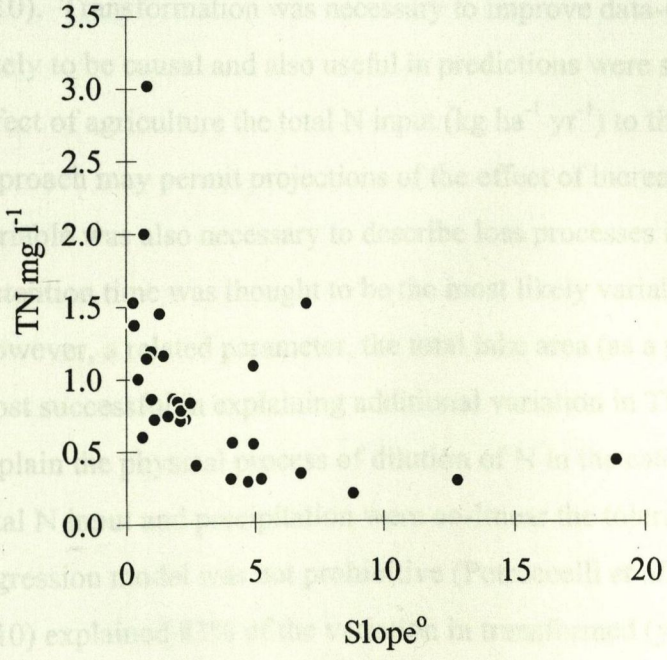


Figure 7.22 Relationship between TN concentration and slope (n = 31).

Table 7.9 Spearman rank correlation table of selected variables which had a high r_S ($\geq \pm 0.5$) with TN.

		X1	X2	X3	X4	X5	X6	X7	X8	X9
X1	Mean net rain (1996/97)	1.00								
X2	Rendzinas & brown earths (pr.)	-0.63	1.00							
X3	Total N input (kg ha^{-1} yr^{-1})	-0.83	0.72	1.00						
X4	Total agriculture (pr.) (CORINE)	-0.87	0.72	0.89	1.00					
X5	Cattle (ha^{-1})	-0.90	0.72	0.88	0.90	1.00				
X6	Mean annual maximum daily temperature °C	-0.53	0.44	0.35	0.53	0.53	1.00			
X7	May mean sunshine hours day^{-1}	0.80	-0.52	0.65	-0.78	-0.78	-0.54	1.00		
X8	Total peatlands (pr.) (CORINE)	0.84	-0.75	-0.82	-0.82	-0.83	-0.55	0.72	1.00	
X9	Slope°	0.53	-0.51	-0.56	-0.70	-0.56	-0.67	0.61	0.51	1.00

Multiple regression was used to explain further variation in transformed ($y^{\wedge 0.1}$) TN (Table 7.10). Transformation was necessary to improve data-distribution. Variables that were likely to be causal and also useful in predictions were selected. To explain the positive effect of agriculture the total N input (kg ha^{-1} yr^{-1}) to the catchment was included. Such an approach may permit projections of the effect of increasing N inputs to catchments. Some variable was also necessary to describe loss processes in the lake which can be substantial. Retention time was thought to be the most likely variable to describe N loss in lakes. However, a related parameter, the total lake area (as a proportion of the catchment) was most successful in explaining additional variation in TN. Net precipitation was included to explain the physical process of dilution of N in the catchment by rainfall. Although the total N input and precipitation were co-linear the tolerance for inclusion in a multiple regression model was not prohibitive (Petruccelli *et al.*, 1999). The final model (Table 7.10) explained 83% of the variation in transformed ($y^{\wedge 0.1}$) mean TN concentration. Additional variables were not significant in explaining further variation.

Table 7.10 Multiple regression for transformed ($y^{\wedge 0.1}$) mean TN (mg l^{-1}). Proportion is denoted by pr. Variables are significant ($p \leq 0.002$), n = 31.

Step	Variable	R^2	Model
1	Total N input (kg ha^{-1} yr^{-1})	0.57	$TN^{\wedge 0.1} = 0.90464 + 0.00150603 \cdot$ Total N input (kg ha^{-1} yr^{-1})
2	Total lake area (pr)	0.75	$TN^{\wedge 0.1} = 0.929637 + 0.00161551 \cdot$ Total N input (kg ha^{-1} yr^{-1}) + total lake area (pr) $\cdot$ -0.289884
3	Mean (96, 97) net $rain^{\wedge 0.1}$	0.83	$TN^{\wedge 0.1} = 1.61311 + 0.00101992 \cdot$ Total N input (kg ha^{-1} yr^{-1}) + total lake area (pr) $\cdot$ -0.353893 + Mean (96, 97) net $rain^{\wedge 0.1} \cdot$ - 0.334587

One test of the success of a model is its ability to predict results that were not used to generate it. To test the success of the model in Table 7.10 published NO_3^- loss data from a field experiment with controlled N inputs were used (Garrett *et al.*, 1992). According to Garrett *et al.* (1992), NO_3^- was by far the dominant fraction lost so the results may be assumed to be close to TN. Factors entered into the model were mean precipitation (884 mm) minus average evapotranspiration (estimated as 506 mm from Rohan, 1986), and the varied N inputs in the field experiment. Predicted TN was close to measured NO_3^- at N application rates of 108 kg ha^{-1} yr^{-1} only (Table 7.11). The difference between predicted and measured N increased with increasing N application rates. Therefore the model may only be successful within the range of nitrogen inputs used to generate it (5.6 to 116 kg N ha^{-1} yr^{-1}).

Table 7.11 Predicted TN and measured NO_3^--N (mg l^{-1}) in leachate. Experimental plots were located in Northern Ireland and received a range of N inputs (kg ha^{-1} yr^{-1}) (Garrett *et al.*, 1992).

Mean N input (kg ha^{-1} yr^{-1})	Measured mean NO_3^- mg l^{-1}	Predicted mean TN mg l^{-1}	Predicted as % of measured
108	3.0	3.0	101
207	5.1	7.2	143
307	8.5	16.1	190
406	16.6	33.7	203
506	16.4	67.3	411

The values predicted from the model (Table 7.10) at varying nitrogen input, precipitation and total lake area (pr.) are presented in Table 7.12. Lake TN concentration was predicted to be highest at low precipitation and high N inputs to the catchment. A high proportion of total lake area in the catchment was predicted to substantially reduce the concentration of TN. Table 7.12 shows that a total lake area (pr.) of 0.1 led to predicted TN that was on average 27% less than for a total lake area of only 0.01.

The model may be useful in predicting future TN concentrations within a limited range. Projections were made for a 90% increase in fertiliser application to grassland and other crops in each catchment, which corresponds to predicted fertiliser application in the year 2020. This figure was derived from the current increasing trend in national fertiliser usage (Figure 7.2). The predicted increase in mean TN ranged from 0 to 2.08 mg l^{-1} (mean 0.39 mg l^{-1}, n = 31) (Table 7.13). However, some caution must be drawn to the use of the model to predict TN increase beyond the range of the data used to generate the model (5.6 to 116 kg N ha^{-1} yr^{-1}). This applies to the seven catchments indicated by an asterisk in Table 7.13.

The model may also be useful in hindcasting TN concentration. The lake TN concentration was predicted for zero fertiliser inputs to agriculture and forestry (Table 7.13). Little difference was predicted in catchments that already receive small fertiliser

inputs. Lakes that currently receive the highest N inputs of 83 to 116 kg N ha^{-1} yr^{-1} (Muckno, Egish, Ramor, Oughter, Gowna and Mullagh) were all located in the north-east of the Republic. These lakes had hindcasted TN concentrations that were 46 - 55% lower than contemporary predicted concentrations. Therefore it is estimated that agriculture currently accounts for half the concentration of TN in these lakes.

Table 7.12 Predicted mean lake TN concentration (mg l^{-1}) for different rates of total nitrogen input to catchments (kg ha^{-1} yr^{-1}), net precipitation (mm) and total lake area (pr.). The different proportions of total lake area were selected to approximate minimum (0.008), mean (0.103) and maximum (0.362) values for the 31 lakes.

Net rain mm	10 kg ha^{-1} yr^{-1}	20 kg ha^{-1} yr^{-1}	50 kg ha^{-1} yr^{-1}	100 kg ha^{-1} yr^{-1}	150 kg ha^{-1} yr^{-1}	200 kg ha^{-1} yr^{-1}
			Total lake area (pr.) = 0.01			
400	1.1	1.2	1.7	2.7	4.2	6.4
800	0.7	0.8	1.1	1.8	2.8	4.4
1200	0.5	0.6	0.8	1.4	2.2	3.5
1600	0.4	0.5	0.7	1.1	1.8	2.9
			Total lake area (pr.) = 0.10			
400	0.8	0.9	1.2	2.0	3.1	4.9
800	0.5	0.6	0.8	1.3	2.1	3.4
1200	0.4	0.4	0.6	1.0	1.6	2.6
1600	0.3	0.3	0.5	0.8	1.4	2.2
			Total lake area (pr.) = 0.30			
400	0.4	0.4	0.6	1.0	1.6	2.6
800	0.2	0.3	0.4	0.6	1.1	1.8
1200	0.2	0.2	0.3	0.5	0.8	1.4
1600	0.1	0.2	0.2	0.4	0.7	1.1

Table 7.13 Measured, predicted and projected (projected for 90% increase and zero fertiliser application) TN concentrations (mg l^{-1}) for the study lakes. An asterisk indicates that projections for 90% increase were outside range used to generate model. Predictions were made using the model in Table 7.10.

Lake	Measured TN mg l^{-1}	Predicted TN mg l^{-1}	Predicted for zero fertiliser	Predicted for 90% increase in fertiliser
Talt	0.19	0.38	0.33	0.43
Maumwee	0.28	0.31	0.31	0.31
Muckross	0.28	0.28	0.27	0.28
Lettercraffroe	0.30	0.30	0.28	0.30
Caragh	0.30	0.34	0.30	0.37
Easky	0.33	0.41	0.41	0.41
Lene	0.40	0.58	0.27	1.12
Bray	0.42	0.32	0.32	0.32
Dan	0.54	0.47	0.46	0.47
Feeagh	0.55	0.55	0.53	0.56
Owel	0.60	0.87	0.51	1.37
Leane	0.71	0.56	0.42	0.71
Bunny	0.72	1.09	0.87	1.32
Doolough	0.72	0.72	0.62	0.82
Rea*	0.74	0.68	0.38	1.11
Moher	0.78	0.76	0.63	0.89
Pollaphuca	0.83	1.00	0.55	1.64
Lickeen	0.84	1.02	0.75	1.32
Ballyquirke	0.86	0.84	0.69	0.99
Graney	0.86	0.96	0.80	1.10
Cullaun	1.00	1.12	0.84	1.45
Mullagh*	1.08	0.60	0.33	1.00
Gowna*	1.14	1.47	0.78	2.51
Ballycullinan	1.16	1.05	0.86	1.26
Dromore	1.19	0.58	0.45	0.69
Gara South	1.37	1.12	0.89	1.36
Inchiquin	1.45	0.99	0.82	1.17
Egish*	1.51	1.33	0.63	2.49
Oughter *	1.53	1.93	1.01	3.36
Ramor*	2.00	1.89	0.97	3.32
Muckno*	3.02	2.30	1.06	4.38

Total nitrogen in the 189 lakes sampled in summer ranged from 0.12 to 2.92 mg l^{-1}. Total nitrogen in the 189 lakes had similar statistical relationships with catchment characteristics as the 31 lakes (Table 7.14 and Table 7.15). Both net precipitation and total nitrogen inputs to the catchments showed similar trends with TN as found in the 31 lakes (Figure 7.23 and Figure 7.24). The relationship between net precipitation and TN found in the 189 lakes, as with the 31 lakes, is likely to be largely a result of the co-linearity between rainfall and the proportion of agriculture in the catchment (Table 7.9). The same predictors of mean TN (n = 31) were significant in multiple regression for summer TN (n = 189) (Table 7.16). However, as summer TN was lower than mean TN the coefficients were different. Sampled lake area (pr) explained substantially less variation than that of the similar parameter for the 31 lakes (total lake area (pr.)) (Table 7.10 and Table 7.16).

Table 7.14 Spearman rank correlation table between summer TN and agricultural and climatic catchment characteristics (n = 189). Only $r_S \geq \pm 0.143$, $p \leq 0.05$ are presented. An asterisk indicates climatic data for other months were also significant.

Agricultural	r_S	Climatic	r_S
Total agriculture (pr.) (CORINE)	0.71	Annual precipitation (mm)	-0.65
Total pasture (pr.) (CORINE)	0.70	Net Annual precipitation (mm)	-0.65
Total N input (kg ha^{-1} yr^{-1})	0.69	August max. temp. °C*	0.61
Pasture high prod (pr.)	0.66	May mean sunshine hours day^{-1}*	-0.47
Cattle (ha^{-1})	0.63	Mean annual maximum daily temperature °C	0.43
Permanent meadow (pr.)	0.60	NO_3 mg l^{-1} deposition kg N ha^{-1} yr^{-1}	-0.30
Sum of rotation under 5 years (pr.)	0.58	Annual mean sunshine hours day^{-1}	-0.27
Silage (pr.)	0.57	Rain NH_4 mg l^{-1} deposition kg N $catchment^{-1}$ yr^{-1}	0.16
Pasture mix (pr.)	0.50	Julian day	0.15
Pasture low prod (pr.)	0.48		
Total grassland (pr.)	0.40		
Rough grazing (pr.)	-0.33		
Sheep (ha^{-1})	-0.28		
All crops (pr.)	0.20		
Natural grasslands (pr.)	-0.17		

Table 7.15 Spearman rank correlation table between TN and land class / soil and morphometric catchment characteristics. Only $r_S \geq 0.143$, $p \leq 0.05$ are presented.

Land class / soil	r_S	Morphometric	r_S
Total peatlands (pr.) (CORINE)	-0.60	Easting	0.46
Peat Bogs unexploited (pr.)	-0.40	Mean catchment elevation (m)	-0.39
Moors and heathland (pr.)	-0.34	Catchment area (km^2)	0.18
		Freshwater (pr.)	-0.16
		Catchment area / lake area	0.16
		Sampled lake area (pr.)	-0.16
		Area of lake (ha)	0.14

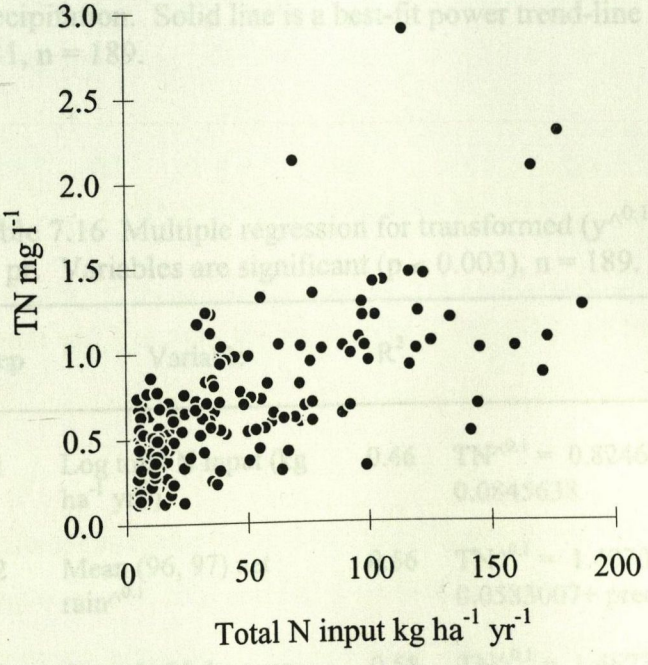


Figure 7.23 Relationship between the summer TN concentration and the total N input to the catchments, n = 189.

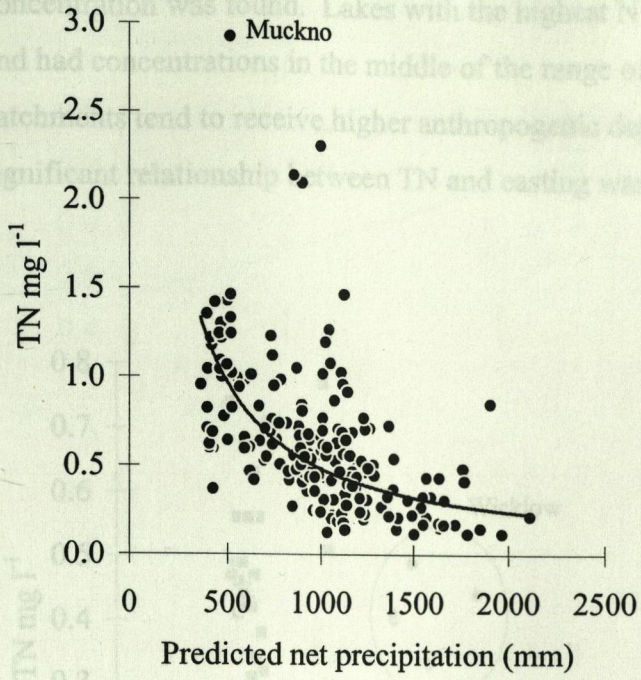


Figure 7.24 Relationship between summer TN concentration and predicted net precipitation. Solid line is a best-fit power trend-line with equation: $y = 456.82x^{-0.9915}$, $r^2 = 0.41$, $n = 189$.

Table 7.16 Multiple regression for transformed ($y^{\wedge 0.1}$) summer TN. Proportion is denoted by pr. Variables are significant ($p \leq 0.003$), $n = 189$.

Step	Variable	R^2	Model
1	Log total N input (kg ha^{-1} yr^{-1})	0.46	$TN^{\wedge 0.1}$ = 0.824666 + log total N input (kg ha^{-1} yr^{-1}) · 0.0845638
2	Mean (96, 97) net $rain^{\wedge 0.1}$	0.56	$TN^{\wedge 0.1}$ = 1.40708 + log total N input (kg ha^{-1} yr^{-1}) · 0.0583007+ predicted net $rain^{\wedge 0.1}$ · - 0.276156
3	Sampled lake area (pr)	0.58	$TN^{\wedge 0.1}$ = 1.46737 + log total N input (kg ha^{-1} yr^{-1}) · 0.0554483 + predicted net $rain^{\wedge 0.1}$ · - 0.299864 + sampled lake area (pr) · -0.109428

To investigate if there was a relationship between atmospheric N deposition and TN concentration in the 189 lakes, other sources of N must be excluded (Allott *et al.*, 1995). Therefore, only 49 catchments that had less than 1% agriculture and less than 5% coniferous forestry were selected. No clear relationship between N deposition and lake

concentration was found. Lakes with the highest N deposition were located in Wicklow and had concentrations in the middle of the range of the 49 lakes (Figure 7.25). Eastern catchments tend to receive higher anthropogenic deposition (Jordan, 1997) but no significant relationship between TN and easting was found ($r_S = 0.253$, $p = 0.08$, $n = 49$).

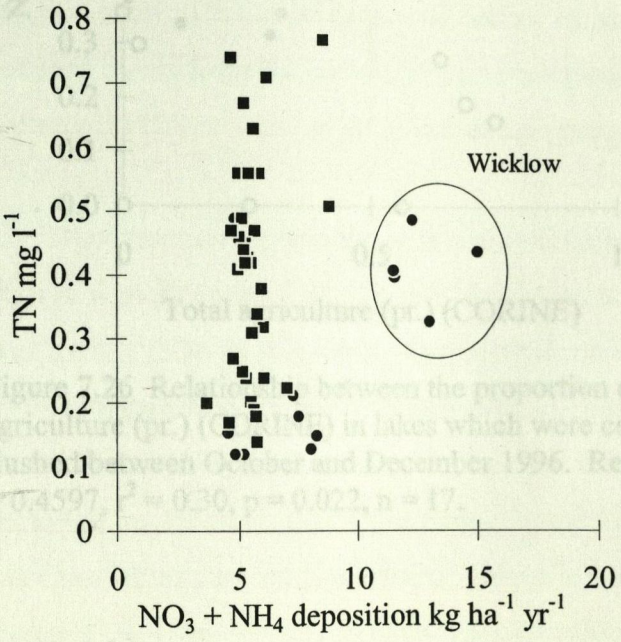


Figure 7.25 Relationship between TN concentration and N deposition. Only catchments which had less than 1% agriculture (CORINE) and less than 5% forestry are included (n = 49).

Differences in the proportions of N fractions were found between the lakes sampled. The proportions of NO_3^- and DON were examined in winter (January 1997) when the effects of biological alteration (NO_3^- uptake or DON release) would be lower. It was found that the proportion of NO_3^- was higher in agricultural catchments and that the proportion of DON was higher in catchments with peat soils (Figure 7.4, Figure 7.26 and Figure 7.27). Lakes that were incompletely flushed (from October to December 1996) prior to sampling in January tended to have lower NO_3^- and higher DON proportions. Analysing proportions rather than concentrations rules out differences owing to rainfall across the catchments. Differences in rainfall should affect concentration but not alter the proportion of the various fractions.

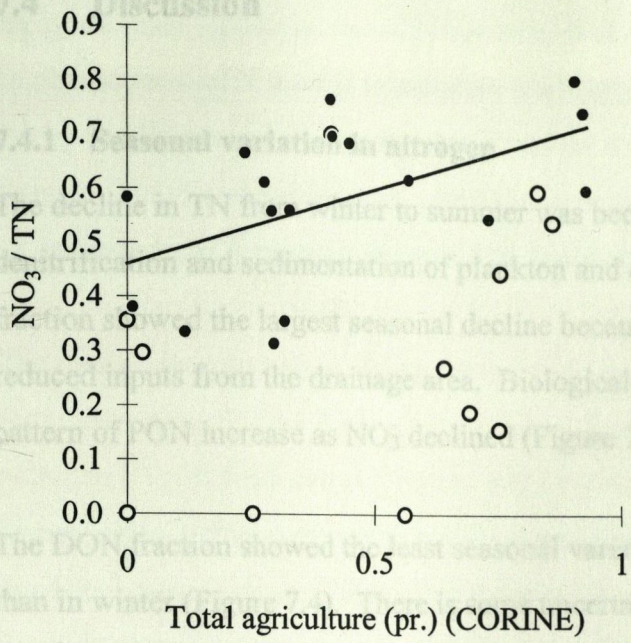


Figure 7.26 Relationship between the proportion of NO_3^- (January 1997) and total agriculture (pr.) (CORINE) in lakes which were completely (●) or incompletely (O) flushed between October and December 1996. Regression line (●) equation: $y = 0.2833x + 0.4597$, $r^2 = 0.30$, $p = 0.022$, $n = 17$.

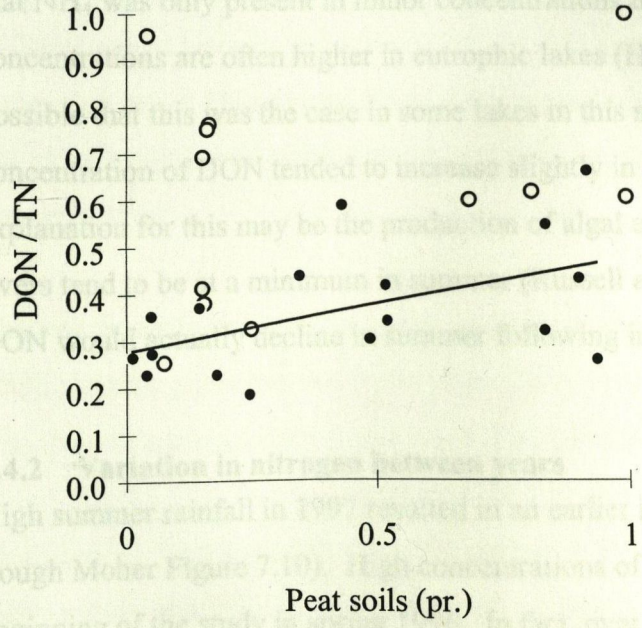


Figure 7.27 Relationship between the proportion of DON (January 1997) and peat soils (pr.) in lakes which were completely (●) or incompletely (O) flushed between October and December 1996. Regression line (●) equation: $y = 0.1974x + 0.2774$, $r^2 = 0.25$, $p = 0.04$, $n = 17$.

7.4 Discussion

7.4.1 Seasonal variation in nitrogen

The decline in TN from winter to summer was because of internal loss processes such as denitrification and sedimentation of plankton and detritus. As would be expected the NO_3^- fraction showed the largest seasonal decline because of biological uptake in the lake and reduced inputs from the drainage area. Biological uptake was apparent in the seasonal pattern of PON increase as NO_3^- declined (Figure 7.9).

The DON fraction showed the least seasonal variation but tended to be higher in summer than in winter (Figure 7.4). There is some uncertainty about the exact composition of what was termed DON in this study. The DON fraction was calculated by subtracting NO_3^- from TDN and therefore may include dissolved fractions other than organic nitrogen (e.g. NH_4^+, NO_2^- and ($CO[NH_2]$)). However, the fact that the DON fraction showed little seasonal variation may indicate that it was mainly composed of recalcitrant dissolved organic nitrogen rather than labile nutrients. This is in agreement with Allott (1990) who found that NH_4^+ was only present in minor concentrations in Clare lakes. However, NH_4^+ concentrations are often higher in eutrophic lakes (Horne & Goldman, 1994) and it is possible that this was the case in some lakes in this study. It is interesting that the concentration of DON tended to increase slightly in summer. The most probable explanation for this may be the production of algal exudates as concentrations in inflowing rivers tend to be at a minimum in summer (Russell *et al.*, 1998). Moreover, allochthonous DON would actually decline in summer following irradiation (Bushaw *et al.*, 1996).

7.4.2 Variation in nitrogen between years

High summer rainfall in 1997 resulted in an earlier increase in TN than in 1996 (e.g. Lough Moher Figure 7.10). High concentrations of TN and NO_3^- were found at the beginning of the study in spring 1996. In fact, over the study period, March and April 1996 were when TN and NO_3^- were at a maximum in most of the lakes. The reason why this period had the highest concentrations of N is uncertain. The most probable reason could be that the drought period experienced in Ireland in 1995 (Mac Cárthaigh, 1996) led to higher N concentrations in the winter of 1995-96, which were still visible in March and

April 1996. Garrett *et al.* (1992) cited several reasons why drought (decreased soil moisture) may lead to increased N concentrations in leachate. These included a reduction in plant uptake of N (owing to moisture stress and reduced availability), less denitrification in dry conditions and a surge in mineralisation at the end of a dry period. Smith and Stewart (1989) and Ferrier *et al.* (1995) have both predicted that dry summers will lead to an increase in NO_3^- concentrations in UK freshwaters.

The mean concentration of TN increased by 81 to 105% between 1981-2 and 1996-7 in four Clare lakes (Figure 7.11 to Figure 7.14). Increases of nitrate have been previously recorded in Irish freshwaters. Tonner and Lennox (1980) found an increase in nitrate in several rivers between the periods 1972-3 and 1976-7 which they attributed to increased fertiliser usage. Lehane (1999) used temporal trends in nitrate concentrations in larger rivers as one of several indicators of the state of the Irish environment. Three rivers (Shannon, Blackwater and Suir) all showed an increasing trend in nitrate from 1982 to 1998. The percentage increase from 1982 to 1996-98 (mean of 1996 and 1998) ranged from 70 to 100%. This increase is similar to that recorded for the four Clare lakes in this study. An increase in NO_3^- concentration and loadings from in-flowing rivers to Lough Neagh has been noted by Smith *et al.* (1982) and Smith & Stewart, (1989). Zhou *et al.* (2000) found a weak upward trend (1974-1997) in mean annual flow weighted concentration of TN and total Kjeldahl N in the inflow to lower Lough Erne. Nitrate did not show a significant upward trend, probably because upstream lakes lowered NO_3^- concentrations.

Most of the increase in TN in Lough Inchiquin was in the NO_3^- fraction (Figure 7.15). A small increase was observed in the particulate organic nitrogen fraction (PON) whereas the dissolved organic nitrogen fraction (DON) showed no increase. Høyås *et al.* (1997) also found that the NO_3^- fraction accounted for the main increase in TN in a Norwegian river in an agriculture catchment between the periods 1966-1974 and 1991-1996. Kopáček *et al.* (1995) found that NO_3^- in the Slapy reservoir in Central Europe had increased between 1959 and 1993 while the concentration of organic nitrogen showed no temporal increase.

The increase in particulate organic nitrogen (PON) from 1985 to 1996-7 in Lough Inchiquin indicated an increase in planktonic biomass. It is unlikely that this increase in

planktonic biomass was stimulated by the increase in NO_3^- as sufficient amounts for algal growth were already present in 1985. As TP concentrations were similar between years (Chapter 6) the most likely explanation for differences in PON is variation in residence time.

Total nitrogen in Lough Inchiquin has increased at a similar rate to national N fertiliser usage (Figure 7.16) which indicates that the likely source of the increased N was from the application of fertiliser. The analysis of such temporal data is a powerful method in isolating fertiliser inputs from other catchment characteristics as an important determinant of lake TN concentration. Previous work using both plot experiments and analysis of time series have shown that increased fertiliser application can lead to an increase in N concentration. Garrett *et al.* (1992) working on fertilised grazed plots in County Down found that the loss of NO_3^- and NH_4^+ increased with increasing fertiliser application but the loss of total Kjeldahl nitrogen (a measure of non-NO_3^- N fractions) was independent of nitrogen input. Smith (1977) and Smith *et al.* (1982) found that mean NO_3^- concentration in major rivers flowing into Lough Neagh was correlated to fertiliser application.

In light of the fact that the two-year period examined followed a drought, some caution must be applied before attributing the 81 - 105% increase in TN in the four Clare lakes solely to increased fertiliser application. The increase may also have been caused by increased mineralisation following the drought in 1995 (Mac Cárthaigh, 1996). Ideally a continuous time series would be available which would allow proper consideration of additional factors affecting TN concentration. Smith and Stewart (1989) found that fertiliser usage only explained 42% of the variation in NO_3^- loading, the inclusion of additional factors (the previous summers rain, current summer air temperature and winter and spring flow) in multiple regression explained a total of 95% of the variation.

The likelihood of an upward trend in TN concentration caused by increased fertiliser application means those empirical models that relate static catchment characteristics (e.g. slope) to TN concentration may only be valid for a limited time period. For example, slope could be used to predict TN (Figure 7.22) but the same model may not be useful in predicting the TN concentration in ten years time if, for example, the fertiliser use in the

catchments increase. The approach used in this study to get around this is to include fertiliser application rates in empirical models.

7.4.3 Variation in nitrogen among lakes

The concentration of TN ranged from a minimum of 0.11 mg l^{-1} in Lough Maumwee to a maximum of 4.48 mg l^{-1} in Lough Muckno (Table 7.5). Summer TN in the 189 lakes ranged from 0.12 to 2.92 mg l^{-1}. These concentrations are much lower than in some other European countries. In the Netherlands, van der Molen *et al.* (1998) have suggested that a suitable target would be to have mean summer TN concentration below 1.35 mg l^{-1}. Only 16% of Dutch lakes had TN below this in 1996, compared with 95% of the 189 Irish lakes sampled.

Multiple regression explained 83% of the variation in TN (Table 7.10). Significant variables ($p \leq 0.0001$) included the total nitrogen input to the catchment (kg ha^{-1} yr^{-1}), net precipitation (mm) and the proportion of total lake area in the catchment. The N input to catchments (kg ha^{-1} yr^{-1}) explained the most variation in mean TN in the 31 lakes (57%). This indicates the importance of N input, which mainly occurred through fertiliser addition to pasture (Table 7.8).

The proportion of total lake area had a negative relationship with TN and explained a further 18% of the variation in multiple regression. This parameter was significant because it indicated the loss of N owing to sedimentation and denitrification within the catchments lakes. The total lake area in the catchment describes N loss for a number of reasons. Firstly it may act as a surrogate for retention time (total lake area was positively correlated with all estimates of t_w, $r_S \geq 0.87$, $p \leq 0.0001$) and a longer retention time increases the duration of loss processes in the lake. A higher proportion of total lake area also means less drainage area, which is the most important source of TN. Dilution of TN by direct precipitation onto the lake may occur in cases where the concentration in precipitation is lower than that of the lake. Also a larger lake area means a larger benthic area which is important in decreasing N by denitrification (Arheimer & Brandt, 1998). Total lake area in the catchment explained more variation than sampled lake area. This is because the loss process in upstream lakes would also be important in determining TN in the downstream lake. The proportion of total lake area explained more variation than

retention time because it acts as a surrogate variable for many catchment processes including retention time. This finding illustrates the importance of lakes in reducing the load of N to the sea.

The negative relationship between TN and net precipitation indicates that a dilution process may be operating. This process is one where a larger volume of precipitation issuing from a soil would have a lower concentration than had a smaller volume passed through. Therefore, the TN concentration may be higher in agricultural areas partly because they receive less precipitation. Hooda *et al.* (1997) found higher NO_3^- concentrations in some streams in Scotland during summer and suggested it was because of a 'concentration effect' where the measured concentration of NO_3^- may be higher owing to less volume passing through the soil and evaporative concentration of NO_3^-. Gasser (1980) collated data from three grassland sites in the UK and found that as precipitation increased the NO_3^- concentration in the drainage water decreased. However, the reverse was true for export; higher precipitation led to higher export. It is therefore important to consider precipitation when relating land use to nitrogen concentration.

There are also other possible explanations as to why net precipitation was significant in a multiple regression along with total N input and total lake area. It is also possible that catchments with high precipitation have a higher proportion of runoff in overland flow thus leading to lower TN concentrations (e.g. Webb & Walling, 1985). Also, TN concentrations would tend to be lower at higher precipitation because of increased denitrification in catchment soils (Hooda *et al.*, 1997).

Before examining the models predictions and projections it was thought necessary to validate the model against independent data. The field experiment conducted by Garrett *et al.* (1992) allowed predictions to be tested against results where the nitrogen inputs were controlled. Predicted TN was only 1% greater than measured NO_3^- at application rates of 108 kg ha^{-1} yr^{-1} (Table 7.11). However, the difference between predicted and measured N increased rapidly with increasing N application rates: concentrations were overestimated by 43% at N application rates of 207 kg ha^{-1} yr^{-1}. There may be several reasons for this discrepancy at higher N application rates. Perhaps loss processes other than leaching were important in the soil at higher N application rates. Denitrification has been found to

increase at higher N application rates (Garrett *et al.*, 1992) and the model may not take this into account. The poor performance of the model may also be because the data used to generate it had a limited range of N inputs (6 - 116 kg ha^{-1} yr^{-1}, Table 7.8). More error may be associated with predictions far outside this range.

Caution must also be applied in the application of the model. The model is certainly likely to be relevant only for similar catchment land uses such as peatland and pasture. It is important to note that catchments with a high proportion of arable land were not included in this study. Most arable farming in Ireland is located in the south-east where there are very few lakes. In addition, because there was some co-linearity between total nitrogen input and precipitation, some caution must be applied in interpreting projections from the model if other factors in the model are held constant (Petruccelli *et al.*, 1999).

In order to hindcast the TN concentration in the study lakes the model (Table 7.10) was used to estimate concentrations when there was zero artificial N application to agriculture and forestry. The model estimated that lakes located in the north-east of the Republic, which currently have the highest artificial N input (83 to 116 kg N ha^{-1} yr^{-1}), had hindcasted TN concentrations that were 46 to 55% of contemporary predicted concentrations (Table 7.13). Therefore, about half of present day TN in these lakes is derived from artificial N inputs to the catchment. Interestingly, Smith and Stewart (1989) found that 50% of mean nitrate load of rivers entering Lough Neagh in Northern Ireland was attributable to N loss from artificial fertilisers. The similar conclusions and the fact that Smith and Stewart (1989) made their estimation using a different approach (time series modelling) corroborates the hindcasted predictions in this study. Therefore, even though Irish TN concentrations are relatively low in comparison with other European countries, TN is elevated in some Irish lakes because of fertiliser usage. Current national and European objectives are to work towards the restoration of both estuarine and freshwaters to natural conditions (Department of the Environment, 1997; Council of the European Communities, 2000). Such models if further validated - especially by sediment cores - may prove useful in guiding remediation.

According to the model in this study, a 90% increase in fertiliser application (predicted for the year 2020) would result in an increase of between 0 to 2.08 mg l^{-1} TN in lake water.

Such increases in TN could have a negative effect by contributing to eutrophication, especially in marine waters (Barnes & Hughes, 1988). Current integration of freshwater and marine water-quality objectives necessitates that more attention now be paid to freshwater N concentrations and more importantly, from a marine perspective, N export (Council of the European Communities, 2000).

Lake TN concentration was predicted to be substantially lower in catchments with a high proportion of lake area (Table 7.12). The model in this study predicted that lakes with a total lake area of 0.1 of their catchments (mean of the 31 lakes) would have 27% less TN than lakes with a total lake area of only 0.01 (minimum of the 31 lakes). The net effect of catchment lakes on reducing TN export may be even greater than this. This is because this study was based on samples taken from the centre of the lake. Additional N loss would occur before water reaches the outflow. Previous work in other countries supports this. Arheimer & Brandt (1998) found that the N load in Southern Sweden was greatly reduced by lakes (30-40 kg N ha^{-1} lake area yr^{-1}) and an average of 45% of annual gross load was reduced during transport. Stewart *et al.* (1976) found than total nitrogen in inflowing waters decreased from 8.47 mg l^{-1} to 3.10 mg l^{-1} after passing through two loughs in Scotland. This represented a decrease of 63% of inflow TN concentration.

The same predictors of TN used for the 31 lakes were also significant in multiple regression for the 189 lakes (i.e. N input to catchment, net rainfall and proportion of lake area) (Table 7.16). A total of 58% of the variation in TN was explained. In contrast to the model for the 31 lakes, that for the 189 lakes indicated that the inclusion of lake area (pr.) explained very little additional variation in TN (3%). The may be because the 189 lakes were sampled in summer when they would already have had a substantial loss of N. Therefore the variation of TN owing to differences in loss of N would have been at a minimum and the usefulness of lake area (pr.) will be less.

No relationship was found between TN concentration and atmospheric N deposition in 49 lakes in non-agricultural catchments. This may be taken to indicate that upland catchments in Ireland are not currently N saturated as has been found in some countries where atmospheric N deposition is high (Allott *et al.*, 1995). Curtis *et al.* (1998), working on 13 upland sites in the UK, noted that significant leaching losses were only apparent when TN

deposition was in excess of 10 kg ha^{-1} yr^{-1}. Maximum deposition calculated in the 49 lakes was 15 kg (NO_3^--N + NH_4^+-N) ha^{-1} yr^{-1}, although this figure is not precise as there are few stations where precipitation chemistry is determined. In addition, the lakes were sampled in summer so this may have reduced the range in TN concentration because of loss processes within lakes.

In the lakes sampled seasonally, the proportion of agriculture (CORINE) had a positive relationship with the proportion of NO_3^- in the lakes in January 1997 ($r^2 = 0.29$, $p = 0.025$, $n = 18$). This relationship was only investigated during winter and in lakes that were completely flushed in the three months prior to sampling in order to lessen the influence of loss processes in lowering the proportion of NO_3^-. The proportion of DON was found to be higher in catchments with peat soils. Previous work supports these findings. Misztal *et al.* (1992) found that NO_3^- comprised 59% of TN (total Kjeldahl + NO_3^-) in streams draining arable land in Poland whereas a higher proportion of organic nitrogen was found in water draining forest and peat bogs (Table 7.2). Høyås *et al.* (1997) recorded that NO_3^- in south eastern Norway constituted 90% of TN lost from agricultural land but only 50% of TN lost from forested catchments. Published work in Northern Ireland reveals similar differences in N fractions with catchment characteristics. Nitrate comprised a much higher proportion of exported N in the pasture-dominated river Main catchment (Smith, 1976) than in the peatland-dominated Loughgarve catchment (Gibson *et al.* 1995b). It is likely that inputs of mineral nitrogen in agricultural catchments are much higher and are more likely to exceed vegetation requirements than in upland peat catchments. Higher proportions of mineral N in catchment soils may therefore lead to higher proportions of mineral N in lakes.

This study showed that NO_3^- was the N fraction that increased in response to agricultural practices. This was evident in the proportion of NO_3^- increasing with the proportion of agriculture in the catchment (Figure 7.26) and also in the increasing trend in NO_3^- with fertiliser usage found in Lough Inchiquin (Figure 7.16). In contrast, the concentration of DON remained relatively constant in Lough Inchiquin. Similar conclusions apply to the Slapy reservoir in Central Europe where over a long period (1959 - 1993) DON showed no increase whereas NO_3^- increased substantially (Kopáček *et al.*, 1995). In addition, Russell *et al.* (1998) found that despite high export of TN in agricultural catchments (19 - 35 kg TN ha^{-1} yr^{-1}), the export of DON was quite low (3 - 6 kg DON ha^{-1} yr^{-1}).

7.5 Conclusions

The main conclusions from this chapter are:

- Total nitrogen displayed a summer minimum and a winter maximum. Nitrate showed the most seasonal variation whereas DON varied little seasonally.
- Most of the lakes had higher nitrogen concentrations at the beginning of the study in 1996 and this was possibly caused by increased mineralisation in the drainage area because of a drought that occurred in 1995.
- An 81 - 105% increase in TN, mainly in the NO_3^- fraction, was found between 1981-2 and 1996-7 in four Clare lakes. This was attributed to increased fertiliser application although higher rates of mineralisation following a drought in 1995 may also have been partly responsible.
- Total nitrogen concentration was most strongly correlated to descriptors of agriculture, which indicates that agricultural activities are a major N source. Multiple regression explained 83% of the variation in TN and significant variables ($p \leq 0.0001$) included the total nitrogen input to the catchment (kg ha^{-1} yr^{-1}), net precipitation (mm) and the proportion of total lake area in the catchment.
- Model predictions for zero fertiliser usage indicated that, for lakes located in the north-east of the Republic, about half of present day TN is derived from artificial N inputs to the catchment.
- No relationship was found between N deposition and TN concentration in 49 lakes with non-agricultural catchments.
- Nitrate was a higher proportion of TN in agricultural catchments and DON was a higher proportion in catchments with peat soils.

8. GENERAL DISCUSSION

This chapter considers themes that were common to several of the earlier chapters, namely, the influence of drought, the effect of elevated summer rainfall, the uniqueness of limestone catchments and changes in lake chemistry over time. Following this, the shortcomings and strengths of the study and an assessment of the overall success of the approach are discussed.

8.1 Re-occurring themes

8.1.1 Influence of drought

One of the re-occurring themes in the thesis was the influence of periods of drought (decreased soil moisture) on freshwater chemistry. This arose because the two years of sampling and analysis followed the drought year of 1995 (Mac Cárthaigh, 1996). Drought may increase N concentrations in leachate by several processes such as reduction of N uptake by plants (owing to moisture stress and reduced availability), less denitrification in dry conditions and a surge in mineralisation at the end of a dry period (Garrett *et al.*, 1992). Like NO_3^-, SO_4^{2-} loss is influenced strongly by mineralisation. Over 90% of S in pasture soils can be in organic form and mineralisation from this pool can account for more than 75% of SO_4^{2-} leached (Sakadevan *et al.*, 1993). A period of drought would be likely to increase mineralisation because of higher temperatures and aerobic conditions. This is supported by Lennox *et al.* (2000) who examined loadings to Lough Neagh in Northern Ireland from 1988-1997 and found that loading increased following dry summers and reached a maximum in 1996. Low moisture content of soils also increases colour, probably by increased micro-organism respiration owing to higher temperature and aerobic decomposition (Naden & McDonald, 1989; Mitchell & McDonald, 1992; Swift *et al.*, 1979).

Given the limited duration of the study an evaluation of the effects of the 1995 drought on lake chemistry was difficult. Ideally, a long time series that preceded and followed the drought would be analysed. Despite this, some evidence was found for a drought-induced increase in concentrations of NO_3^- and SO_4^{2-} (See Chapters 4 and 7). In contrast, no evidence was found to indicate that the drought in 1995 led to an increase in colour (See

Chapter 5). The decline in SO_4^{2-} from early 1996 to late 1997 in lakes in Cavan and Monaghan suggested that concentrations were higher immediately following the drought and then declined (Figure 4.11). Comparing the results of this study to those from a survey in the early 1970s (Flanagan & Toner, 1975) revealed that concentrations of SO_4^{2-} were higher in 1996-7 in the counties of Cavan, Monaghan and Westmeath. The magnitude of this increase was partly attributed to the size of the organic S pool built up from past fertiliser additions (Table 4.22). Evidence for a drought-induced increase in NO_3^- was that the maximum concentration mainly occurred in the spring that followed the drought (22 out of 29 lakes had maximum NO_3^- in March and April 1996). Sampling commenced in the spring of 1996 so it is possible that concentrations were higher prior to this. In addition, four Clare lakes had higher NO_3^- in 1996-7 than in 1981-2 (Table 7.4). However, the relative importance of increased fertiliser application and drought could not be distinguished. In contrast, no evidence was found for a higher colour in 1996. This was attributed to the severity of the drought being below that where an increase in colour would be observed (Mitchell & McDonald, 1992).

There are several implications that arise from the likely association between the 1995 drought and the chemistry of the lakes. Firstly, this means that comparison with previous or future chemical data on these lakes should take cognisance of the preceding climatic conditions. This should be done on a catchment basis, as although effects may apply across a region (e.g. Clare), the resultant effect on lake chemistry may also be dependent on the amount of an element in the organic fraction of a catchment's soils (i.e. SO_4^{2-}). Secondly, any relationships defined between catchment characteristics and lake chemistry may only be strictly valid under similar climatic conditions. Similar statistical relationships will probably be found but the coefficients will be different for many elements. Alternatively, models could be developed that take climatically driven seasonal variation into account.

Thirdly, isolation of a drought effect on lake chemistry may have connotations for future climate change. Climate change in Ireland is likely to bring drier summers and higher precipitation in the winter (Sweeney, 1994). This study indicates that such a change may result in higher concentrations of NO_3^- and SO_4^{2-} in freshwaters. Higher NO_3^- as a result of climate change in Northern Ireland and Scotland has also been anticipated by Smith and Stewart (1989) and Ferrier *et al.* (1995). Given the anticipated increase in both winter

precipitation and NO_3^- concentration the increased export may have implications for eutrophication of estuarine and coastal waters. Implications of a higher SO_4^{2-} export have been less emphasised: possibly because it is not a limiting nutrient in the aquatic environment. However, the implications for the terrestrial environment may be more serious. One would expect that there would be an initial increase in pasture growth in response to higher SO_4^{2-} in the soil water (Murphy, 1991); however, a continued loss of the magnitude found in the Cavan and Monaghan lakes (on average 40 kg ha^{-1} yr^{-1} higher than deposition at Clones) might lead to a reduction in soil fertility over the long term.

8.1.2 Effect of elevated summer rainfall

Rainfall during the summer of 1997 was considerably higher than in 1996 and led to an earlier increase than usual in the concentrations of N, P and colour (Figure 5.13, Figure 5.14, Table 6.2, Figure 7.9). The effects of summer rainfall were dependent on the amount of rainfall, land cover and management, lake residence time, and lake morphometry. For example, the highest increase in colour was observed in lakes with peatlands and short residence times (e.g. Lough Ballyquirke Figure 5.13) and substantial increases in nutrient concentration were found only in lakes that had a high proportion of agriculture in their drainage area (e.g. Loughs Gowna, Ramor and Inchiquin Table 6.2).

The responses of Loughs Inchiquin and Ramor to increased rainfall in August are compared in Table 8.1. The increase in nutrient concentration was higher in Lough Ramor than in Lough Inchiquin despite rainfall being higher at the latter. This was probably a result of the intense nature of agriculture in Lough Ramor's catchment in comparison with Lough Inchiquin (Chapter 2). The net rainfall estimate for August in Lough Ramor appears low (Table 8.1) but this may be an underestimate of actual runoff because the rainfall was intense and occurred over two days in August (Kurz, 2000) whereas the figures in Table 8.1 were calculated by subtracting evapotranspiration from rainfall for each month. Following nutrient input in August, chlorophyll *a* in Lough Ramor reached a very high concentration of 185 μg l^{-1} whereas it only increased slightly in Lough Inchiquin (6.9 μg l^{-1}) (Table 8.1). The low chlorophyll *a* in Lough Inchiquin was probably because of its shorter retention time and greater depth in addition to the lower nutrient concentrations. In contrast, Lough Ramor had ideal conditions for algal growth: a large

nutrient input, low flushing, large algal inoculum, low mean depth and high solar irradiation.

Another, less common, result of high summer precipitation was the decline in O_2 as a result of increased humic substance input. Winter O_2 concentrations in the surface waters of Lough Dan in 1997 were 80% saturated compared with 100% in 1996 (Figure 5.29). Concentrations as low as 3 mg l^{-1} were recorded at the sediment-water interface, which may have implications for profundal invertebrate communities. The timing of rainfall in summer rather than autumn may have intensified colour release. Summer rainfall follows a period when colour 'production' is at a maximum in the drainage area owing to aerobic mineralisation. In addition, early and intense rainfall means less colour loss by adsorption to mineral soils.

The importance of summer precipitation in altering freshwater chemistry was also demonstrated in a concurrent study in 1997. Kurz (2000) conducted a field experiment in Wexford and found that 150 mm of rainfall between the 3rd and 4th of August resulted in overland flow which accounted for 41% of the export of MRP for 16 months. The pathway of P export – in overland flow was important as this pathway typically results in a high P concentration in runoff. Such a finding indicates that a high frequency of sampling is needed to measure P loads accurately. High summer precipitation events may be rare: Tunney *et al.* (2000) suggested that they might only occur less than once every 30 years.

As with drought, the high summer rainfall in 1997 should be taken into account when comparisons are made between years.

Table 8.1 Selected chemical variables, rainfall and flushing in Lough Inchiquin and Ramor in 1997.

Lake	Date	Colour mg l^{-1} PtCo	Chl *a* µg l^{-1}	TP µg l^{-1}	TN mg l^{-1}	TSi mg l^{-1}	Net rainfall mm	Flushing $month^{-1}$
Inchiquin	14/01/97	33	0.6	33	1.66	0.88	31	0.39
Inchiquin	01/02/97						181	2.29
Inchiquin	09/03/97	29	1.1	28	1.77	0.71	29	0.37
Inchiquin	09/04/97	23	5.0	23	1.59	0.39	-7	-0.09
Inchiquin	04/05/97	20	3.0	12	1.39	0.16	-5	-0.15
Inchiquin	03/06/97	19	5.3	6	1.23	0.09	25	0.16
Inchiquin	01/07/97	20	4.5	12	1.32	0.30	26	0.33
Inchiquin	**11/08/97**	**47**	**6.9**	**41**	**1.44**	**0.66**	**149**	**1.88**
Inchiquin	17/09/97	48	2.5	32	1.20	0.83	66	0.83
Inchiquin	12/10/97	48	1.9	36	1.25	0.97	132	1.66
Inchiquin	01/11/97						113	1.43
Inchiquin	10/12/97	43	1.2	39	1.49	1.09	166	2.10
Ramor	21/01/97	52	14.9	61.8	3.12	3.02	26	0.30
Ramor	01/02/97						126	1.42
Ramor	12/03/97	51	70.4	62.4	3.31	0.69	8	0.09
Ramor	15/04/97	42	30.2	60.3	2.21	0.34	-9	-0.11
Ramor	15/05/97	58	37.6	92.5	1.82	0.87	-4	-0.16
Ramor	18/06/97	41	92.6	72.3	1.30	0.44	22	0.09
Ramor	08/07/97	38	30.1	59.4	1.30	0.45	19	0.22
Ramor	**20/08/97**	**57**	**184.9**	**204.5**	**2.09**	**2.41**	**15**	**0.17**
Ramor	24/09/97	44	56.6	104.9	1.25	4.10	12	0.14
Ramor	21/10/97	83	27.1	110.9	1.95	3.42	86	0.98
Ramor	01/11/97						99	1.12
Ramor	03/12/97	64	20.3	80.6	2.29	3.48	129	1.46

8.1.3 Limestone catchments

Lakes with limestone drainage areas had distinctive chemical characteristics in relation with catchment characteristics. In addition to higher Ca^{2+} and alkalinity these lakes typically had lower colour and most notably lower P and K than lakes whose catchments were otherwise similar.

Lakes with limestone drainage areas were listed in Chapter 2 (Table 2.11) as Loughs Ballycullinan, Bunny, Cullaun, Dromore, Inchiquin, Rea, Gara South, Lene and Owel. These lakes typically had a low colour and Loughs Lene, Owel and Rea never had a colour greater than 10 mg l^{-1} PtCo (Figure 5.11). There may be two explanations why these lakes had low colour. Firstly, the humic substances may have been precipitated by $CaCO_3$: Steinberg & Muenster (1985) noted that dissolved organic matter can be co-precipitated by calcium carbonate, although high concentrations of fulvic acid can prevent precipitation of calcium carbonate by sorbing to the spiral dislocation of the calcite crystal and forcing it to grow slower. Secondly, most lakes with limestone drainage areas had lower proportions of surface drainage (Figure 2.6). The passage of water through the mineral soils of these catchments may have resulted in lower colour as McDowell & Likens (1988) recorded a 90% decrease in DOC after passing through a mineral soil. Lough Gara South differed from the other calcareous lakes in having a very high colour (76 – 223 mg l^{-1} PtCo). This was possibly because of the high percentage of peat soils in the catchment (35%) and also because of the higher proportion of surface drainage (Figure 2.6).

The export of TP increased linearly with the proportion of agriculture in the catchments studied. However, drainage areas with well-drained soils, which corresponded mainly to limestone catchments, tended to export less TP than expected (Figure 6.11). It was reasoned that this was mainly because of a greater adsorption potential of the soils owing to their higher infiltration capacity. Other processes such as increased precipitation owing to higher Ca^{2+} in the soils and $CaCO_3$ in freshwaters may play a minor role (Chapter 6).

In support of this, Tunney *et al.* (2000) suggested that higher P application to limestone soils might be compatible with good water quality. Johnes *et al.* (1994a, b) and Johnes (1996) used lower export coefficients to predict TP in rivers with limestone catchments compared with other catchments.

Export of K^+ from limestone catchments was lower than would be expected from the amount of agriculture in their catchments (Figure 4.16). Lough Ballycullinan was an exception, having very high export of 14 kg K^+ ha^{-1} yr^{-1} owing to point source pollution. The lower K^+ export may have been because of a greater adsorption capacity in the soils. This is supported by Culleton *et al.* (1996) and Coulter *et al.* (1999) who noted that limestone soils with clay minerals have fertility problems because of K^+ fixation.

The preceding discussion illustrates the distinctiveness of limestone lakes and demonstrates the difficulties in relating catchment characteristics to lake chemistry for a diverse series of lakes. Treating the lakes separately in groups may improve predictions in some cases but not always. For example, when a separate set of P export coefficients was applied to the catchments of limestone lakes the predicted values were not related to the observed (Figure 6.15, $r^2 = 0.03$, $p = 0.634$, $n = 9$). Here the phosphorus dynamics of limestone catchments proved too complex to be predicted by a coefficient approach.

8.1.4 Changes in lake chemistry over time

The changes in lake chemistry over time were also a theme of this study. Apart from seasonal fluctuations that are well-documented the reason for changes over time could be separated into four causes: direct fertiliser losses, drought induced, changes in soil chemistry, and storm induced. Apart from direct evidence for change, the models used to hindcast N and P concentration inferred that chemistry has changed over the longer term.

The increase in application of N fertiliser (Figure 7.2) was probably responsible for the increased TN concentrations in four lakes in County Clare between 1981-82 and 1996-97. However, as drought is known to increase N in leachate then this may also have been a factor.

Increased mineralisation during the drought in 1995 was suggested as the reason why SO_4^{2-} was higher in 1996-7 than in 1973-4. The increase in SO_4^{2-} was also partly attributed to the size of the organic S pool. The highest increases in SO_4^{2-} were found in the intensely farmed north-east which were likely to have a higher amount of organic S in their soils from past fertiliser additions. Similarly, the build up of soil K^+ as a result of fertiliser addition was also proposed as the reason why K^+ concentrations had increased since

1973-4 in this region (Table 4.23). In contrast, although the national increase in soil P has been linked to higher P in leachate (Tunney *et al.*, 2000) no evidence for an increase in TP in three Clare lakes was found. This may be because of high adsorption capacities of the soils in their drainage areas or that there has been no increase in soil P in this region since the early 1980s.

Fourthly, lake chemistry changed over a shorter time scale in response to storm events. Figure 4.4 shows that Cl^- increased markedly after January 1997 in western lakes and only returned to previous levels in the following December. This was a result of increased sea-salt deposition from westerly storms during the winter of 1996-7.

The implications of these temporal changes in lake chemistry are that the relationships and models produced may only be useful over a limited time period, depending on the element being examined. For example, the positive relationship found between the proportion of agricultural land in the catchment and K^+ export (Figure 4.16) may change over time as an increase in soil K^+ leads to more K^+ export per unit area.

Comparisons with previous data were useful in isolating the influence of certain catchment characteristics or processes. The examination of a time-series may be likened to a laboratory experiment where many characteristics are held constant (e.g. geology, land cover) and a few are varied (e.g. fertiliser use, climate). For example, finding higher K^+ in 1996-7 than in 1973-4 in the north-east agricultural region pointed to increased soil K^+ as the likely causal factor. Unfortunately, there are no complete time-series on lakes in the Republic of Ireland and where there is infrequent historical data it can be of dubious quality. The 1973-4 An Foras Forbartha preliminary survey of Irish lakes was used for comparisons of K^+ and SO_4^{2-} but unfortunately the data on P concentrations are unreliable. The difficulties encountered in this study in identifying changes in lake chemistry and their causes underlines the urgent need for frequent chemical monitoring with accompanying information on quality control and quality assurance. Maintaining standards will not be an easy task in Ireland as monitoring is devolved to many local authorities. Although, improvements are imminent as the new framework directive on water quality will require regular monitoring of lakes and critically "Estimates of the level of confidence and precision of the results provided by the monitoring programmes shall be given in the [river

basin management] plan." (Annex 5, paragraph 1.3, Council of the European Communities, 2000).

8.2 Evaluation of research approach and success

The aim of this study was to examine the relationships between catchment characteristics and lake chemistry in Ireland. The primary hypothesis was that lake chemistry could be predicted from catchment characteristics. Here, as frequently found in science, the hypothesis was used as a vehicle with which to discover new facts rather than as an end in itself (Beveridge, 1961). The measure of its success is therefore an assessment of the new contributions to science rather than whether the hypothesis was proved or disproved. These contributions are summarised in Chapter 9.

The approach taken to predict lake chemistry was statistical rather than process based. While this may lead to sound predictions it simplifies the complexity of reactions in the environment. A process-based approach would have been impossible given the diversity of catchments and range of chemical substances examined. Generally, the statistical relationships did not represent causal mechanisms; instead these were inferred with regard to processes likely to be described by the catchment characteristics. Such an approach is feasible because catchment characteristics often act as surrogates for the processes that determine lake chemistry.

As with all research, the approach was moulded by financial and logistical constraints. A line needed to be drawn between useful science and unachievable aims within these constraints. These constraints determined the methods used which in turn dictated the confidence placed in the results and conclusions. The major areas where compromises were made between resources and quality of results are now discussed.

In this study the catchment area was defined from topographic maps. The problems associated with defining catchments by their topographic rather than phreatic (water) divide were discussed in Chapter 2 and included error in the extent and position of the catchment with resultant uncertainties in runoff, retention time and other information dependent on geographic accuracy such as stocking density, geology, and so on. One solution to this would have been to employ tracers to define the actual catchment.

The estimations of export made in Chapter 4 for the various elements may be criticised at several levels. Firstly, flushing of the lake was based on monthly runoff rather than a direct measurement of the outflow. This means that export figures will contain error associated with the assumption that the topographic divide coincides with the phreatic divide. Therefore the total amounts of the elements exported from the lake may be approximate. However, the export was expressed per unit area of the catchment (kg ha^{-1}). This will reduce the error associated with inaccurate catchment areas: for example, if the catchment area is underestimated by 10 km^2 then this will lead to an underestimate of the runoff and the total material exported but if this is expressed per unit area the error should be small assuming that the omitted catchment area exports a similar amount of material to that of the topographic catchment (Figure 8.1).

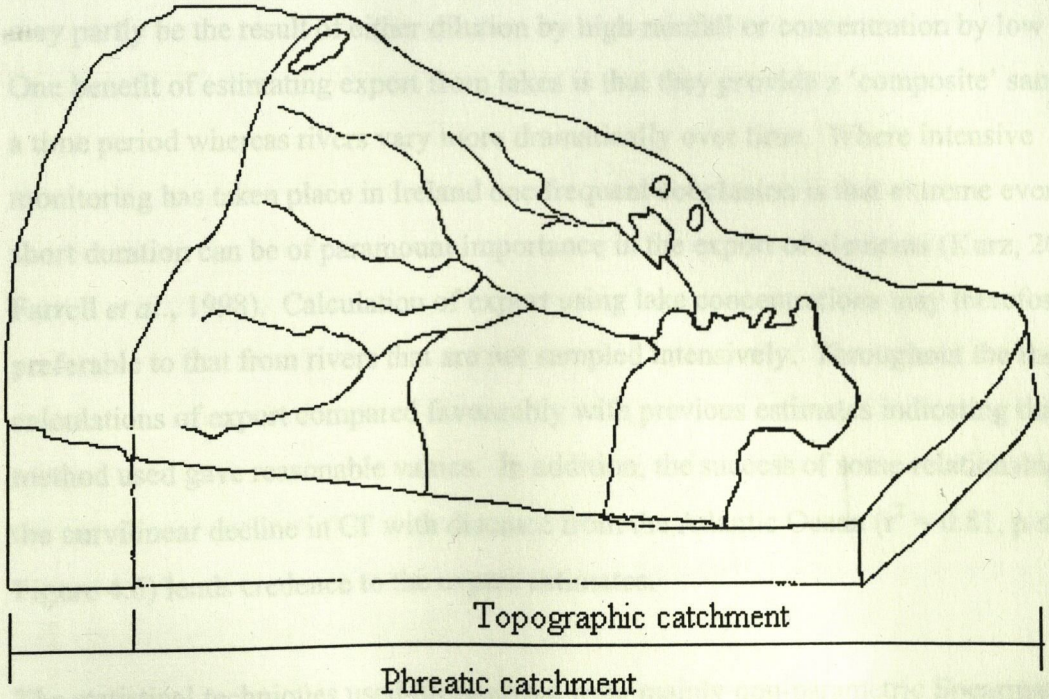


Figure 8.1 A hypothetical example where the topographic definition of the catchment area underestimates the phreatic catchment. If the portion of the phreatic catchment excluded has similar characteristics (e.g. geology, rainfall) as the rest of the catchment then estimates of element export per unit area (kg ha^{-1} yr^{-1}) should be valid. However, the total flux of material will be underestimated.

Another possible criticism is that estimates of export were based on mid-lake concentrations and therefore neither represent input to nor export from the lake. The estimates would be expected to be intermediate between these values. The importance of this will depend on the loss rate which is particular to both the element and the lake being examined. Retention time is probably the most important source of between lake variation in loss rates. This may not be a significant drawback as exports were only calculated for conservative elements or compounds. Where loss processes would be expected to be important (e.g. Si) then estimates of catchment export were not made. In the case of TP, the input concentration was estimated from the mid-lake concentration using an established model (Foy, 1992). An ideal but costly solution would be to automatically measure discharge and chemistry at inflowing and outflowing rivers.

It can be concluded that the attempts to estimate export were extremely valuable. Firstly, as the 31 lakes had a wide variation in precipitation then it was imperative to examine export rather than concentration. This is because the concentration of an element in a lake may partly be the result of either dilution by high rainfall or concentration by low rainfall. One benefit of estimating export from lakes is that they provide a 'composite' sample over a time period whereas rivers vary more dramatically over time. Where intensive monitoring has taken place in Ireland one frequent conclusion is that extreme events of a short duration can be of paramount importance in the export of elements (Kurz, 2000; Farrell *et al.*, 1998). Calculation of export using lake concentrations may therefore be preferable to that from rivers that are not sampled intensively. Throughout the thesis, calculations of export compared favourably with previous estimates indicating that the method used gave reasonable values. In addition, the success of some relationships such as the curvilinear decline in Cl^- with distance from the Atlantic Ocean ($r^2 = 0.81$, $p \leq 0.0001$, Figure 4.6) lends credence to the export estimates.

The statistical techniques used for analysis were mainly non-parametric Spearman rank correlation and linear regression. Correlation and regression were the most commonly used methods in the literature cited in this work and were considered to be the most appropriate following consultation in TCD. One of the inadequacies of the statistical analysis was that it took place using mean values for the 31 lakes even though they were sampled at two different intensities – four to six times for 20 lakes and eight to ten times for 11 lakes in 1996-7. The importance of this was tested for NO_3^-, TN and TDN in

Chapter 7. Table 7.3 shows that there was very little difference between the means calculated at the two different sampling intensities. Differences are likely to be even lower for conservative elements. One of the avenues not explored in this thesis was the importance of the geographic position of different catchment attributes. In addition to using the proportion of different land covers for analysis it could have been beneficial to weight them according to their proximity to the lake. It would be expected that an area of peatland would have a greater influence if it were adjacent to a lake rather than in the upper reaches of the catchment.

One of the strengths of the current research is the comprehensiveness of the description of the catchments. However, some additional data would have been beneficial. Detailed information on the point sources to some of the lakes would have been useful. In addition, information on the number of pigs in a catchment would have complemented the information on cattle and sheep. Unfortunately, this information was not available owing to data confidentiality measures. Similarly, information on soil P concentrations was only available at poor resolution (10 km^2) and over broad intervals of concentration (3 mg l^{-1} Morgans P) (Tunney, 1997).

This study would no doubt have been improved if the suggestions above were implemented. However, this would have required unrealistic expenditure on both equipment and personnel. Focusing on fewer lakes in more detail may seem like one solution but this would have lead to the work being less representative of limnetic systems in Ireland. For example, upland catchments that received high rainfall tended to have unique chemistry (e.g low colour) but were only represented by four lakes: Caragh, Leane, Muckross and Maumwee (Figure 5.21). In the context of both the objectives and resources, the approach taken led to many useful contributions to Irish limnology and these are summarised in the next chapter.

9. SUMMARY CONCLUSIONS, KEY CONTRIBUTIONS AND FUTURE RESEARCH NEEDS

This study is the first comprehensive attempt to relate lake chemistry to catchment characteristics in the Republic of Ireland. The study has yielded several findings, outlined below, that are new in an international context. In addition, there are no other published works detailing seasonal variation in chemistry across a broad range of lake types in Ireland. Therefore, this study is a historical record against which future changes in the environment may be compared. This was recognised from an early stage and every effort was made to ensure the results were of high quality. With regard to this, the work included an accurate record of station position using a GPS, rapid initial processing of samples, quality control, quality assurance and full documentation of results (Appendix 2).

9.1 Major ions

The calculation of export of the major elements for the 31 catchments was the first such attempt in the Republic of Ireland. The principal catchment influences on export were rock type, deposition of marine salts and agricultural practices. Sodium and chloride export had a curvilinear decline from the west coast indicating that deposition of sea-salts was the source. Examining export rather than concentration led to the discovery of a good curvilinear fit whereas previous work that related concentration to easting only found approximate trends (Webb, 1947). Further work in Ireland may focus on quantifying the contribution of aerosol deposition to total deposition using a transect of gauze nets mounted during dry westerlies (See Gustafsson & Franzén, 2000). Sea-salt deposition was also important with respect to other elements. In upland western catchments comparisons between the export of SO_4^{2-}, K^+ and Mg^{2+} with that of Cl^- revealed that sea-salt deposition accounted for approximately 60% of export from catchments. In contrast, element budgets in lowland catchments were heavily modified by agricultural practices. In Cavan and Monaghan, where agriculture was most intensive, over 86% of K^+ export was from non-marine sources. The linear relationship between K fertiliser application and non-marine K^+ export indicated that agricultural inputs were the source. Moreover, evidence was found that K^+ concentration has increased in the Cavan/Monaghan region since the early 1970s. This was attributed to the accumulation of K^+ in soil over the last 50 years rather than increased K^+ application, which has remained constant. Similarities may

be drawn with the accumulation of soil P and a resulting increase in export to freshwater (Tunney, 1990; Tunney *et al.*, 2000). With the exception of Cavan and Monaghan, the similarity of the Cl^- to SO_4^{2-} ratio between atmospheric deposition and export indicated that SO_4^{2-} inputs and outputs were in balance. In Cavan and Monaghan SO_4^{2-} export was substantially higher than atmospheric deposition and this was attributed to increased mineralisation of soil organic S following the drought of 1995 (Mac Cárthaigh, 1996). Prior to this, in the early 1970s, the ratio of Cl^- to SO_4^{2-} indicated that export of SO_4^{2-} was of similar magnitude as atmospheric deposition. This contrasted with Lennox *et al.* (2000) who found that SO_4^{2-} export to Lough Neagh increased following dry summers but was always substantially higher than atmospheric deposition. Further work should aim to resolve whether SO_4^{2-} export in Cavan and Monaghan usually exceeds atmospheric deposition or whether this is only a response to increased mineralisation. This work provides the SO_4^{2-} export estimates sought by the Irish Agricultural research body 'Teagasc' (Murphy, 1991), but further work needs to take place to determine if the losses of SO_4^{2-} recorded threaten soil fertility over the longer term.

Rock type was found to be a major influence on Mg^{2+} Ca^{2+} and Si. The amount of chemical weathering in catchments located on resistant rock types was investigated by calculating the export of non-marine base cations (C_B). Catchment area (m^2) divided by mean catchment relief explained 94% of the variation in C_B ($r^2 = 0.94$, $p \leq 0.0001$, $n = 13$, Figure 4.21). The independent parameter: catchment area (m^2) divided by mean catchment relief was developed specifically for use in this study from the concept of a relief ratio used for rivers which is calculated by dividing relief by a horizontal distance (Strahler, 1964). This approach is an improvement on previous attempts to explain C_B. Johnson *et al.* (1994) were unsuccessful in their attempt to relate C_B to differences in H^+ inputs in 28 felsic catchments. Following more testing, this parameter may be useful in assessing the risk of acidification as well as being a parameter alongside which the effects of other catchment characteristics may be assessed (e.g. H^+ inputs, forestry and rock type).

9.2 Colour

A significant proportion of the 187 lakes sampled in summer had high colour (25% >57 mg l^{-1} PtCo). Similar to findings in North America by Rassmussen *et al.* (1989), colour was found to be highest in lakes with peatland catchments, short residence times and few upstream lakes.

Colour had a bell-shaped relationship with precipitation (Figure 5.25). The ascending limb, where colour increased with rainfall, was a result of an increasing proportion of peat bogs, increased colour export and short residence time. The descending limb, where colour decreased with rainfall, was interpreted in the light of Naden and McDonald's (1989) concept of a store of colour in a catchment. This concept asserts that there is a finite amount or store of colour in a drainage area that may be released to freshwaters over a period. The descending limb therefore represented a process whereby colour was lowered owing to dilution of the store of colour in the drainage area by high rainfall. It was initially thought that the low colour in such lakes was a result of the pristine nature of their peatlands. However, this study indicates that this may not be the main reason as these peatlands were found to export similar amounts of humic substances as others receiving less rainfall (Figure 5.22). This is the first description of such a relationship across a series of lakes and adds support to Naden and McDonald's (1989) concept of a store of colour in a catchment. Further work may seek to relate microbial activity in a series of peatland catchments to riverine DOC export. Radiometric dating of DOC would determine if the colour was derived from recent (post-1950s) carbon sources indicating that it was sourced from the aerobic surface layers of peat. This should be done in winter when algal exudates are a lower proportion of DOC. An alternative hypothesis, that the peatland volume rather than the aerobic surface layer is the source of humic substances in leachate, could also be examined. In such a study it would also be useful to determine peatland type and health as well as drainage pathways.

Inter-annual variation in colour was determined mainly by the amount of rainfall. Previous work indicated that a drought may lead to increased colour (Mitchell & McDonald, 1992). This phenomenon was not observed following the 1995 drought probably because it was not severe enough.

This study also found a weak but significant decrease in colour with increasing sunshine hours from north to south. That colour declines linearly with irradiation is well known (Engstrom, 1987; Jefferson-Curtis & Schindler, 1997) but such a trend has not been identified in field data previously.

It was also found that colour significantly reduced transparency and in certain cases may decrease the oxygen concentration in lake waters. This is the first indication in Ireland of humic-substance-induced oxygen-decline but the phenomenon is well known in Florida lakes (Miles & Brezonik, 1981; Crisman *et al.*, 1998).

9.3 Phosphorus

The 31 lakes examined had a very wide range of TP concentrations (1 - 344 $\mu g\ l^{-1}$). This contrasts with Northern Ireland and England where few lakes were found to have a TP concentration less than 10 $\mu g\ l^{-1}$. However, in Scotland 73% of lakes had TP less than 10 $\mu g\ l^{-1}$ (Foy & Bailey-Watts, 1998).

In contrast to national trends, no increase in TP concentration was found in three lakes in County Clare since 1981. It was reasoned that this was mainly because of a greater adsorption potential of limestone mineral soils owing to their higher infiltration capacity. In County Clare further study should focus on obtaining information on farm management and soil P over the last 20 years. A field experiment on calcareous soils under Irish climatic conditions would also be beneficial.

Catchment characteristics that described agriculture (mainly pasture) were the most strongly correlated with TP export and concentration in both the 31 and 189 lake data-sets. Wet soils exported more TP than dry soils. Wet soils were identified according to Daly (2000) and comprised the sum of the soil types: gleys, peaty gleys, peaty podzols, peats and rocks expressed as a proportion of the drainage area. These soils are likely to have impaired drainage which may increase TP export by promoting overland flow and also by reducing infiltration and subsequent adsorption. These results support those of Daly *et al.* (2000) who found river MRP concentrations were higher in Irish catchments with wet soils.

Two export coefficient models were applied. The model of Jordan *et al.* (2000) used coefficients based on CORINE land cover in Northern Ireland but was unsuccessful in accurately predicting TP export ($r^2 = 0.26$, n = 30). The model of Johnes *et al.* (1994a, b) allowed three sets of export coefficients to be applied to upland, limestone and lowland catchments. Overall, the model of Johnes *et al.* (1994a, b) explained 64% of the variation in observed TP export (n = 30). Considering the three groups separately, only the predictions made for six lowland catchments were significantly correlated with the observed loads. Predictions were substantially in excess of observed export but as there was a good relationship between predicted and observed loads then this approach may be successful if the coefficients were lowered. Further research may focus on a larger set of lowland agricultural catchments with emphasis on selecting export coefficients according to soil P.

Combining the models of Johnes *et al.* (1994a, b) and Tunney *et al.* (2000) produced hindcasted estimates of TP export in 1950. It was estimated that TP export to six lowland lakes in agricultural catchments has increased by between 51 and 150% since 1950.

9.4 Nitrogen

This was the first study in Ireland to examine seasonal variation in the concentration and fractions of nitrogen in a diverse series of lakes. A wide range in concentration was found and this data should provide a useful reference for future comparisons. Future NO_3^- increases could be caused by increased agricultural inputs, higher rates of mineralisation owing to global warming or increased atmospheric deposition.

An 81 - 105% increase in TN, mainly in the NO_3^- fraction, was found between 1981-2 and 1996-7 in four Clare lakes. This may have been caused by either increased fertiliser application or higher rates of mineralisation following a drought in 1995. As mineralisation was invoked as a mechanism that led to higher SO_4^{2-} in north-eastern lakes then this mechanism may have been mainly responsible for the increase in NO_3^-.

Total nitrogen concentration was most strongly correlated to descriptors of agriculture, which indicates that agricultural activities are a major N source. Multiple regression

explained 83% of the variation in TN and significant variables ($p \leq 0.0001$) included the total nitrogen input to the catchment (kg ha^{-1} yr^{-1}), net precipitation (mm) and the proportion of total lake area in the catchment. The multiple regression indicated that concentrations were highest in catchments that received large amounts of N fertiliser, low precipitation and where lakes were a small proportion of the catchment area. The model predicted that lakes with a total lake area comprising 10% of their catchments (mean of the 31 lakes) would have 27% less TN than lakes where total lake area comprised only 1% (minimum of the 31 lakes).

Model predictions for zero fertiliser usage indicated that, for lakes located in the north-east of the Republic, about half of present day TN is derived from artificial N inputs to the catchment. This result was in agreement with the conclusion of Smith and Stewart (1989) for rivers flowing into Lough Neagh in Northern Ireland. Therefore, even though Irish lake TN concentrations are relatively low in comparison with other European countries (van der Molen *et al.*, 1998), TN is elevated in some Irish lakes because of fertiliser usage.

No relationship was found between N deposition and TN concentration in 49 lakes with non-agricultural catchments. This may be taken to indicate that upland catchments in Ireland are not currently N saturated as has been found in some countries where atmospheric N deposition is high (Allott *et al.*, 1995). However, this analysis used summer TN which may not have been ideal for detecting N saturation. Further analysis should focus on seasonal concentrations of N fractions in both atmospheric deposition and freshwaters in upland catchments in the east. Nitrate was a higher proportion of TN in agricultural catchments and DON was a higher proportion in catchments with peat soils.

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