…as yet there was no field shrub on earth and no grass of the field had sprouted, for the Lord God had sent no rain upon the earth and there was no man to till the soil, but a stream was welling up out of the earth and was watering all the surface of the ground…

Genesis 2: 5-6

ANALYSIS OF TRACE ELEMENTS IN IRISH FRESHWATERS BY ICP-MS

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A thesis submitted to Dublin City University for the award of

Master of Science

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AUTHOR'S DECLARATION

I herby certify that this material, which I now submit for assessment on the programme of study leading to the award of Master of Science is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: Fionnuala O'Connor
I.D. No.: 98970747
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ABSTRACT

Analysis of Trace Elements in Irish Freshwaters by ICP-MS

Fionnuala O'Connor

Ireland's largely unpolluted surface waters are one of the most valuable natural resources of the island. Until the 1970's there was very little information available on the quality of Irish water bodies. Since then, drinking water legislation has required the monitoring of certain specific parameters and the problem of eutrophication has resulted in extensive investigation of nutrient levels. In more recent years, however, the availability of modern analytical techniques has greatly assisted routine monitoring of waters for a wider range of chemical parameters.

Over the period 1998-2001 thousands of samples from Irish rivers, lakes and canals were analysed by the Central Fisheries Board using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS), a method that allows for rapid and sensitive multi-element measurements. The purpose of the analyses was primarily to increase knowledge of Irish surface water chemistry. It was also hoped that the work would assist in the understanding of biological processes and begin the development of a database of chemical "signatures" for Irish waters.

This thesis attempts to summarise and interpret a large quantity of analytical information obtained from about 230 sites chosen from the larger dataset of sampling locations on Irish lakes, rivers and canals. Sixteen elements were routinely analysed, resulting in approximately 100,000 individual measurements during this study.

In Chapter 3 eighteen lakes of varying size and location are compared and contrasted. The distinctive characteristics of twenty-eight rivers to the east and west of Lough Corrib are studied in Chapter 4 and differences in the water chemistry of the four main canal systems are investigated in Chapter 5. In each of these specific areas, temporal and spatial variations in the concentrations of major and minor elements were studied. The effects of local geology was also considered and found to play a large part in the chemical composition of surface waters.

It is anticipated that the knowledge gained from this preliminary investigation of trace elements in Irish waters will advance more in-depth future studies in this area.

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ABBREVIATIONS

AQUAFOR	1997 study involving three universities, forestry and fisheries sectors
CFB	Central Fisheries Board
COFORD	National Council for Forest Research and Development
EC	European Community
EEC	European Economic Community
EIFAC	European Inland Fisheries Advisory Commission
EPA	Environmental Protection Agency
ERU	Environmental Research Unit
EU	European Union
GNP	Gross National Product
MAC	Maximum Allowable Concentration
OECD	Organisation for Economic Co-operation and Development
OPW	Office of Public Works
SAC	Special Area of Conservation
SIL	International Association of Theoretical and Applied Limnology
SPA	Special Protection Area
TAM	Tourism Angling Measure
US EPA	United States Environmental Protection Agency
US NAS	United States National Academy of Sciences
WHO	World Health Organisation

PUBLICATIONS AND CONFERENCES

1. Publications:

A Baseline Study of Metal Ion Content of Irish Canals by ICP-MS
Fionnuala O'Connor, Brendan Duffy, Trevor Champ, Dermot Diamond
Inter. J. Environ. Anal. Chem., **83**, 7-8, pp 713-725.

2. Oral Presentations:

Advances in the Measurement and Management of Water Quality
Trevor Champ and Fionnuala O'Connor
International Year of the Ocean Conference, Dublin Castle, 2 December, 1998

Application of ICP-MS in Freshwater Fisheries
Fionnuala O'Connor
Spectroscopy and Chromatography Seminar, University College Cork (22 September 1998) and Dublin City University (23 September 1998)

Statistical Analysis of Irish River and Lake Water Chemistry
Fionnuala O'Connor, Trevor Champ, Brendan Duffy, Dermot Diamond
Environ 2000, University of Ulster, Jordanstown, 28-30 January 2000

3. Poster Presentations:

Statistical Analysis of Irish River and Lake Water Chemistry
Fionnuala O'Connor, Trevor Champ, Brendan Duffy, Dermot Diamond
2000 Winter Conference on Plasma Spectrochemistry, Fort Lauderdale, Florida, 10-15 January, 2000

4. Conferences attended:

1. The 6th International Conference on Plasma Source Mass Spectrometry, University of Durham, England, 13-18 September, 1998
2. Winter Conference on Plasma Spectrochemistry, Fort Lauderdale, Florida, 10-15 January, 2000
3. Winter Conference on Plasma Spectrochemistry, Phoenix, Arizona, USA, 6-12 January, 2002

5. Data dissemination:

Data collected during this project has contributed to the development of the 2001 Dangerous Substances Regulations by the Department of the Environment and Local Government (DOELG).

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CHAPTER 1

1. INTRODUCTION

'Fresh water is a finite and vulnerable resource, essential to sustain life, development and the environment.'

First Principle from the International Conference on Water and the Environment, Dublin, 1992

In January 1992 an International Conference on Water and the Environment was held in Dublin, Ireland.[1] It was attended by 500 participants from 114 countries. The statement and report from the conference provided guidelines for the Earth Summit at Rio in June 1992. The participants of the conference agreed on four guiding principles as a basis for discussion and the future planning of water resource management. In recent years, the first principle (quoted above) has been increasingly recognised and emphasised in the management of Ireland's natural water resources. It is also the basis for the Water Framework Directive (2000/60/EC) published in the official Journal of the European Commission in December 2000.[2]

1.1 Ireland's Freshwater Resource

Ireland has a unique richness of freshwater resources, perhaps unparalleled elsewhere in Europe. It is Ireland's geography and location that have resulted in the presence of such a valuable natural asset. Ireland is located in the zone of westerly atmospheric circulation of middle latitudes, with the Atlantic Ocean to the north, west and south.[3] Thus, the country is greatly influenced by Atlantic weather systems. The warm North Atlantic Drift also has an effect on sea temperatures, and all these factors result in a temperate, maritime climate. This, along with Ireland's geographical separation from the large cities and industrial centres of Europe has undoubtedly helped to protect the quality and relatively unpolluted nature of Irish waters.

The oceanic climate also provides Ireland with a relatively high effective rainfall of 700mm per annum (annual average rainfall of 1,150mm with an average annual loss from evapotranspiration of 450mm). This gives the country an average run-off of 31 m^3/capita/day, which is amongst the highest in Europe.[4] About 65% of this drains away directly as surface run-off through the river systems,[5] and the remainder seeps into the earth to become groundwater – eventually emerging as springs or inflows to rivers and lakes. Thus, surface water and ground water are intrinsically linked.

Surface freshwaters cover approximately two per cent of the land area of Ireland (Figure 1.1) (145,000km^2) – twice the European average, and four times that found in England and Wales.[6] Twenty per cent of the country is - or was at one time - bog land. Surface freshwaters are used for many purposes including public supply, agriculture, industry and recreation. Groundwater provides approximately 20-25% of Irish drinking water supplies.[7] In general, groundwater is under-utilised, although in the future it may increasingly be used as a source of emergency water supplies, for energy production, aquaculture and bottled waters. However, at present Ireland has a relatively low water demand in absolute terms.

All these factors have combined to provide Ireland with a valuable natural resource which is the envy of Europe but which also presents a huge challenge in its protection, management and development.

Figure 1.1: Surface drainage in Ireland [♣]

1.2 Water pollution and legislation

Up until the first half of the twentieth century, Ireland escaped much of the water pollution that was becoming an increasing problem in other developed countries. This was a consequence of the low population density, the relatively high rainfall, the low

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[♣] *Source: Modified from Central Fisheries Board digitised fisheries maps* level of industrialisation and the fact that the largest cites are located on the coast. However, since the second half of the twentieth century our natural waters have been under increasing threat from industry, intensive agriculture and urbanisation.

Water is used for many different purposes, e.g. drinking supply, bathing, fisheries, agriculture, industrial, etc… Each water use is sensitive to different pollutant levels and so has specific water quality requirements. For example, dissolved oxygen concentration is important for aquatic life, but has less importance for bathing or recreational pursuits. The particular requirements for each water use are referred to as Water Quality Criteria.[5] Agencies such as the US Environmental Protection Agency (US EPA), the European Union (EU), the European Inland Fisheries Advisory Commission (EIFAC) and the World Health Organisation (WHO) have published guideline criteria for many different water uses, e.g. bathing water, drinking water, aquatic life (details of some of the more relevant guidelines and directives can be found in Appendix A).

The Directives and decisions on water uses issued by the European Union have a legal status in all member countries including Ireland,[5] e.g. Drinking Water Directive (80/778/EEC) and the Freshwater Fish Directive (78/659/EEC), and as with all EU Directives, they must be transposed into the formal legislation of the member state. The Member State is obliged to choose the appropriate form and method of implementation most in conformity with national constitutional requirements. (In Ireland, transposition of Directives by means of statutory instruments has been criticised for its immunity from political commentary which is afforded to primary legislation implemented by Acts of the Oireachtas. There is a suggestion that some Irish regulations relating to EU

Directives and transposed by means of this informal legislation may be in conflict with the Irish Constitution).[8]

The EU Directives list criteria that must be adhered to for concentrations of various constituents in the water. The mandatory value listed in these directives for each chemical parameter is called the "I" value. More stringent guidelines - "G" values – are also given which represent a desirable condition. Any member nation may set their own standards that can be more stringent than either of these values, but no country may set standards less stringent than the "I" values[5].

Many countries have adopted their own criteria, taking into account their own specific circumstances. For example, in 1978 the Department of the Environment in Ireland issued a document entitled "Water Quality Guidelines", which took into consideration the requirements for Irish waters[5]. Once criteria have been established, the regulating agency in the country can introduce Water Quality Standards that have the status of a legal requirement. In most situations, where the water body is required for several uses, the standards will be based on the most stringent of the criteria applying to them. In Ireland, the setting of standards for water quality is provided for in the Local Government (Water Pollution) Act, 1977 and the Amendment Act of 1990.

EU member countries are required to monitor any of their national waters that have been designated under each Directive, and must communicate the resulting data. Under the Habitats Directive (92/43/EEC), waters may now be designated for protection because of the presence of a particular habitat or species of flora or fauna. Areas so designated are called "Special Areas of Conservation" (SAC's) or in the case of birds "Special Protection Areas" (SPA's). There is a large database of SAC's and SPA's in

Ireland, and this is monitored by the National Parks and Wildlife section of the Department of the Environment, Heritage and Local Government (previously Duchas). This database is continuously updated and revised.

EU member states are required under Council Directive 76/464/EEC (CEC 1976), to reduce pollution by certain defined dangerous substances discharged into the aquatic environment. This directive was one of the first water related Directives to be adopted. The purpose of the Directive was to eliminate pollution from certain substances (List I) and reduce pollution from other substances (List II). Mercury and cadmium are included in List I and twenty other metals are included in List II.[9] Progress in implementing this Directive was very slow, and in the 1990's the European Commission began infringement procedures against many of the Member States. Some of the cases are still before the European Court. Amendments to Directive 76/464/EEC in 1986[10], 1988[11] and 1990[12] listed specific criteria for discharge of certain List I substances.

As mentioned above, an important step was taken by the European Union in 2000 with the establishment of the Water Framework Directive for Community action in the field of water policy.[2] The document opened by stating: *"Water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such"*. This statement is a firm reminder of the First Principle drawn up by the International Conference on Water and the Environment eight years previously in Dublin.[1] Previously, most EU Directives were drafted to protect a specific end use, e.g. freshwater fish, shellfish, waters for abstraction as potable supplies, etc... This new Directive, however, offered protection to the entire ecosystem and so indicated a change in direction in water policy. The Water Framework Directive also repeals and replaces various older European Directives, including Council Directive 76/464/EEC and its amendments when it states: *"The provisions of this Directive take over the framework for control of pollution by dangerous substances established under Directive 76/464/EEC. That Directive should therefore be repealed once the relevant provisions of this Directive have been fully implemented."*

In July 2001 the Irish Government issued the Water Quality (Dangerous Substances) Regulations, 2001[13] which gave further effect to EU Council Directive 76/464/EEC and supported the EU Water Framework Directive. Included in the regulations were new Irish standards for concentrations of arsenic, chromium, copper, lead, nickel and zinc in waters (Table 1.1). Two different standard concentrations were given for each metal, taking into consideration the fact that metals are known to be more toxic to fish (and other aquatic life) in soft waters rather than hard waters (EIFAC reports on zinc[14], cadmium[15], chromium[16] and copper[17] in the 1970's and 1980's).

Table 1.1: Irish standards for trace metals in waters[13] [♣]

Substance	**Irish Regulations 2001 (Maximum Admissible Concentrations)**	
	Hardness < 100 mg/l $CaCO_3$	***Hardness > 100 mg/l $CaCO_3$***
Arsenic (μg/l)	25	25
Chromium (μg/l)	5	30
Copper (μg/l)	5	30
Lead (μg/l)	5	10
Nickel (μg/l)	8	50
Zinc (μg/l)	8-50	100

It is important to assess a water supply in relation to all its possible uses, noting that absence of specific pollutants above a "critical concentration" may permit use of the water for certain purposes, but the same water may be unsuitable for another purpose. Logically, the effect of toxic substances should be much greater on organisms such as fish living in the water than on humans that use the water for drinking supplies or other

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[♣] Note: Only the values given for metals in fresh waters are quoted purposes. Water has often been considered adequate for fish as long as there is no obvious mortality[18] but degradation of the habitat and sub-lethal effects on fish physiology and behaviour can occur at much lower than lethal concentrations of contaminants. For this reason, recent guidelines by many agencies have specified criteria for aquatic life considerably lower than recommended values for the same substance in drinking water (Appendix A).

In 1978 a European Directive was issued relating to the quality of fresh waters for support of fish life (Directive 78/659/EEC). This Directive defined salmonid and cyprinid waters and listed guideline and mandatory values for each type of water for 14 different parameters. The only metal elements included were copper and zinc, and different values were given for these elements depending on the water hardness (Table 1.2 & Table 1.3).[19] It must be noted that the values listed for both these elements are considerably lower than the EU criteria for drinking water (see also Appendix A).

Table 1.2: Criteria for Total Zinc from Directive 78/659/EEC[19]

	Water Hardness (mg/l $CaCO_3$)			
	10	***50***	***100***	***500***
Salmonid waters (mg/l Zn)	0.03	0.2	0.3	0.5
Cyprinid waters (mg/l Zn)	0.3	0.7	1.0	2.0

Table 1.3: Criteria for Dissolved Copper from Directive 78/659/EEC[19]

	Water Hardness (mg/l $CaCO_3$)			
	10	*50*	*100*	*300*
Copper mg/l	0.005	0.022	0.04	0.112

1.3 Methods of analysis

Over the past number of decades, as laboratory analytical techniques have improved and developed, it has been possible to determine the presence of chemical parameters in waters to a greater degree of precision and accuracy. In particular, there have been important advances in recent years in the quality and range of instrumentation used for the analysis of cations – the primary focus of this work.

The earliest lake survey carried out by An Foras Forbartha in 1975[26] used Atomic Absorption Spectroscopy (AAS) for determination of four elements – sodium, potassium, iron and manganese. The EPA continued to use this method for several decades and in 1994 carried out analysis (published in their 2001 report) for 13 metals in 76 samples using AAS. This is a method with very good specificity but which unfortunately requires each element to be analysed separately and so multi-element determinations are time consuming.

During the 1990's Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) became popular in laboratories because of its multi-element capabilities, although the detection levels were very similar to the most modern AAS instruments on the market. In many laboratories both techniques were used in conjunction for element analysis, e.g. in the chemical measurements carried out for the AQUAFOR reports in 1997.[45 - 48] These reports were the result of a detailed study involving three universities (UCD, TCD, UCC), the forestry and fisheries sectors and funded under the EOLAS Higher Education Industry Co-operation.

The most recent EPA survey on dangerous substances in 2001[52], which summarised 28 metals in 117 samples, used the most modern of low level analytical techniques – Inductively Coupled Plasma Mass Spectrometry (ICP-MS). This is the same technique as was used in the present study and it has many advantages over older methods of analysis – namely, multi-element capability, speed, selectivity and sensitivity. This analytical method will be discussed in greater detail in Chapter 2.

1.4 Development of freshwater quality measurement

There are many physical, chemical and biological characteristics of water which all combine to give an overall picture of the water quality. For example, dissolved oxygen, coliform bacteria, temperature, nutrients, trace metals and pesticides are some of the parameters which need to be considered when describing the quality of water in a river, lake, canal or other water body. Some extremely detailed studies have been carried out on Irish waters, and many different subjects reported on. The background to these will now be outlined briefly.

1.4.1 Early Studies

Modern analyses of Irish freshwater has its origin in the 1950's and 1960's when agencies such as the Inland Fisheries Trust (now the Fisheries Boards), the Salmon Research Trust (now incorporated into the Marine Institute) and a section of An Foras Forbartha (now EPA), began carrying out chemical and biological surveys of Irish rivers and lakes.[20] At this time, aquatic studies also began to increase in the universities, particularly in zoology departments. Most of the work carried out concentrated on gathering information about the physical and physicochemical characteristics of Irish waters, e.g. parameters such as water hardness, pH, alkalinity, oxygen, etc... These parameters also provided valuable information on the suitability of waters to produce and support fish populations. In 1971 Kennedy and Fitzmaurice published the results of an extensive study on the growth of brown trout in Irish waters.[21] They found ample justification for equating alkaline waters with fast growing trout, and also found the same patterns with other fish species.[22, 23] Despite the limitations of only measuring basic parameters, this work provided a significantly greater understanding of the condition of Irish waters and identified some deterioration in water quality over the years. In 1977 Toner stated that since 1960 there had been a marked increase in pollution incidences, including fish kills in rivers and algal 'blooms' in lakes, and suggested that an increase in urban population and intensification of agricultural practices had played a part in this.[24]

1.4.2 Focus on eutrophication

1.4.2.1 Lakes

In the early 1970's a shift in emphasis occurred when the problem of eutrophication in many Irish lakes became apparent (Figure 1.2). Kennedy and Fitzmaurice commented on the need for further research in 1971 when they noted an absence of adequate data on the amounts of phosphate and nitrate in Irish waters.[21] The numbers of nutrient assays (specifically nitrogen and phosphorus) by the Inland Fisheries Trust and An Foras Forbartha increased and several lake-monitoring projects were initiated. The IFT began weekly measurements of phosphorus and nutrients in Loughs Sheelin, Ennell, Derravaragh and Owel in 1971. For a period, the tributary streams of Lough Sheelin were sampled intensively every day and flows recorded in order to calculate the loading of nutrients to the lake (a scaled-down version of this work still continues to this day). In 1975 regular sampling was commenced in the western lakes (Conn, Corrib, Carra, Mask, Arrow and Inchiquin) and this was extended to many small lakes in the Erne system in 1976.[25]

Analysis of these large numbers of samples was made possible thanks to new analytical instruments available to laboratories. The IFT used a Technicon AA2 segmented flow analyser for nitrogen and phosphorus analysis at this time. This technology, which was originally developed for laboratory blood testing, was adapted well to multi-parameter nutrient analyses. Instrument design and performance improved gradually over the years to give better sensitivities and limits of detection. By the 1980's the IFT were using a Skalar continuous flow analyser and this was used until the purchase of a computerised system in 1997.

Figure 1.2: Shoreline algal bloom as a result of nutrient enrichment ♣

Inset: close-up of green algae in water at the shore

An Foras Forbartha published a Preliminary Survey of Irish Lakes in 1975.[26] The report presented the results of a survey of 41 lakes, which commenced in 1973 and described itself as "the first overall examination of lakes on a systematic basis". It gave general information on each lake, results from basic physical and chemical tests of the water and listed the dominant planktonic groups found in the lake. The report also commented that this information was available for the first time in the case of many of the lakes.

♣ *Source: Central Fisheries Board, reproduced with permission.*

The impact of eutrophication in Ireland was first considered in detail at a seminar in Killarney in May 1977. The meeting recognised that the quality of water in many Irish lakes had deteriorated dramatically, and that the Irish pure water resource was at risk[27]. Many leading scientists attended the seminar from Ireland and Europe. Following from this, John, Champ and Moore published work in 1982 that compared and contrasted the changing status of vegetation in four midland lakes and they reported evidence of artificial nutrient enrichment.[28] In 1982 the Organisation for Economic Co-operation and Development (O.E.C.D.) published a fixed boundary classification scheme based on the concentration of total phosphorus, chlorophyll and transparency [29]. Table 1.4 summarises the OECD classification, which is now widely used for categorising the trophic status of lakes.

"The State of the Environment" report by An Foras Forbartha in 1985[5] stated that of at least 1,500 lakes in Ireland with area greater than 10 hectares, less than 150 had been examined since 1970. Of the 39 lakes examined, 19 were found to be eutrophic. The report concluded that eutrophication was affecting some of the country's important fishery lakes and that this was a cause for concern.[5]

Table 1.4: OECD Classification of Lake Waters[29]

Category	Mean Total P mg/m^3	Mean Chlorophyll mg/m^3	Mean Transparency m
Ultra-oligotrophic	≤ 4	≤ 1.0	≥ 12
Oligotrophic	≤ 10	≤ 2.5	≥ 6
Mesotrophic	10 – 35	2.5 – 8	6 – 3
Eutrophic	35 - 100	8 – 25	3 – 1.5
Hyper-eutrophic	≥ 100	≥ 25	≤ 1.5

1.4.2.2 Rivers

River monitoring also commenced on a regular basis in the 1970's. In 1972 An Foras Forbatha published the first report on a National Survey of Irish Rivers.[30] In the survey 121 rivers were examined chemically and/or biologically and the water quality of each river was classified with reference to an arbitrary five-point scale (Table 1.5).

Table 1.5: Quality Rating Scale [30]

Q-value	Description
Q5	Good quality
Q4	Fair quality
Q3	Doubtful quality
Q2	Poor quality
Q1	Bad quality

The scale was developed by defining the relationship of water quality to the composition of macroinvertebrate fauna in the river. This Quality Rating Scheme with minor modifications has been improved and today forms the basis for classification of water and long-term monitoring of trends by the EPA. A sixth classification – Q0 - is used occasionally where possible toxic pollution is suspected. The 1972 report concluded that there was significant pollution on some stretches of Irish rivers and that 17% of the rivers examined were in a less than satisfactory condition. It was pointed out that there would inevitably be an increase in pollution as industrialisation became more widespread.

Two further reports by An Foras Forbartha in 1974[31] and 1980[32] continued the survey of river water quality, concentrating mostly on physico-chemical parameters such as pH, alkalinity, hardness, dissolved oxygen, ammonia and nutrients. These reports showed little change in overall water quality since 1972 but continued to warn about the need for increased monitoring to protect against future pollution.

The Environmental Research Unit (ERU) continued the work of An Foras Forbartha in the 1980's, and issued a series of reports on river water quality based on the same quality scale. In 1992 the Environmental Protection Agency was set up and since then they have published several reports on the quality of public drinking water supplies in Ireland, the most recent of which appeared in 2002 based on 22,453 samples taken in the year 2001[33].

A comprehensive EPA report in 1996 stated that by 1990 virtually all of the major rivers and streams had been surveyed to form an "acceptably representative national baseline".[34] The report concluded that 71% of rivers/streams and 61% of the lakes examined in the period 1991-1994 were in a satisfactory condition.

1.4.3 The SIL Congress 1998

In 1965, the first annual meeting of an informal Freshwater Research Group was held in Ireland and this culminated in 1992 with the establishment of a National Commission for Hydrobiology.[20] The Commission organised annual meetings of the research group and maintained a register of research workers having an interest in freshwater studies. In 1998 the register listed 188 scientists. The Commission organised three scientific seminars related to inland waters during the 1990's.

In 1985 members of the Freshwater Research Group decided to invite SIL (International Association of Theoretical and Applied Limnology) to hold a future Congress in Ireland and a SIL Congress Committee was set up. The Congress was eventually held in 1998 in Dublin. In preparing for the Congress, the Committee recognised that individuals and organisations were carrying out a considerable amount of research in Ireland, but this information was largely unpublished and difficult to access. In response, three volumes were published in time for the Dublin Congress in 1998, covering a wide range of topics related to Irish inland waters (e.g. macrophytes, invertebrates, fish, flora, etc…).[6,20, 35] It was hoped that the Congress would encourage freshwater researchers in Ireland to present their information to the scientific community on a more regular and organised basis in the future.

1.4.4 Recent publications

In 1999 the EPA published a comprehensive report on Water Quality in Ireland between 1995 and 1997.[36] The report presented data from surveys of 13,000 km of river channel and 120 lakes, and concluded that Irish waters remain in good condition because of the limited pressures on them compared to other countries. However, the report also stated that the greatest problem in Ireland was still eutrophication control and that there was also a deteriorating trend in river water quality.

A 25-year monitoring programme on eight of Ireland's primary fishing lakes was published in 1998, and this work described how total phosphorus concentration and chlorophyll levels are significantly correlated.[37] In 1999 McGarrigle and Champ suggested a management strategy for Loughs Conn and Mask – two of the largest lakes in western Ireland.[38] A baseline investigation on Lough Carra – another important western lake – was published by King and Champ in 2000.[39] In 2000, McCarthy *et al.*

reported on the water quality and trophic status of these three western lakes, along with Loughs Corrib, Carrowmore and Cullin, as a result of an extensive survey from 1995-1997.[40]

The EPA Millennium Report in 2000 stated that *"over 13,000km of river channel is subject to regular chemical and/or biological sampling."*[41] The report outlines the river biological monitoring programme at 3,200 locations once every three years and a less extensive chemical programme where 2,100 locations had been covered in total at the date of the report. (The frequency of the chemical sampling was not specified in the report). Thus, many small rivers and mountain streams may rarely, if ever, have been analysed for chemical parameters. The same report also stated that *"only a minor proportion of the estimated 6,000 lakes over 1 hectare have been surveyed for water quality status to date."*

1.4.5 Focus on Acidification

Investigations were undertaken in the late 1980's and early 1990's by An Foras Forbartha and the Environmental Research Unit to determine the degree of sensitivity to acidification in Irish waters. The studies concentrated on areas of the west and northwest where there are many lakes in areas of base-poor bedrock, and thus the waters have a limited buffering capacity. Results of the investigations were published in 1986[42] and 1991[43] and indicated that acidification of surface waters due to atmospheric pollution was not a significant problem in Ireland. Some evidence of acidification in rivers from afforested catchments was found, however.

Interest continued to develop in this area, particularly in studies of the effects of coniferous forestry on surface waters. In 1990 Allot *et al.* reported on the acidification of surface waters in Connemara and South Mayo.[44] They reported a relationship between upstream forest cover and the degree of acidity in streams. This theme continued in 1997 with the publication of a four-volume report by the National Council for Forest Research and Development (COFORD) on the relationships between precipitation, surface water chemistry and forestry in various parts of Ireland.[45,46,47,48]

In 2000, Aherne and Farrell reported the sensitivity of Irish lakes to acidification based on geology and soil type, but did not take into account the possible acidifying effects of forestry. They stated that although Bowman reported acidification in some areas in 1991, no large-scale studies on acidification of Irish surface waters had been carried out previously. They restricted sampling to 201 lakes in acid-sensitive regions and found that 35% of the sampled lakes had a pH lower than 5.3 and thus were sensitive to acidification.[49] They found most of the acid-sensitive lakes in the mid-east and northwest of Ireland. They also stated that 44% of lakes had a pH lower than 6.0, a value below which detrimental effects on freshwater fauna have been previously recorded. For example, Howells *et al.* reported in 1990 that aluminium toxicity to fish is greatest between pH 5.0 and 6.0 when the hydroxy forms $Al(OH)_2^+$ and $Al(OH)^{2+}$ predominate.[50]

1.4.6 Trace element and metal analysis of Irish waters

Due to the wide range of topics related to water quality and the necessary importance given to subjects such as eutrophication and acidification, little attention has been given in the literature over the years to trace element and metal concentrations in Irish waters.

The 1974 report on river water quality by An Foras Forbartha[31] reported results for copper and zinc in all the samples collected over the course of the study. It is not specified what method of analysis was used for the determinations, but given that the same agency used AAS for their lake survey in 1975, it is probable that this technique was used. The report concluded that no gross pollution by metals was found in the rivers surveyed, although significant concentrations were found at a few sites near mining areas (Table 1.6). It was noted in the discussion that in some cases metal toxicity to fish is greater than to humans (see also Section 1.2 above). While useful for providing an idea of the overall metal concentrations in Irish rivers, the data contained in this report is quite limited and in many cases values were found to be well below detection levels of the measurement technique. Some other extremely toxic elements for aquatic life were not measured in the survey (e.g. aluminium, cadmium) and others were only measured on some samples (e.g. lead, chromium, nickel).

Table 1.6: High metal concentrations reported in 1974 by An Foras Forbartha[31]

Metal	Kilmastulla (Silvermines)	White River	Navan mining area
Lead (mg/L)	0.02-0.40	-	< 0.05 – 0.107
Zinc (mg/L)	0.02-2.3	0.1-0.58	0.008-0.021
Copper (mg/L)	Max 0.2	-	Max 0.03
Nickel (mg/L)	-	0.4-1.15	-
Chromium (mg/L)	-	0.006-0.70	-

Monitoring of drinking water supplies in the 1980's and 1990's by the ERU and EPA included analysis of several trace metals – aluminium, iron, manganese, lead, copper, zinc and cadmium. Again, it is probable that AAS was used for determinations as it was still being used by the same agency for metal analysis as late as 1994 (see Section 1.3). Most of the results during the 1980's and 1990's complied with drinking water standards, but some exceedances were noted for aluminium, iron, manganese, lead and copper.[51] The 1999 EPA report on Water Quality in Ireland from 1995-1997 measured iron and manganese in groundwaters, aluminium in forested areas and selected heavy metals in certain rivers with known contamination problems.[36] The report clearly stated that whilst the measurement of toxic contaminants in freshwaters is generally not included in regular water quality monitoring, where problems with metals, pesticides and polychlorinated biphenyls (PCBs) have occurred, they are monitored on a regular basis.

In 1999-2000 the Environmental Protection Agency carried out a survey of dangerous substances in surface freshwaters – the majority of which were rivers previously studied in the river water quality reports mentioned above. The survey covered pesticides, organic compounds and eight toxic metals selected with reference to the List 1 and List 2 substances in the EU Dangerous Substances Directive (CEC 1976)[9]. Another 20 trace elements and metals were also measured during the survey and were presented in the report for reference purposes (Table 1.7). ICP-MS was used for metal analysis during this survey. This work was a follow-up to a previously unpublished survey from 1994 and both sets of results were published in 2001.[52] It was the first comprehensive report listing trace element and metal concentrations in Irish waters – and even still it contained information only on 74 river sites. Of these, 53 sites were sampled once and 21 were sampled on two or more occasions. A total of 117 samples were taken. The report acknowledged that there is limited knowledge of the occurrence of these substances in Irish waters and recommended their further investigation and ongoing monitoring. Finally, a report on drinking water quality in Ireland by the EPA in 2001 listed exceedances for some of the metal elements in public and ground water supplies – for example there was fourteen exceedances for copper and six for lead.[33] Further details of these exceedances were not given in the printed report, but were made available in electronic format by the EPA.

Table 1.7: Elements reported in EPA Dangerous Substances report 1999-2000

List 1 substances (according to 76/464/EEC)	Cadmium, Mercury
List 2 substances (according to 76/464/EEC)	Arsenic, Chromium, Copper, Lead, Nickel, Zinc
Other potentially dangerous substances	Selenium, Tin, Silver, Aluminium, Barium
Other metals measured for reference	Beryllium, Boron, Sodium, Magnesium, Potassium, Calcium, Vanadium, Iron, Manganese, Cobalt, Molybdenum, Antimony, Thallium, Thorium, Uranium

1.5 Factors influencing element concentrations

1.5.1 Geology

Undoubtedly the most important factor influencing the concentration of the alkali and alkaline earth metals (Periodic Table Group I and Group II) in surface waters is the underlying geology of the catchment basin from which the waters originate.

Rocks are aggregates of minerals and each mineral is in turn made up of atoms of the chemical elements. Eight elements make up more than 98% of all rocks (Table 1.8).[53] The other chemical elements appear as trace constituents of the common rocks and may also become so concentrated in certain small areas that they can be mined commercially (e.g. copper, lead, barium).

Table 1.8: Average composition of crustal rocks, in terms of elements[53]

ELEMENT	SYMBOL	PERCENTAGE
Oxygen	O	46.71
Silicon	Si	27.69
Aluminium	Al	8.07
Iron	Fe	5.05
Calcium	Ca	3.65
Sodium	Na	2.75
Potassium	K	2.58
Magnesium	Mg	2.08
		98.58 %

It is widely accepted that water plays a major part in the weathering of bedrock (through hydration and oxidation, reduction, dissolution and decomposition) and that rivers and streams contribute more to the wearing away of the continents than all the other agents of erosion combined. It follows that the chemical composition of the bedrocks themselves should then be reflected in the surface water chemistry of the rivers, lakes and streams causing the weathering and erosion.

In certain areas where there is a concentration of metal ores in bedrock (e.g. copper, lead, zinc) the local water chemistry may reflect the presence of these metals.

1.5.2 Forestry

By 1900 woodland cover in Ireland was reduced to about 1% and from then until 1980 it was government policy (in latter years reinforced by the EC Common Agricultural Policy) that land suitable for agricultural production should not be devoted to forestry.[54] Recent afforestation policies in Ireland have increased the land area under forestry to almost 9%, and a further increase is projected to 17% by 2030.[41] Nearly 80% of all the plantings are of two coniferous species – sitka spruce and lodgepole pine, neither of which are native Irish species, but both of which grow well on poor peaty soils in high rainfall and humidity. Blanket bog has been used for many forestry plantations in the 1980's and 1990's.

However, forestry plantations on peatland pose many environmental problems. As well as soil depletion and erosion, coniferous forests filter atmospheric pollutants, create an acid needle litter in the soil and run-off may lead to acidification of streams and rivers, which directly affects the river ecology.[55, 48, 47] In addition, drainage design in the plantation can cause problems of sediment, flash flooding and leaching of aluminium and other metals from the poor peaty soils.[45] Elevated concentrations of aluminium in rivers and streams can be an indication of acidification in forested areas as this element is easily leached from the soil and rocks under acidic conditions.

1.5.3 Mining

Whilst the number of base metal exploitation mines in Ireland is not large, they nevertheless have a local impact on the environment (Figure 1.3). Mining residues accumulate at the various mine dumps and tailings ponds, e.g. Avoca, Tynagh, Silvermines and Tara. There is a constant long-term risk of pollution to waterways in these areas from leachate coming from the mine tailings. Leachate from old disused mine-workings in Ireland contains mainly metals such as lead, copper and zinc in the highest concentrations (often >100mg/l), and other metals such as cadmium, chromium, manganese, nickel and aluminium in lower concentrations <1mg/l). Furthermore, the highly acidic nature of mine leachate (<pH3) can leach elements such as aluminium and manganese from soils and rocks it passes over.

Figure 1.3: The effect of mine leachate on the Avoca River [•]

[•] *Source: Central Fisheries Board, reproduced with permission.*

Ireland is currently Europe's largest producer of zinc concentrate, accounting for an estimated 35% of the total zinc output in Europe.[56] The zinc is mined at three different locations, all opened in the last forty years – i.e. Tara Mines (Co. Meath), Lisheen (Co. Tipperary) and Galmoy (Co.Kilkenny). All three mines produce lead and zinc, and Tara also produces silver. Unlike the older mines near Kilmastulla and Navan which impacted heavily on the local environment (see Section 1.4 above), environmental legislation now requires effluent treatment prior to discharge in order to comply with the Water Pollution Act 1963 and the EPA Act 1992. Nevertheless, these mines could pose some threat to local surface waters, in particular the Boyne, Drish and Goul rivers respectively. Long-term monitoring of local streams and rivers will reveal the impact, if any, the mines will have on the local aquatic environment, and will also provide the Fisheries sector with an opportunity to investigate the possible impacts of sub-lethal levels of metals in the natural environment.

1.5.4 Point source pollution

The EPA Millennium Report[41] stated that most instances of serious river pollution were due to sewage discharges, with the remainder attributed to agriculture or industry in roughly equal proportions. Instances of slight to moderate pollution were mostly eutrophication related and have been mainly attributed to agricultural practices.

Localised pollution instances, whether from sewage, agriculture or industry immediately cause a change in the trace element concentrations of the local river or stream where the pollution occurs. Knowledge of the pollution source can give an indication of what chemical elements would be expected in higher concentrations downstream of the source location. For example, sewage pollution would be expected to increase the concentration of elements such as sodium, potassium and zinc (as well as phosphorus, nitrogen and ammonia). Consequently, analysis of the polluted water and identification of chemical elements present in elevated concentrations can assist in identifying a possible source of pollution.

1.5.5 Miscellaneous wastes

Metal elements can find their way into surface waters from many different sources, and especially as a result of human waste disposal.

Municipal and industrial sludges as a waste product from treatment plants contain high levels of metals such as copper, zinc, chromium, nickel, cadmium, lead and iron.[5] Prior to 1998, this sludge was frequently dumped at sea, and other times disposed of in landfill sites where there is potential to leach into groundwater and then small drains, streams and eventually rivers and lakes. Landfill sites are also filled with a variety of other metal-containing wastes e.g. aluminium cans, scrap metal, refrigerators, washing machines and other pieces of broken or unwanted furniture. Discarded batteries contain lead and mercury. Electroplating waste contains copper, cadmium, cobalt, lead and nickel. Abandoned vehicles in the countryside contribute a large amount of ferrous and non-ferrous metals to the environment as they disintegrate slowly over a long period of years. Indeed, fish kill statistics unfortunately are testament to the fact that leachate from these sources enters surface waters occasionally with devastating results on the fish.[57]

1.6 <u>The role of the Fisheries Boards in Inland water management</u>

The Central and Regional Fisheries Boards are the State agencies responsible for conserving and managing Ireland's inland fisheries resources. Many of the extensive waters of Ireland still contain abundant stocks of wild fish, attracting thousands of recreational anglers each year. In 1996 it was estimated that anglers contribute almost €100m to Irish GNP, supporting about 3,750 jobs.[58] This figure has not changed significantly since 1996. However, from being the most popular tourist activity in Ireland less than a decade ago, angling is now rated as the third most important outdoor tourist activity in Ireland after golf and walking.

Protecting and promoting Ireland's angling resource presents a difficult challenge in modern times, with increasing problems from invasive species, over-fishing, reduced stocks and pollution. The Fisheries Boards devote much time and energy to combating water pollution and monitoring water quality in the rivers, lakes and canals of Ireland. The Boards recognise the importance of good water quality for aquatic ecosystems. The aquatic habitat is a dynamic environment, and thus not only the fish, but also all other fauna and flora are adversely affected when a river or lake is damaged by pollution. It is widely accepted that the presence of healthy fish is one of the best indicators of water quality.

Unfortunately, long term systematic monitoring shows that whilst the occurrence of seriously polluted rivers has decreased since 1971, the percentage of high quality unpolluted rivers has also decreased (Figure 1.4). These trends show the gradual deterioration in water quality over the past few decades and highlight the need for continued protection, monitoring and conservation work.

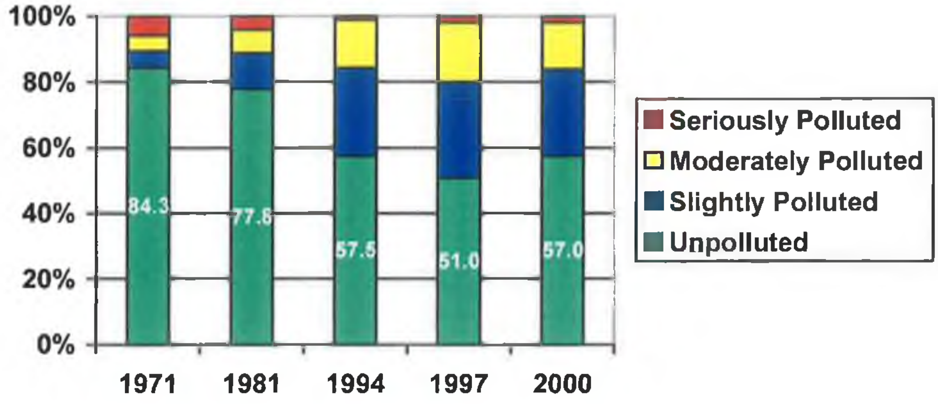

Figure 1.4: Trends in Irish River Water Quality 1971-2000 [41 58 59]

The Strategic Development Plan for Inland Fisheries 1998-2002 identified a number of key actions necessary to maintain and improve water quality. One of these actions was to upgrade specialist laboratory services and equipment. In 1997 and 1998 the laboratory at the Central Fisheries Board was upgraded with the help of EU Tourism Angling Measure (TAM) funding. The purpose of the upgrading was to enhance the capability of the Fisheries Boards to monitor the chemical characteristics of aquatic habitats, to improve pollution detection and prevention and to extend the national database of information on the composition of Irish freshwaters. One of the pieces of equipment purchased by the CFB was an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) for the low level analysis of trace elements and heavy metals in river, lake and canal water – a facility not previously available to the Fisheries Boards.

1.7 Aims and Objectives

This thesis describes a study carried out from 1998-2001 as part of a larger investigation into the concentrations of trace elements and metals in Irish surface waters by the Central Fisheries Board. The purpose of the large investigation was to increase the national database of information in this area, possibly leading to establishment of chemical “fingerprints” for specific rivers and lakes. It was hoped that this would eventually assist in the understanding of biological processes and possibly facilitate pollution detection and tracing. The main objective of the more detailed study described in this thesis was to assist the understanding and interpretation of results collected in the larger investigation, and to explore more thoroughly the similarities and differences in the chemistry of waters in various parts of the country.

During the period of this investigation, water samples were taken from many recognized and potentially important fisheries. Some of these sites were already part of long-term monitoring programmes and others were included in shorter-term EU funded development projects. Specific areas were selected for particular focus in this thesis in order to reduce the huge amount of data collected over the course of the project to a manageable level. The particular samples used for detailed interpretation were chosen to represent the variation in the larger dataset, i.e. a selection of important fishing lakes in different parts of the country (Chapter 3), an important river catchment which highlights the effect of geology on water chemistry (Chapter 4) and finally the four major canal systems (Chapter 5). The general conclusions drawn from these areas represent well the findings at all the other sample sites around Ireland.

All water sampling for the duration of this project was carried out by Central or Regional Fisheries Board staff (with the exception of Lough Lene and Lough Derravaragh samples that were collected by Westmeath County Council). Sample treatment and analysis was carried out exclusively by the author. Results from the analyses were examined mathematically, graphically and statistically mainly by the author with some assistance from colleagues in Dublin City University in order to identify patterns and trends in the collected data.

CHAPTER 2

2. INSTRUMENTATION AND METHODS

2.1 History of ICP-MS

Since the 1960's interest has increased in methods of analysis with the capability to measure several or many elements rapidly at trace levels and relatively quickly and reliably.[60] The replacement of the flame in atomic emission spectroscopy with the inductively coupled plasma (ICP) source became a very important step in the 1970's. This resulted in a huge rise in popularity for ICP-AES analysis, which allowed rapid scanning (and later sequential analysis) of large numbers of elements. However, even this technique had its limitations due to emission lines from high concentration elements in the sample matrix interfering with analyte lines. The search continued for an alternative multi-element method of analysis with the speed and ease of ICP-AES.

It soon became apparent that the only method suitable for multi-element, trace level analysis would be a system involving mass-spectrometric detection[61] – where individual elements could be separated based on their atomic mass after being first ionised. It was widely accepted that ICP was a good ion source, but there remained a problem in how to extract the ions from the plasma into the high vacuum required for the MS. Much research was carried out into this problem in the late 1970's and early 1980's, with the main focus of the work being the problem of the boundary between the extremely hot plasma and the low-pressure vacuum system.[61, 62, 63, 64, 65, 66] The first successful spectra were produced in 1981 at the University of Surrey, and the first commercial instruments were available by 1984. Since that date there has been a huge amount of development and improvement in ICP-MS technology – a subject beyond the scope of this text, but reviewed annually by the Journal of Analytical Atomic Spectroscopy (JAAS) in their Atomic Mass Spectrometry update.[♣]

The JAAS review in 1999 had 298 references to MS related publications in the previous year.[67] The 2000 review covered only a period of 10 months and listed 319 references.[68] The 2001 review acknowledged that the use of more modern ICP-MS related techniques has been gathering momentum[69], e.g. Laser-Ablation sample introduction, the incorporation of collision or reaction cells into the ICP-MS, and the use of single and multiple collector magnetic sector MS systems. The large number of publications each year highlights the constant growth, development and improvement of ICP-MS technology to this day.

2.2 Principles of ICP-MS

2.2.1 Plasma formation

The plasma is formed in a quartz tube torch by the transfer of energy from a Radio Frequency (RF) supply to an inert gas (usually argon). The RF supply is applied to a load coil of copper tubing surrounding the torch at a frequency of 40MHz and a power of 1-2kW. The load coil is cooled internally by a circulating water flow. A high stream of argon entering the torch is seeded with electrons from a Tesla discharge coil.[70] These electrons interact with the magnetic field of the load coil and gain energy, which causes them to ionise argon atoms by collision. The eddy current formed by fast moving electrons and cations, causes further ionisation, and a flame shaped plasma is formed where temperatures range from 6,000-10,000K. Most of the energy is coupled to the outer region of the plasma, creating a skin effect. In the instrument used for this work, the load coil consisted of two interlaced 2-turn coils, instead of a 4-turn coil found on

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[♣] This review also includes other types of mass spectrometry, e.g. thermal ionisation mass spectrometry (TIMS), glow discharge mass spectrometry (GDMS) and others.

other instruments. This arrangement where a front-grounded coil is interlaced with a rear-grounded coil creates an electrically neutral plasma, which allows for more efficient transfer of energy to the plasma, and thus more favourable plasma conditions for production and sampling of ions[71]. (Figure 2.1)

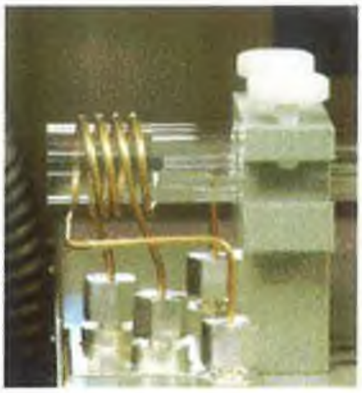

Figure 2.1: Varian ICP-MS torch and coils arrangement [♣]

There are normally three separate supplies of argon gas delivered to the torch in order to sustain and stabilise the plasma (Figure 2.2). The main plasma support gas (~15 L/min) is delivered by a side tube to the outermost area of the torch, creating a vortex flow which also serves to cool the inside walls of the torch, and to centre and stabilise the plasma. An auxiliary gas flow (~1 L/min), also delivered via a side tube, keeps the hot plasma away from the tip of the innermost injector tube.

The innermost concentric tube (injector) of the torch carries the nebuliser gas from the sample introduction system. This gas flow (0-1 L/min) punches a channel in the main plasma, and cools the centre to about 5,000-7,000K. The gas in this central channel is mainly heated by radiation and conduction from the outermost parts of the plasma. Thus, because of the physical separation between the outer and innermost parts of the

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[♣] *Source: Varian Inc. – reproduced with permission* plasma, the chemical composition of the sample delivered to the central channel can vary substantially, without affecting the processes that sustain the plasma.[60]

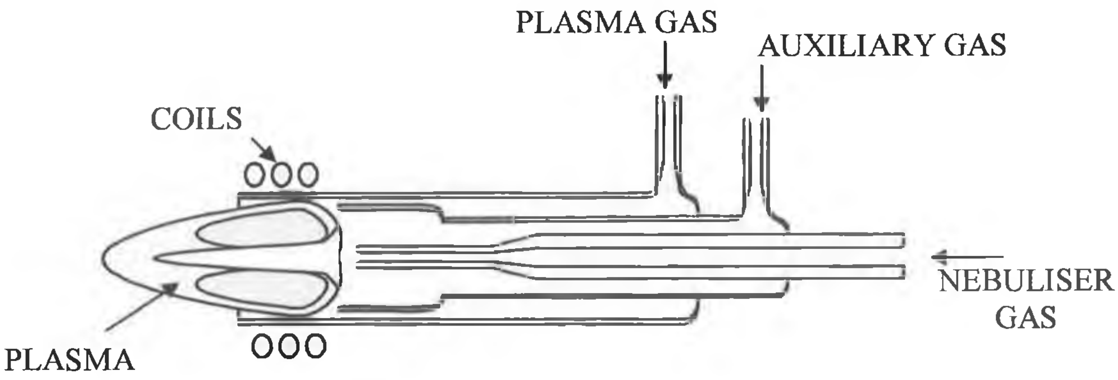

Figure 2.2: Torch design showing the three different gas flows ♣

2.2.2 Sample Introduction

Samples are most often introduced to the plasma in the form of a fine liquid aerosol. The most popular liquid sample introduction methods are pneumatic nebulisation[60], ultrasonic nebulisation[72], thermospray vapourisation[73] and direct injection nebulisation[74]. By far the most widely used is pneumatic nebulisation, which is easy to use and relatively stable despite being inefficient. It is also possible to introduce gases (by hydride generation[60, 75] and direct injection[60, 76]) and solids (by laser ablation[77] and arc/spark[78]). There have also been publications in the literature describing novel and unique sample introduction methods.[79] However, as the majority of ICP-MS applications involve the analysis of liquid samples, including the work carried out in this study, further discussion will consider only liquid samples.

Liquid samples are pumped to a sample introduction assembly where they enter a nebuliser (in this work a concentric glass nebuliser was used) and are mixed with a high

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♣ *Source: Varian Inc. – reproduced with permission* flow stream of argon gas, forming a fine aerosol. This aerosol enters a spray chamber – in this work the spray chamber was made from inert Teflon – where a turbulent flow allows only the smallest droplets to pass into the ICP-MS system (typically those <15μm[80]). Only about 1% of the original sample solution reaches this stage.[60] The instrument set-up used in this work had an external sample introduction assembly (ESIA). This meant that aerosol formation and droplet selection in the spray chamber was carried out at room temperature, to avoid the possibility of drift from radiated heat inside the plasma compartment of the ICP-MS system.

From the spray chamber, the smallest selected droplets pass to the central capillary (injector) tube of the glass torch located inside the ICP-MS. These droplets are injected into the centre of the plasma where the liquid water is evaporated (desolvation). Next, the remaining salts are volatised and dissociated into their constituent atoms. These atoms are excited and ionised before leaving the plasma to enter the next stage of the instrument. The entire process from injection through to ion formation is summarised in Table 2.1 and is very rapid (estimated to be approximately 50μs).

Table 2.1: Analyte solution history from introduction to final ionisation [61]

Location	**State**	**Event**
Sample vessel	Solution	Aspiration or pumping
Nebuliser	Aerosol droplets	
Spray chamber	Selected droplets	Dia. >4μm rejected*
Torch capillary	Droplets	Transport to plasma
Plasma central channel	Droplets	Desolvation
Plasma central channel	Salt particles	Volatilization
Plasma central channel	Molecular vapour	Dissociation
Plasma central channel	Atoms	Excitation and ionisation
Free space	Atoms and ions	Exit from torch

* Literature values for selected droplet size vary depending on spray chamber and conditions used

2.2.3 Ion sampling and beam focusing

Upon leaving the plasma, the ions pass through a sampling orifice approximately 1mm in diameter behind which is a vacuum of approximately 10^{-4}Torr. This reduction in pressure causes the gas to expand and form a supersonic jet. The central part of this jet is further sampled through a smaller orifice in the skimmer cone of about 0.5mm in diameter.

After the ions leave the skimmer cone they enter the high-vacuum chamber, which contains the mass analyser – but first they must be focused into a narrow beam. This is done with ion lenses – the basic operation of which is similar to electron lenses used in television sets. The ion lenses consist of several cylindrical shaped electrodes strung together, and the voltages applied to these electrodes can be varied in order to focus the analyte ions into a narrow beam. A central disc – called the "photon stop" - is also incorporated, which collects neutral species and prevents photons from the plasma from reaching the detector (Figure 2.3).

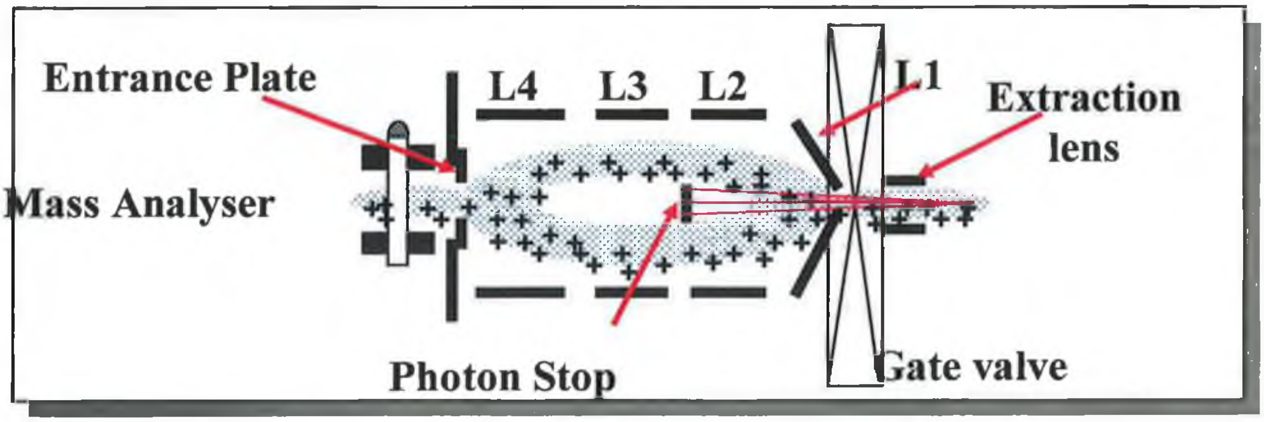

Figure 2.3: Schematic diagram of the ion optics *

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* *Source: Varian Inc. – reproduced with permission*

2.2.4 *Mass scan & detection*

In order to measure individual species, the ion beam needs to be separated on the basis of the atomic mass of the ions. This is carried out by a quadrupole mass analyser or mass filter, which consists of four straight metal rods, opposite pairs of which are connected together. DC and RF voltages are applied to each pair – the DC voltage being positive for one pair and negative for the other. The RF voltages have the same amplitude but are opposite in sign[60]. Varying these DC and RF voltages allows different masses to find an electro-statically stable path through the quadrupole rods. During analysis the RF-DC voltages are altered in a rapid scanning sequence that successively allows ions of a particular mass to pass unhindered through the rods to the detector. Other ions are ejected from the quadrupole and removed by the vacuum (Figure 2.4).

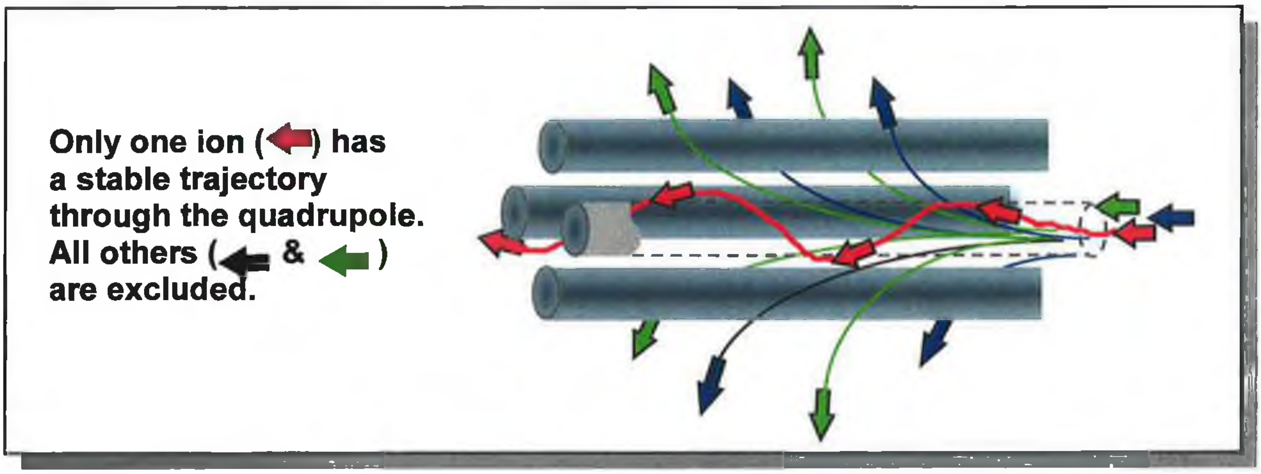

Figure 2.4: Ion path through the quadrupole ♦

Detection of the ion beam signal is carried out using an off-axis discrete dynode electron multiplier (DDEM) detector. Electron multiplier detectors are common in mass spectrometry when the ion current is less than 10^{-15}A. The positively charged ion beam is accelerated by a high negative charge (2,000-3,000V) on the dynode detector and the

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♦ *Source: Varian Inc. – reproduced with permission* current is then magnified by 15-18 individual dynodes that are coated with a metal oxide that has high secondary emission properties[70]. These secondary electrons are constrained by a magnetic field, causing them to strike successive dynodes (Figure 2.5). The gain of this type of detector can typically range from 10^5 to 10^7. The detector is positioned in an off-axis position to ensure that background neutral species and photons are not detected. Output from the detector is transferred to computer where it is displayed as a "counts per second" value for each mass unit measured.

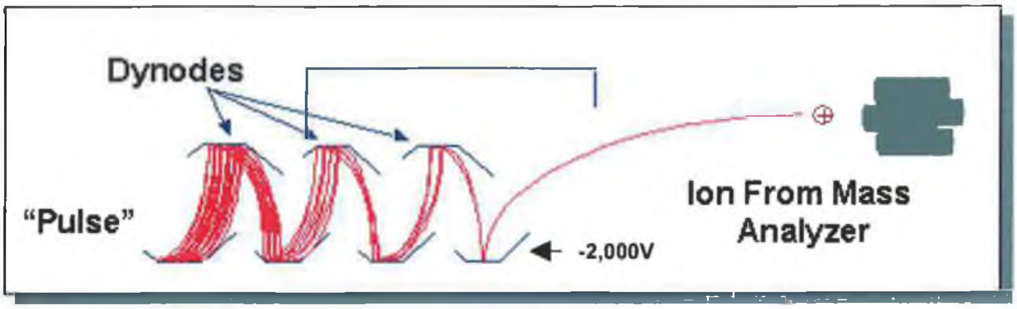

Figure 2.5: Ion detection ♣

2.3 Applications of ICP-MS

ICP-MS has been used for elemental analysis in a wide range of fields, including clinical, environmental, geological, petrochemical and nuclear industry applications. It is also widely used in the water industry and for certification and validation testing (e.g. Certification of Community Bureau of Reference Materials (BCR) reference materials[81, 82]).

In 1986 Taylor *et al.* used ICP-MS to determine trace metals in reference water samples, and stated that this method of analysis is a powerful tool to assist the assessment of trace elements in water systems.[83] Since that date, because of its high sensitivity, specificity

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♣ *Source: Varian Inc. – reproduced with permission* and low detection limits, ICP-MS has been routinely used in analysis of surface and ground waters. This was re-iterated by Cave *et al.* in their Environmental Analysis update in 2001[84]. (A review of environmental analysis applications is published annually by JAAS, last in March 2002[85]).

2.4 Problems & Interferences

Despite the advantages of ICP-MS over many other methods of multi-element analysis, this technology is not without interferences and other problems associated with the instrumentation and sample matrix. These issues will now be discussed in further detail.

2.4.1 Problems associated with instrumentation

2.4.1.1 Plasma stability

An electrically neutral plasma is one of the most important things to have in order to ensure an efficient transfer of ions from the plasma compartment (at atmospheric pressure) to the vacuum region behind the cones interface.[86] If there is electrostatic coupling between the plasma and the metal cones, electrical arcing can occur which causes many problems such as an increase in doubly charged species and a spread in the kinetic energy of the sampled ions. It also decreases the lifetime of the cones by increasing the orifice size. In the instrument used for this work, the use of an inter-laced coil arrangement reduced this problem.[71]

A stable plasma is also vital for trace level analytical work – and this is again achieved through hardware design with a good steady RF power supply that is coupled efficiently to the plasma. Without plasma stability there can be fluctuation in the ion signal produced.

2.4.1.2 Instrument cleaning

The design of a mass-spectrometer instrument is such that much of the sample material that enters it will remain there, unless it is immediately drawn away by the vacuum pumps. Over time the detector, quadrupole and ion focusing lenses become coated with material, thus reducing their sensitivity. The ion lenses, which receive most of the deposits, need to be regularly removed for cleaning – in modern instruments this is normally carried out by a trained service engineer as part of preventative maintenance. In time, the detector, and possibly the quadrupole also require replacement or re-conditioning due to lost of sensitivity from build up of deposit. In an ICP-MS, the other main area where deposit is formed is on the cones at the plasma/vacuum interface. These cones need to be removed and cleaned regularly in order to avoid loss of signal, increased %RSD and drift caused by deposits around the sampling orifice.

2.4.1.3 Resolution & peak height

As described above, quadrupole mass analysers select ions based on their stability through a rapidly scanning field. The ability of the quadrupole to separate different masses so that they do not overlap at the detector is called its "resolution". Many factors influence the resolution of a quadrupole, including its shape, diameter, length, operating power supply, operating vacuum, applied voltages, and the motion and kinetic energy of the ion beam.[87] There are no moving parts in the quadrupole, and the user normally adjusts the resolution by changing the ratio of the DC and RF voltages. As the ratio is increased, resolution also increases, and the result is that the number of ions transmitted to the detector decreases.[60] Thus, there is a constant compromise between instrument resolution and sensitivity.

2.4.2 *Non-spectroscopic and matrix effects*

2.4.2.1 Effect of acid concentration[80]

A change in acid concentration from one sample to the next causes a transient signal change that can last several minutes. The magnitude of this change increases as the difference in the acid concentration increases. Acid concentration directly affects the droplet size distribution in the spray chamber – a higher acid concentration reduces the evaporation of water from the aerosol droplets. Changes in acid concentration are also thought to induce changes in the plasma itself and in the transmission of ions to the detector. Using a constant acid concentration across standards, samples and rinse solutions eliminates this problem.

2.4.2.2 High dissolved solids

One of the earliest observations from work on ICP-MS was that it was not tolerant to solutions containing high levels of dissolved solids. The use of a very small ion-sampling aperture at the plasma interface caused problems with blocking and signal drift over a very short time. The aperture size has been increased in more modern instruments, but rapid signal loss at the beginning of an analytical run may still occur. This effect can be minimised by priming the system for about 20 minutes before analysis with a solution of similar composition to the samples.[60] Indeed, by careful optimisation of instrument conditions, solutions with very high salt content have been analysed using ICP-MS with extremely good stability. However, it is generally recommended that the concentration of matrix components be kept below 0.2%. Concentric glass nebulisers are also susceptible to high levels of dissolved solids because of the small orifice of the central capillary tube through which the sample solution passes. Nebulisers designed to handle higher levels of dissolved solids (such as ICP-AES nebulisers and crossflow designs) are not generally used for ICP-MS work because they are not as efficient at creating small aerosol droplets.[88] Changes in salt concentrations between samples can result in effects similar to those occurring with changes in acid concentration (see above). Therefore, it is good practice to group samples according to similar matrices.

2.4.2.3 Space-charge effects

ICP Mass Spectrometry is susceptible to severe, mass dependent chemical matrix effects that cause defocusing of the ion beam. High concentrations of matrix elements (e.g. sodium) can repel analyte ions, causing a reduction in signal. In general it is found that if high concentrations of low mass elements are present, the high mass elements are affected, and the same is true in reverse.[80] Mathematical correction using internal standards, which are well chosen across the mass range of interest, can reduce the problem of space-charge effects.

2.4.2.4 Suppression and enhancement (memory) effects

Insufficient wash out times between samples can result in memory effects. This is more pronounced with certain “sticky” elements such as boron, thallium, lithium, mercury, etc… Careful method development can reduce or eliminate this problem. Dirty cones, torch, sample introduction assembly or ion optics can also lead to enhancement effects. Signal suppression can occur due to build up of deposit on the cone apertures leading to a reduced orifice size. Suppression can also occur due to blocking in the nebuliser. Space-charge effects (see above) can also cause suppression of the ion beam signal.

2.4.3 *Spectroscopic Interferences*[60]

2.4.3.1 Isobaric

Isobaric interference occurs when two elements have an isotope with practically the same mass. In reality, the mass differs by a very small amount, but not enough for the instrument to resolve sufficiently (e.g. ^{64}Ni has a mass of 63.9280 and ^{64}Zn has a mass of 63.9292). Most elements in the periodic table have isotopes that are free of isobaric overlap, and these isotopes can be chosen for analysis to eliminate the possibility of this interference. However, there are other elements where the most abundant isotope is subject to isobaric interference, and in this case a less abundant isotope, which is free of interference, must be chosen for measurement. In some cases where an element has no isotope free of interference, or where the isotope is of too low an abundance for measurement, a correction equation must be used to correct for the effect of the interfering ion. Isobaric interference can also occur due to overlap with argon – the plasma gas – or with krypton and xenon, which can exist as impurities in liquid argon supplies. In general, however, the low mass elements (<m/z 36) are free of isobaric interferences, and even mass isotopes are more likely to suffer from isobaric overlap than odd isotopes.

2.4.3.2 Polyatomic

Polyatomic interference results from the short lived formation of molecular ions between isotopes of H, C, N, O, S, Cl & Ar in the plasma or from constituent species of the acids/solvents used in sample preparation, or from combination of any of these with the analyte atoms (e.g. ^{40}Ar^{35}Cl interferes with ^{75}As). These molecular ions can overlap with elemental isotopes of interest. A large number of different polyatomic species can be formed, but these are only significant up to about 82 amu.[89] Careful consideration of sample preparation and sample matrix can help to reduce the effect of these polyatomic interferences. For example, it has been shown that HNO_3 is the best choice of acid, which results in the least complex pattern of polyatomic peaks – and indeed the pattern produced in a HNO_3 matrix is identical to that produced in deionised water since the constituent elements are already present in air entrained by the plasma. [60, 90]

2.4.3.3 Oxides

Oxygen is introduced to the plasma in the form of water in each aerosol droplet. The formation of refractory oxides in the plasma reduces the measured signal for those elements with the highest oxide bond strength. The oxide ions appear at M+16, i.e. $^{40}Ar^{16}O$ appears at m/z 56 and interferes with ^{56}Fe. This problem is reduced as much as possible during instrument set up when the rate of oxide formation for cerium is measured (this element forms oxides most readily and has the highest oxide bond strength). The RF power and nebuliser gas flow have a significant effect on the level of oxides produced.[91]

2.4.3.4 Doubly charged ions

Most ions are produced in the ICP-MS as singly charged (i.e. $M \rightarrow M^+$), but some multiply charged ions can also occur (i.e. $M \rightarrow M^{2+}$). This is dependent on the second ionisation potential of the particular element.[92] Only those elements with a second ionisation energy lower than the first ionisation energy of argon will undergo any significant M^{2+} formation (i.e. typically alkaline earths, some transition metals and the Rare Earth Elements). The plasma stability and nebuliser flow also affects the rate of formation of these species. The result of doubly-charged ion formation is firstly a loss of signal for the singly charged species (the measured species at the detector) and secondly as an isobaric overlap at half the mass of the parent element, i.e. the doubly charged ion for ^{138}Ba appears at m/z 69, and interferes with ^{69}Ga. However, the number of elements affected by doubly charged species is few, and in many cases it is possible to use an alternative isotope.

2.5 Materials and Methods

2.5.1 Instrumentation

A Varian Ultramass 700 ICP-Mass Spectrometer fitted with a Varian SPS-5 Autosampler was used for analysis during this work. Sample introduction was via a concentric glass nebuliser (K style) coupled to a Sturman-Masters Spraychamber.

2.5.2 Sampling Procedure

Samples were collected during the study by various Central and Regional Fisheries Board staff. Most of the samples were taken as "grab samples" from bridges or banks using a plastic bucket from which new 150ml polypropylene bottles were filled. Lake samples were taken from a boat. Samples were transported to the laboratory in Dublin as soon as was convenient by bus, rail, courier or by the field staff themselves.

Upon receipt in the laboratory the samples were stored in a refrigerator until nutrient analysis was completed (the main purpose of most Fisheries Board sample collections). They were then passed over for trace element analysis (the secondary purpose of sample collection) where an aliquot was taken from each bottle stored and acidified with HNO_3 to preserve the metal ions in solution. Samples were analysed as soon as possible for trace elements and metals using the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

2.5.3 Standards and calibration

Ready-prepared Merck multi element stock standards were used for calibration. These standards were purchased containing on average 25 different elements. Over the course of the project the elements included in analysis varied somewhat due to slightly different mixes of standards used. Calibration was carried out using working standards prepared from the Merck stock standards. All standards were prepared in Nalgene plastic volumetric flasks (100ml and 200ml). MilliQ water (18 Mega-Ohm) was used for all dilutions and a matrix of 1% (V/V) nitric acid (Aristar Grade) was used for all standards.

Standards were in the range 10-500 μg/l for most elements and 50-1000 μg/l for higher concentration elements. The ICP-MS software used linear calibration curves to calculate individual element concentrations. The software automatically flagged any result above the calibration range. For the purposes of this study these high results were considered acceptable because of the extremely linear nature of this method of analysis. However, it must be noted that this was only necessary for elements present in particularly high concentrations such as calcium and sodium.

Samples were prepared in 30ml plastic screw-top tubes using an adjustable hand-pipette with plastic tips. Solids in the sample were allowed to settle before the liquid portion was removed by pipetting. Filtering and centrifuging the samples was avoided in order to avoid contamination at low levels. The liquid portion was diluted by a factor of 10 with Milli-Q water (18 Mega-Ohm) and acidified to 1% (V/V) with HNO_3 (Aristar Grade). The samples were allowed to stand for a minimum of 16 hours before analysis as recommended in US-EPA Method 200.8 [93].

2.5.4 Analytical methods

A quick and reliable method of analysis was required in this study because of the large number of samples to be analysed. When selecting elements for analysis, consideration was given to the parameters listed in the drinking water and fisheries/aquatic life directives. Other elements that could be analysed in a normal analysis run using standard ICP-MS operating conditions were also included (e.g. cobalt and strontium). Unfortunately it was not possible to include several environmentally important elements such as mercury, selenium and arsenic because sufficiently validated analytical methods for these elements using ICP-MS were unavailable. It is anticipated that the Central Fisheries Board can address this deficit in future studies.

Sixteen elements were routinely measured in the samples analysed. For the purposes of this thesis they shall be classified as follows:

- "GI/GII" refers to Periodic Table Group I and Group II elements – i.e. Na, K, Mg, Ca, Sr and Ba
- "Metals" refers to the remaining ten elements – i.e. Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn

The high concentrations of the GI/GII elements (in particular calcium, magnesium, potassium and sodium) in many samples made analysis by ICP-MS difficult. However, due to their low ionisation potentials, it was possible to use alternative instrument conditions - known as "cool" plasma – to measure these elements. "Cool" plasma has been shown to be suitable for these elements where low detection limits are required[94], but it also proved useful for analysis at high concentrations in this study because it reduces the mass spectrometer detector signal. Iron was also analysed using the "cool" conditions due to interference from argon oxide (ArO) under normal conditions. Typical standard and cool plasma operating conditions are summarised in Table 2.2.

Table 2.2: Typical operating conditions for normal and cool plasma conditions

	Normal Conditions	**Cool Plasma Conditions** (Fe, Ca, Mg, K & Na)
RF Power:	1.28 kW	0.7 kW
Plasma flow:	17.0 L/min	18.0 L/min
Auxiliary flow:	1.05 L/min	1.00 L/min
Nebuliser flow:	0.95 L/min	1.22 L/min
Sample uptake:	1 ml/min	0.8 ml/min

Internal standards used under normal conditions[♦] were scandium, yttrium, rhodium and terbium – selected to represent the range of analyte masses. These were prepared in one solution at approximately the same concentration as the highest calibration standard and were introduced continuously into the sample stream by using a T-piece between the pump and the spray chamber. Each element was assigned the internal standard closest to its atomic mass.

The instrument software was completely automatic and during analysis took five replicate measurements of each standard and sample presented. The software then automatically processed the raw data received from the detector (count/sec values) and returned a mean value for each element. A calibration for all elements was carried out when all the standards had been presented and a calibration coefficient was reported. The sample results were then each processed in turn by the instrument software and a concentration value calculated based on the most recent calibration. The instrument software also measured the internal standard signals with each sample and automatically

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[♦] No internal standard was used under "cool plasma" conditions because there is no suitable element for this purpose under these conditions.

calculated and corrected for any drift that may have occurred during analysis from the original internal standard signal. At the end of the analysis run, the results file was then exported to Microsoft® Excel and Minitab® for manual processing.

2.5.5 *Quality procedures*

Certified quality control standards purchased from Promochem UK were included in each analysis run, with acceptance criteria of ± 10% the certified value. Methods were developed using NIST standard 1643d, and a 10% dilution of surface water standards SPSW1 and SPSW2 were used as daily QC checks. A preparation blank (MilliQ water/1% v/v Aristar Grade HNO_3) was also analysed with each set of samples to determine background metal levels present in the dilution water and nitric acid used.

2.5.6 *Data analysis*

Initial investigation of results was carried out with Microsoft® Excel using simple plots and tables of the data. Many trends and patterns were identified using these basic methods. Following this, some multivariate analysis was carried out using Minitab®. The technique used was Principal Component Analysis (PCA) [95, 96]. There has been a rapid increase in the number of papers being published using various chemometric techniques for aiding the analysis and interpretation of environmental data since the early 1990's. For example, PCA has been successfully applied to the analysis of drinking water[97], sediments and seawaters[98, 99, 100] and to the temporal evolution of groundwater composition[101], while Alberto *et al.* used the technique to study the spatial and temporal variations in water quality in a river basin [102].

Another technique – Discriminant Function Analysis (DFA) – has been applied to the identification of origin of Atlantic salmon[103], the interpretation of geochemical development in Managed Retreat sites in the UK[104] and grouping of locations in Hong

Kong to select environmental and toxicity data[105]. Classification5 techniques, such as DFA, are used to predict group memberships using *a priori* information. Environmental problems however tend to be orientated towards identifying factors responsible for the state of a given system, and so techniques such as PCA are more popular in comparison. A detailed discussion of the results collected during this study follows in Chapters 3, 4 and 5.

CHAPTER 3

3. LAKE WATER ANALYSIS

3.1 Introduction

Ireland contains an abundance of natural lakes, with the majority of these located in the midlands, west and northwest. It is estimated that there are at least 1,500 lakes in Ireland with area greater than 10 hectares[5], and 6,000 lakes with an area greater than 1 hectare[41]. Many of the smaller lakes are used as local potable water sources, and the larger lakes are renowned for their angling potential – particularly the hard-water lakes of the midlands and west.

As discussed in Chapter 1, very little information was available on the water quality of Irish lakes before 1971 when systematic investigations began. Since then there has been some extensive studies carried out, concentrating mainly on chlorophyll and nutrient concentrations. In 1999 the results of surveys on 120 lakes was published by Lucey *et al.*, but of these lakes more than one-third were sampled only once during the study period of 1995-1997. A comprehensive assessment of 200 Irish lakes was completed and published by the EPA in 2001 and this report refers to all the major published lake studies that have been carried out in Ireland.[106] The report also recognises that there is still a limited amount of knowledge on Irish lake water chemistry, and identifies nutrient enrichment and acidification as the two main environmental problems affecting lakes.

The trace element composition of eighteen Irish lakes shall be examined in detail in this chapter. The lakes represent a wide range of size, geological characteristics, water hardness and geographical locations. Further details of the lakes sampled can be seen in Table 3.1, and Figure 3.1 indicates their locations.

3.2 Trace elements in lakes

Although the information on nutrient and chlorophyll concentrations in lakes has increased in recent years, there was very little information available on the trace element and heavy metal concentrations in Irish lake water before the present study was undertaken. Work carried out in other countries, however, gives some hints as to the trends that may also be found in Irish lakes.

There is evidence that the growth of plankton and other organisms in lake water at different times of the year can lead to fluctuations in trace element concentrations. A study carried out on three clean lakes in Argentina by Markert *et al.* found that there was an accumulation of the elements K, Ca, Mg, Fe, Cu and Zn in phytoplankton living in the lakes.[107] The study also reported that there was a general 100- to 1000- fold accumulation of these elements in the organisms compared to the surrounding environment. Work by Hamilton-Taylor *et al.* also found evidence of metal uptake (in particular Zn) by phytoplankton.[108]

Concentrations of trace elements in lake water are also dependent on the pH of the water and the level of suspended solids. In the previously mentioned study, Hamilton-Taylor *et al.* also found that there was increased sorption of the metals Cu, Pb and Zn onto particulates in natural lake waters with increasing pH.[108]

Of course, the main factor determining the chemical composition of lake water is the nature of the surrounding catchment, the local geology and the characteristics of the tributary rivers and streams. It is these issues, along with an examination of the temporal trends in element concentrations that will form the basis of the following discussion of Irish lake water chemistry.

3.3 Sample collection

For the purposes of this work, there was no specific selection process for one lake over another, because the samples used were those that had been collected by Regional Fisheries Board staff as part of long-term nutrient and chlorophyll monitoring programmes. (The only exception to this was the Lough Lene and Lough Derravaragh samples, which were collected by Westmeath County Council.)

The samples were collected in plastic screw-top bottles (various sizes of bottles were used) and all the samples were taken between March 1998 and December 2001. The number of times each lake was sampled during the study period is listed in Table 3.1. Most of the lakes were sampled monthly, with a few exceptions:

- Lough Sheelin was sampled more frequently at random intervals as the opportunity arose.
- Loughs Lene and Derravaragh were only sampled in the summer months (April-September).
- Lough Melvin was only sampled during summer months (May-September) from 1998 to 2000
- Allua was sampled most months from 1999 to 2002, but there were some months when no sample was taken.

Samples were transported by train or bus to Dublin within one-to-two days of collection, and collected by courier on arrangement. Upon arrival in the Central Fisheries Board laboratory in Dublin, the samples were analysed for nutrients, chlorophyll and other chemical parameters before transfer to the ICP-MS laboratory for trace element analysis as outlined in Chapter 2.

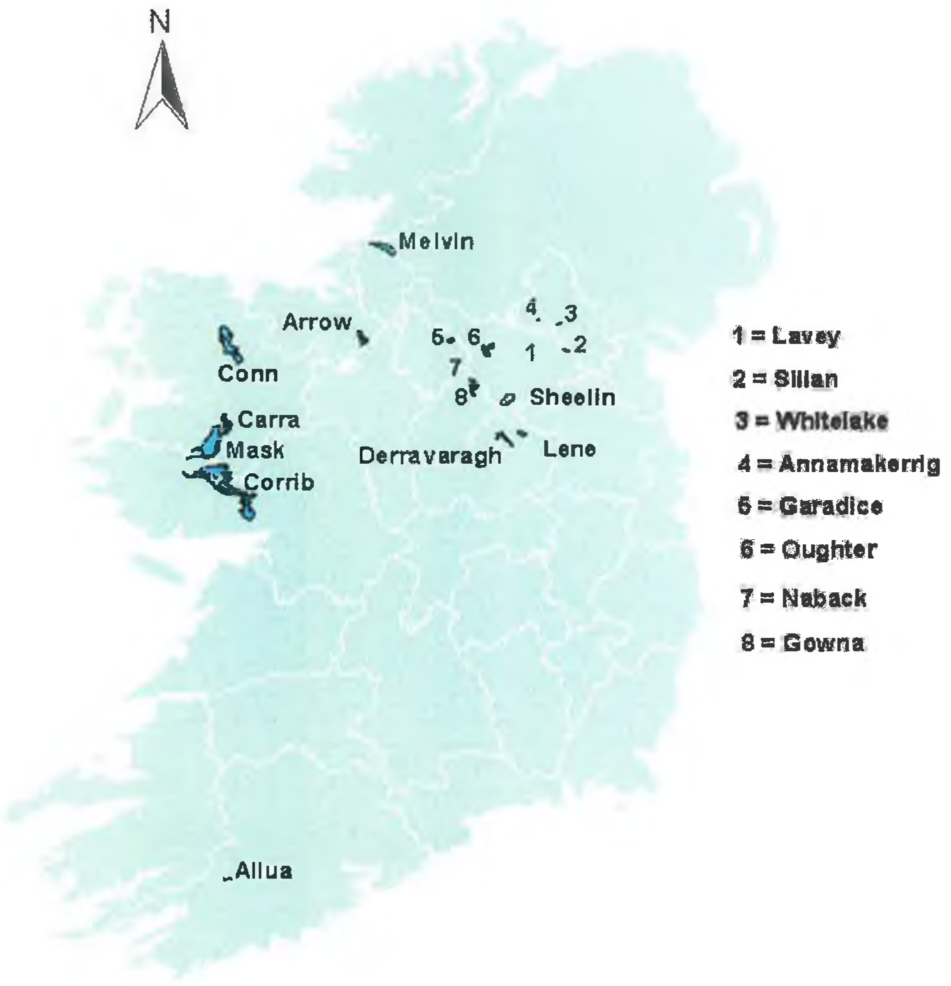

Figure 3.1: Locations of lakes studied [*]

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[*] *Map created by author using Geographical Information System software at Central Fisheries Board*

Table 3.1: Size, geology and samples taken from lakes studied [26 38 109]

Lake Name	County	Area of lake (hectares)	No. sample sites on lake	General geological characteristics of district	No. sampling occasions: Mar '98 – Dec '01 [⊕]
Allua	Cork	130	9	Old Red Sandstone	33-39
Annamakerrig	Monaghan	35	1	Ordovician	47
Arrow	Sligo	1,250	1	Carboniferous limestone	43
Carra	Mayo	1,500	2	Carboniferous limestone, shales, sandstones	43-44
Conn	Mayo	5,000	4	Carboniferous limestone	47
Corrib	Galway, Mayo	17,000	3	Carboniferous limestone, granite, schists, gneiss	41-45
Derravaragh	Westmeath	1,100	2	Carboniferous limestone	22
Garadice	Leitrim	360	1	Carboniferous limestone	46
Gowna	Longford, Cavan	1,100	2	Ordovician, Silurian	47
Lavey	Cavan	13	1	Silurian Quartzite	47
Lene	Westmeath	430	3	Carboniferous limestone	22
Mask	Mayo, Galway	8,294	1	Carboniferous limestone, Silurian, Ordovician, shales, sandstones	43
Melvin	Leitrim, NI	2,125	8	Carboniferous limestone	10
Na Back	Longford	12	1	Ordovician	48
Oughter	Cavan	1,300	2	Carboniferous limestone, Silurian, Ordovician	47
Sheelin	Cavan, Westmeath, Meath	1,900	1	Carboniferous limestone, shales, sandstones, Silurian, Ordovician	71
Sillan	Cavan	140	1	Ordovician	47
Whitelake	Monaghan	54	1	Silurian Quartzite	47

[⊕] A range of values here signifies a difference in the number of sampling occasions for different sites on the lake.

Table 3.2: Mean element concentrations for each lake sample site*

Lake	Ca	K	Mg	Na	Ba	Sr	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Allua 1	6.16	0.74	1.35	6.95	2.82	13.86	48.21	0.45	0.39	0.91	0.88	56.35	20.52	0.89	0.25	3.23
Allua 2	5.81	0.79	1.28	6.89	2.56	12.99	50.95	0.60	0.36	3.59	1.43	62.94	15.27	2.09	0.20	49.92
Allua 3	5.66	0.76	1.27	6.90	2.69	12.93	47.88	0.39	0.32	0.99	1.12	49.02	21.18	0.44	0.18	8.01
Allua 4	5.83	0.76	1.24	6.90	3.18	15.90	48.79	0.33	0.34	4.76	2.38	62.55	30.16	2.49	0.53	12.49
Allua 5	5.69	0.75	1.23	6.91	3.76	16.62	46.61	0.42	0.37	4.41	2.41	56.52	15.14	2.81	0.98	6.06
Allua 6	5.68	0.77	1.22	6.94	2.67	13.94	47.87	0.36	0.48	2.92	1.37	53.53	19.08	1.97	0.34	7.05
Allua 7	5.65	0.77	1.22	6.93	3.25	14.13	46.46	0.45	0.36	3.20	1.78	57.12	29.89	2.22	0.64	14.93
Allua 8	9.47	0.84	1.41	7.81	3.98	19.77	36.01	0.25	0.49	1.52	1.32	80.40	22.94	1.67	0.18	20.92
Allua 9	5.78	0.76	1.24	7.03	2.53	13.52	41.13	0.38	0.52	1.21	1.45	41.39	11.92	0.93	0.17	6.67
Arrow	53.85	1.37	3.70	9.04	24.30	112.02	6.91	0.57	0.51	3.14	1.25	135.40	5.09	2.76	0.23	4.15
Carra CC	67.52	2.62	4.39	12.84	24.09	185.94	5.41	0.60	0.40	3.25	2.58	202.04	1.26	3.35	0.65	5.05
Carra Tl	77.91	2.81	4.93	12.96	24.50	236.43	8.09	0.53	0.30	3.18	2.64	209.80	1.72	3.34	0.82	7.46
Conn N	43.56	1.58	4.33	12.57	30.10	207.61	16.36	0.57	0.47	2.73	1.28	149.72	4.59	2.88	0.32	8.17
Conn S	43.26	1.60	4.40	12.73	29.82	197.60	10.81	0.53	0.29	2.32	1.16	134.00	2.56	2.49	0.27	5.77
Conn Cbay	45.00	1.63	4.64	12.84	30.94	235.32	22.37	0.43	0.36	2.70	1.46	140.65	7.78	3.18	0.19	5.12
Conn Tbay	44.89	1.61	4.41	12.73	32.03	217.70	33.61	0.41	0.45	3.16	1.37	200.51	29.48	3.15	0.32	5.46
Corrib Lwr	51.46	1.71	3.48	10.63	27.43	145.23	8.27	0.54	0.34	2.90	1.06	124.21	2.99	2.72	0.26	5.41
Corrib Upr	46.01	1.56	3.08	10.19	33.37	114.01	7.98	0.37	0.36	1.95	0.98	103.51	2.95	2.25	0.18	4.97
Corrib Dp	47.20	1.62	3.16	10.34	33.89	117.67	7.31	0.51	0.32	2.30	1.64	114.24	3.79	2.63	0.41	5.00
Derra D	75.50	2.51	8.93	8.35	43.40	293.90	6.85	0.43	0.47	4.81	1.13	141.40	4.79	6.54	0.10	7.66
Derra F	79.54	2.53	8.84	8.45	43.47	310.36	7.27	0.49	0.43	4.45	1.19	161.22	4.05	6.53	0.17	4.43
Lene1	44.10	1.06	4.07	6.32	11.11	231.21	7.68	0.58	0.45	3.14	0.53	94.92	10.35	4.27	0.15	3.11
Lene2	42.87	1.09	4.08	6.47	11.05	228.16	6.88	0.72	0.39	3.18	0.44	108.80	8.14	3.82	0.16	3.10
Lene3	42.58	1.10	4.12	6.45	12.11	227.94	6.16	0.33	0.59	3.22	0.57	104.90	7.74	3.41	0.20	2.92
Mask	52.07	1.88	3.31	10.77	38.73	137.51	12.01	0.51	0.35	2.51	2.80	141.64	4.27	2.78	1.21	8.20
Melvin 1	24.70	1.19	3.22	9.91	23.39	154.31	13.02	0.41	0.35	0.76	3.27	65.98	1.08	1.04	0.16	4.00
Melvin 2	23.66	1.15	3.11	9.72	23.34	153.40	15.86	0.27	0.37	1.05	3.62	57.07	0.70	1.26	0.24	23.82
Melvin 3	24.08	1.15	3.13	9.68	23.37	152.25	11.38	0.40	0.25	1.68	2.11	86.79	1.11	1.14	0.13	3.48
Melvin 4	24.05	1.16	3.11	9.74	23.62	153.03	12.58	0.13	0.35	2.16	2.75	55.21	0.81	0.89	0.15	2.22
Melvin 5	23.66	1.15	3.07	9.63	24.44	153.31	12.14	0.44	0.27	1.27	2.52	79.46	0.85	1.49	0.15	2.57
Melvin 6	23.93	1.18	3.12	9.68	24.76	153.65	12.82	0.44	0.38	2.15	4.29	61.74	1.31	1.44	0.25	5.43
Melvin 7	23.98	1.26	3.10	9.68	24.43	154.63	14.31	0.94	0.40	2.43	4.00	65.60	0.70	2.13	0.21	4.05
Melvin 8	23.84	1.17	3.10	9.72	24.61	152.80	12.26	0.80	0.39	2.21	3.37	75.19	0.80	1.45	0.27	4.49
Sheelin	68.09	3.58	10.85	8.65	52.48	172.34	8.03	0.46	0.39	2.60	1.48	143.02	10.96	3.25	0.34	4.27
Gowna Nth	15.66	3.19	3.30	7.60	13.51	49.79	9.02	0.95	0.33	1.26	2.08	55.22	15.19	4.27	0.65	3.45
Gowna Sth	27.94	2.99	4.64	7.81	23.57	108.10	11.02	0.57	0.36	1.70	2.02	98.02	9.86	4.40	0.68	3.47
Garadice	27.76	1.59	3.17	7.11	15.42	120.88	34.39	0.50	0.36	1.73	2.93	257.59	7.70	4.06	0.88	5.16
Oughter Eon	32.47	3.76	4.71	10.08	32.89	125.79	18.25	0.47	0.48	1.78	2.23	123.67	12.60	3.48	0.69	2.50
Oughter Cha	33.00	3.84	4.77	10.28	33.79	126.80	20.73	0.60	0.51	2.07	2.50	146.59	16.40	3.54	0.63	3.06
Whitelake	30.26	5.32	4.35	9.66	21.71	87.66	17.80	0.57	0.61	2.27	2.92	151.57	15.42	5.38	1.12	5.25
Sillan	21.43	4.16	3.84	8.31	23.15	68.58	9.90	0.68	0.60	1.70	2.09	55.74	22.90	2.86	1.36	3.58
Annamakerrig	38.81	5.71	4.17	8.99	25.10	94.23	7.10	0.60	0.55	2.37	1.00	98.26	7.39	2.47	1.13	3.35
Lavey	35.80	3.43	6.27	8.50	34.22	100.66	8.89	0.62	0.59	2.26	1.65	107.54	9.24	2.95	0.64	3.26
Naback	15.74	2.30	3.81	6.60	15.21	45.42	20.36	0.64	0.59	2.40	2.55	98.96	7.35	2.27	0.84	4.91

Details of sampling locations can be found in Appendix B, Table B.1
Standard deviations can be found in Appendix B, Table B.3

3.4 **Results and Discussion**

3.4.1. Initial observations of results

The most immediate observation from visual inspection of the results was the wide range in GI/GII concentrations between the lakes (in particular calcium, magnesium, sodium and potassium). Iron, manganese, strontium, aluminium and barium also showed quite a large variation in concentrations. The concentrations of heavy metals (such as lead, cadmium, copper, etc...) were extremely low in all the lakes studied. Table 3.2 shows the overall mean values for each element in each of the lakes studied. More detailed statistics (max, min, etc...) can be found in Appendix B.

Fluctuation in element concentration was noticed for some major elements during the period of a year, and for other elements there seemed to be little variation. Also, within individual lakes there was variation noted in the element concentrations measured at different sample sites. These observations will now be discussed in greater detail.

3.4.2. Spatial variation between lakes

Even before a detailed examination of the results, it is clear that local geology has a significant influence on the chemical composition of lake water. A more thorough study of GI/GII concentrations confirms the significant spatial variation between different lakes. In order to estimate the extent of this variation, mean concentrations were calculated for each element for each lake over the duration of the study. From these mean values, some conclusions can be drawn which relate the lake to the geology of its catchment as listed in Table 3.1. A general discussion of the results can be found in Appendix B.

3.4.2.1 Calcium & Magnesium

The mean calcium concentrations measured in this study ranged from 5.65-79.54 mg/l. The mean values for magnesium ranged from 1.22-10.85 mg/l. Literature values for water hardness (directly related to calcium and magnesium concentrations) in Irish lakes show a similar large variation, i.e. in the 1975 report by An Foras Forbartha[26], a total hardness range of 15-250 mg/l is reported. This translates approximately to calcium concentrations of between 6-100 mg/l[♥], a similar range to that found in the 18 lakes under discussion in the present study. As might be expected, lakes located in rich limestone catchments have the highest values – e.g. Derravaragh, Sheelin, Carra and Mask. Those lakes on the hardest rocks (granite, gneiss, schist, sandstone) have the lowest values (e.g. Allua). Lakes on Ordovician and Silurian strata have an intermediate range of values.

3.4.2.2 Sodium

It has been previously established that the sodium content of Irish lake water is very much influenced by precipitation, which contains sodium, derived of sea spray.[106, 110, 111] The lakes along the west coast are known to have higher concentrations, due to the Atlantic influence and prevailing winds. Analysis results during the present study confirmed this, with Lough's Conn and Carra having the highest concentrations of sodium (approximately 12mg/l), closely followed by Mask and Corrib (~10mg/l). The inland lakes had the lowest concentrations of sodium with values ranging from 6.89-10.28mg/l.

[♥] [Calcium] = ([Hardness]/100)*40, magnesium contribution is disregarded for simplicity.

3.4.2.3 Potassium

Results by An Foras Forbartha in 1975 suggested that lakes lying on Ordovician or Silurian strata have higher than average concentrations of potassium, with the average range reported as 0.5-2.5 mg/l.[26] Three lakes – Egish, Muckno and Ramor – were identified as having levels greater than this at 4.5mg/l, 3.2mg/l and 3.6mg/l respectively. This theory was supported during the present study where the lakes of the Cavan/Monaghan area, which has an Ordovician/Silurian bedrock, contained the highest concentrations of potassium, e.g. Annamakerring, Whitelake, and Sillan all had potassium concentrations greater than 4mg/l. Other midland lakes such as Sheelin, Gowna, Oughter and Lavey had quite high levels also (>3mg/l), but the other lakes in the west and south, and including some midland lakes on limestone bedrock had values less than 3mg/l.

3.4.2.4 Barium & Strontium

Although present in much lower concentrations, both of these alkaline earth metals loosely follow the trends seen with their closely related Periodic Table Group II species – calcium and magnesium – i.e. higher concentrations are found in harder waters. Barium values from analysis of the lakes in this study ranged from 2.53 – 52.48 µg/l, with the limestone lakes (Derravaragh, Sheelin) having the highest concentrations, and the soft water lakes having lower concentrations (Allua, Gowna, Garadice). Interestingly, Lough Lene has quite a low concentration of barium (11.05-12.11µg/l), despite the fact that it has a relatively high concentration of both calcium and magnesium compared to the other lakes. This is an example of how – whilst general trends can be observed – individual lakes possess their own unique chemistry related to local geology, catchment characteristics and possibly hundreds of other influencing factors.

Strontium is present in the lakes at higher concentrations than barium, but the same general trends found in the other Group II elements are also true for this element and it seems to be particularly closely related to calcium. Strontium ranges from 310.36µg/l in the hardest water lake (Derravaragh) to 12.93µg/l in the softest water (L.Allua). Loughs Conn, Carra, Sheelin and Lene also have high concentrations of strontium.

3.4.2.5 Aluminium

The aluminium concentration in the lakes studied ranged from 5.41-50.95µg/l – a range that is well below the maximum recommended in drinking water regulations (Appendix A). Because most of these lakes are well buffered with high GI/GII concentrations and neutral pH, these levels should not pose any danger to fisheries or aquatic life. However, it must be noted that the highest concentrations of aluminium occur in the softest water, from areas of hard rock and therefore possibly prone to acidic "episodes", which may subsequently cause a lowering of the lake pH from time to time. The highest aluminium was found in Lough Allua (36.01-50.95µg/l), and the lowest aluminium concentrations were found in the harder water lakes such as Carra, Lene, Derravaragh, Arrow, Corrib, Sheelin and some of the smaller midland lakes (all <10µg/l).

3.4.2.6 Iron

Iron proved to be quite a difficult element to measure with accuracy using ICP-MS, especially in the harder water lakes, due to interference from calcium in the analytical method. Ideally, another method of analysis should be used for this element, but unfortunately this was not possible during the course of the project.

However, the results obtained were generally in the same range (non-detectable up to a maximum of 1.0mg/l) as reported by An Foras Forbartha in 1975.[26] The greatest deviation from the mean was found in the harder water lakes – again, a possible consequence of the difficulties associated with the analytical method. Unsurprisingly, Lough Garadice had the highest mean iron concentration of all the lakes (257.59µg/l). This is presumably due to the proximity of the "Iron Mountains" – an upland area rich in iron deposits, from which the Yellow River and Aghascashlawn River tributaries flow into the lake (see also Chapter 5).

3.4.2.7 Heavy Metals

Eight heavy metals completed the suite of sixteen elements used for this study – i.e. cadmium, cobalt, chromium, copper, manganese, nickel, lead and zinc. The mean concentrations of all these elements in the lakes were very low, and all well below the maximum admissible concentrations stated in the Irish and EU Drinking water regulations. (Appendix A)

Cadmium and cobalt had the lowest concentrations with mean values ranging from 0.13-0.95µg/l and 0.25-0.61µg/l respectively. There was no indication of a trend in the cadmium concentrations in hard or soft water lakes. However, the highest cobalt concentrations were found in the small midland lakes of Ordovician and Silurian geology. These lakes also displayed the highest mean concentrations of lead – with the overall lead concentration for all the lakes ranging from 0.10-1.36µg/l.

The highest levels of zinc were found in Lough Allua, the softest water lake, which also had some of the highest levels of manganese. Manganese was also found in high concentrations in one of the Lough Conn sites – Tolans Bay (see also Section 3.4.3.2) and in some of the smaller midland lakes. The effect of shallow water in bays and small lakes, local influence of tributary rivers, mixing of sediment and reduction of oxygen content could contribute to higher manganese concentrations.

Nickel and chromium were found in slightly higher levels in the harder waters. Nickel levels were also relatively high in some of the smaller midland lakes, and chromium was found in some of the Lough Allua sites at higher concentrations than the rest of the lake (a possible explanation being the proximity of metal fish cages adjacent to these sampling points). Finally, copper was found in the highest concentrations in Lough Melvin and the smaller midland lakes from harder geological areas.

3.4.3. Spatial variation within individual lakes

Irish lakes are generally well mixed bodies of water. Nevertheless, their size, geographical location, shape and the composition of tributary rivers and streams can result in much local variation in the chemistry of an individual lake. Several of the lakes under study during this work were sampled regularly at more than one location, e.g. Conn, Carra, Corrib, Gowna, Oughter, Allua, etc... Examination of the different concentrations of elements at different sites in these lakes allows a better understanding of the nature of lake water chemistry. It must be remembered that the composition of lake water is extremely dynamic and can also vary temporally as well as spatially (temporal variation will be discussed in Section 3.4.4). This makes it difficult to define ‘typical’ compositions for particular sites. However, it is useful to broadly discuss the spatial variations observed during this work, as a first step towards a possible detailed study on the cyclical trends in trace elements within individual lakes.

3.4.3.1 Corrib

The upper basin of Lough Corrib is fed by a variety of hard-water streams to the east and soft-water streams to the west, coming from catchments of very different geologies. This will be discussed in greater detail in Chapter 4. However, as would be expected, the chemistry of the main lake water in the upper basin is a mixture of the extremes in hard and soft water chemistry, and has intermediate values for most elements.

The lower basin of Lough Corrib is mostly fed by the River Clare and River Cregg – both of which are large alkaline rivers flowing from a limestone catchment. This lower basin is relatively shallow, and thus the lake water chemistry would be expected to reflect the chemistry of the main tributary rivers. However, because the outflow from the entire lake is to the extreme south (Corrib River), the lower basin also receives flow from the upper basin, which reduces the overall hardness of the water. Nevertheless, the chemistry of the lower basin water was found to be slightly harder than that of the upper basin water (particularly noticeable were higher values for calcium, magnesium and strontium).

3.4.3.2 Conn

Four different locations were sampled from Lough Conn during the course of this study. Midlake samples were taken from each of the basins - north and south and the other two samples were taken closer to shore at Cloghans Bay and Tolans Bay (Figure 3.2).

The two midlake samples had very comparable results for all elements, but a slightly greater concentration was detected in the northern basin for some elements, namely aluminium, iron, manganese and zinc (Figure 3.3). This may be explained by re-suspension of sediments in the exposed and relatively shallow upper basin, a phenomenon also noted by the EPA in 2001.[112]

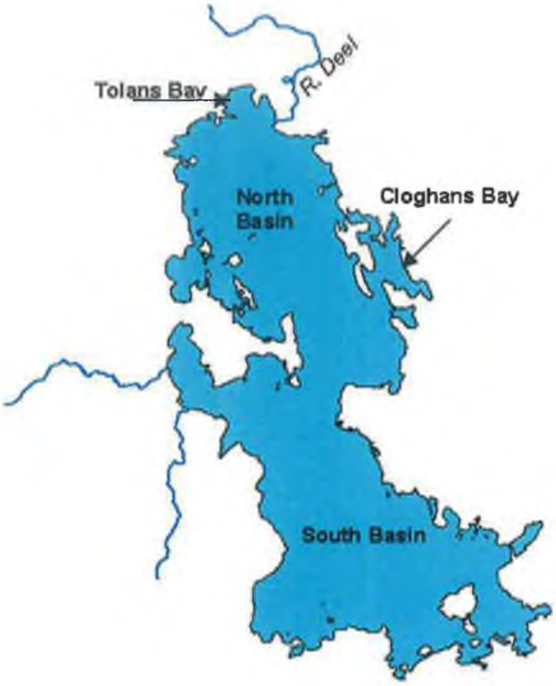

Figure 3.2: Sampling locations on Lough Conn [*]

In general, the bay samples had higher concentrations of elements than the midlake samples, with the most notable increases seen for aluminium, iron and manganese. Tolans bay had particularly high concentrations of these elements and this may be explained by its proximity to the River Deel inflow and the possible influence of sediment originating from the river discharge. From the map (Figure 3.2) it can be seen how Cloghans bay is more sheltered and does not have a major inflowing river nearby.

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[*] *Map created by author using Geographical Information System software at Central Fisheries Board*

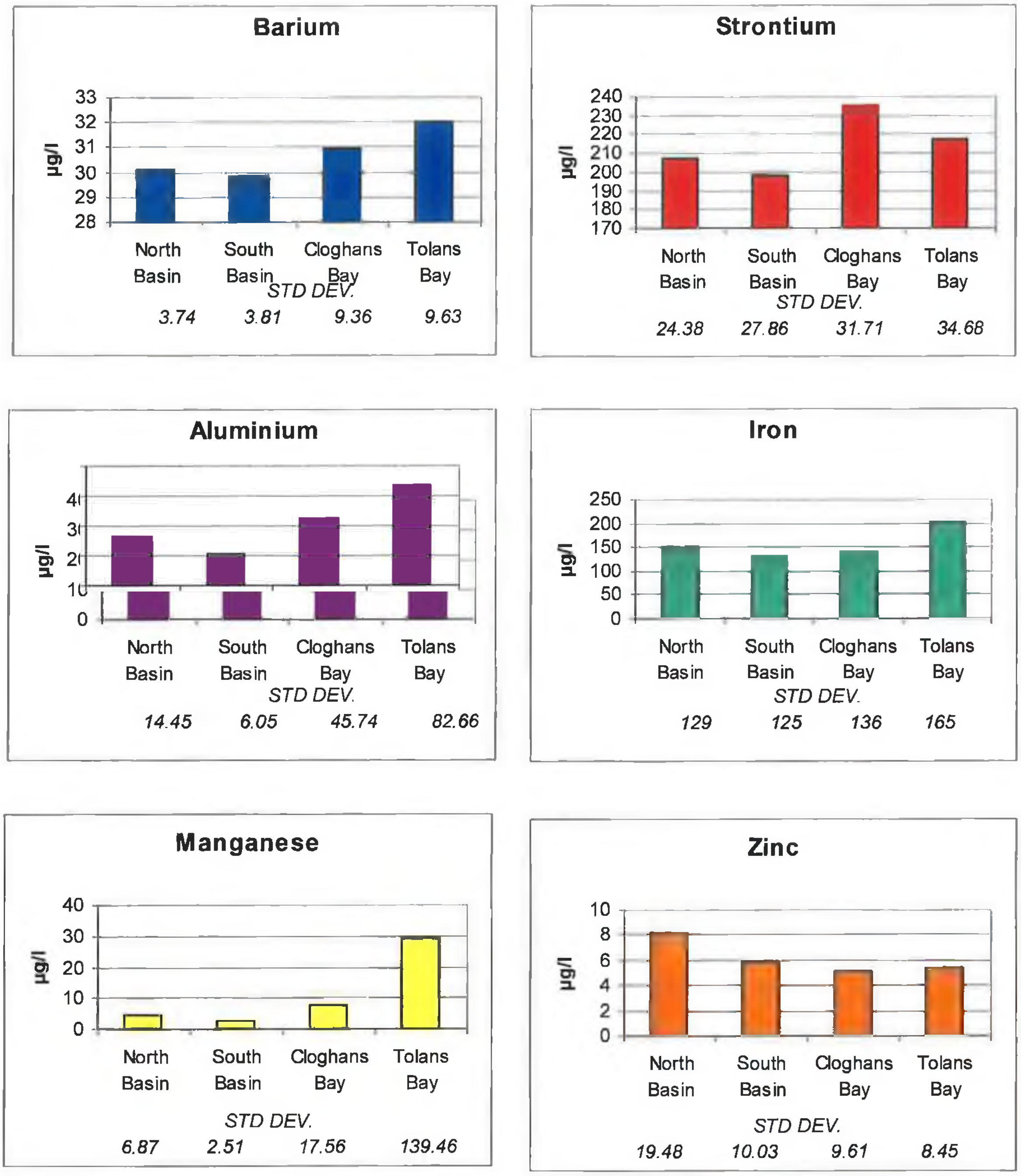

Figure 3.3: Mean elemental concentrations at four locations on Lough Conn

Information taken from Table 3.2 and Appendix B, Table B.3

3.4.3.3 Carra

Several small streams feed this shallow (mean depth 1.75m[39]) hard water lake, and the outflow is to Lough Mask (Figure 3.4). It was sampled in two locations – close to Castlecarra at the northern end of the lake and beside the Twin Islands in the southern basin. The sample at Twin Islands was found to be slightly harder than that at Castlecarra (i.e. Group II elements had higher concentrations), but there was little difference in the concentrations of the Group 1 elements and heavy metals.

Figure 3.4: Southern basin of Lough Carra with Lough Mask in the background [*]

3.4.3.4 Gowna

Gowna has two main sections – divided into north and south by Dernaferst Bridge, and samples were taken at each side of this bridge. The water in the northern section is softer than that in the south, and indeed there was a considerable difference in the concentrations of elements in the two samples taken from this lake, even though their geographical locations were relatively close. The northern sample had a lower concentration of Group II elements (calcium, magnesium, barium and strontium) than the southern sample, e.g. strontium concentration in the northern sample was 49.79µg/l and in the southern sample was 108.10µg/l - a considerable difference for samples taken

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[*] *Source: Central Fisheries Board – reproduced with permission*

from the same water body and very close in location. Iron and aluminium showed a similar trend with higher levels in the southern sample. However, manganese had an opposite pattern, with a higher concentration in the northern sample. Group I elements (potassium, sodium) and many of the heavy metals had fairly similar concentrations at the two locations in this lake.

3.4.3.5 Oughter

Oughter is not a particularly large lake but it has a very complex and irregular shape due to the drumlin landscape of this part of County Cavan. Most of the surrounding catchment is limestone, but the lake water is only moderately hard because the main feeders (Erne and Annalee Rivers) flow over insoluble Ordovician and Silurian rock. Regular samples were taken at two different locations on the lake, and there was very little difference between the concentrations of elements at the two locations, despite the unusual topography of the lake.

3.4.3.6 Melvin & Lene

These two lakes have a fairly uniform physical shape, and so little variation in water chemistry would be expected at different sample points across the lake area. Although both lakes have quite different catchment geologies from each other, it was found that their chemical characteristics had a lot in common as there was little variation in the chemical composition of the water in different sites on both these lakes, as illustrated in Figure 3.5.

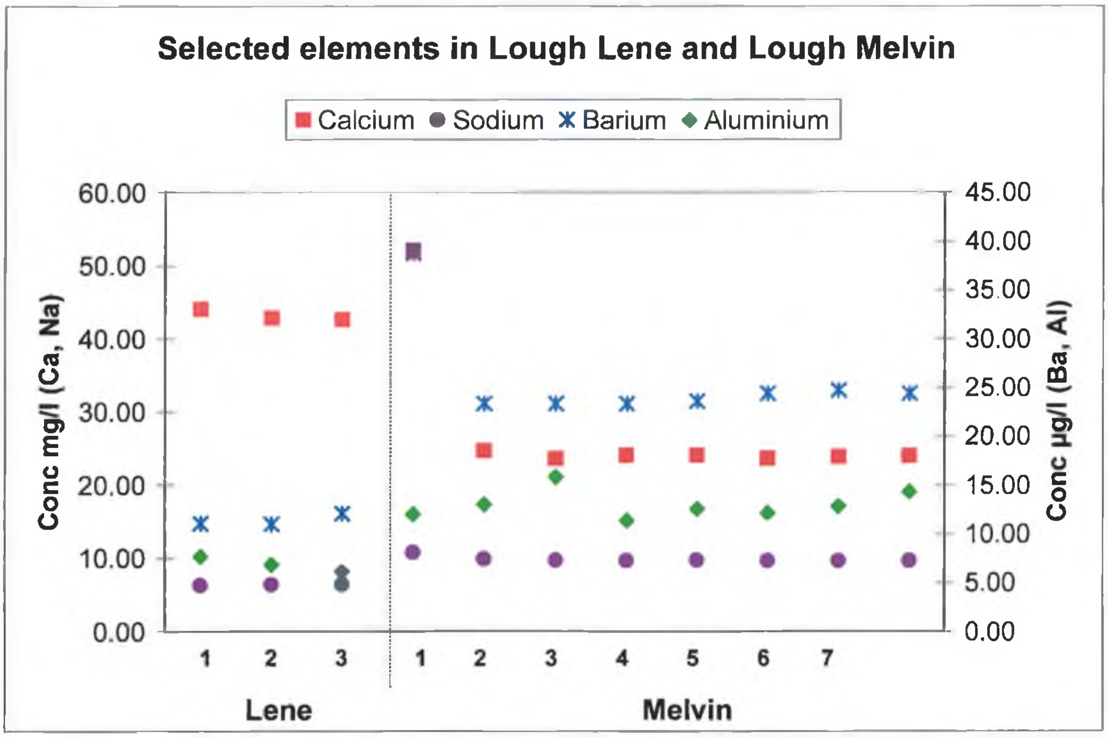

Figure 3.5: Mean values for Ca, Na, Ba and Al in Loughs Lene and Melvin

Data taken from Table 3.2
Standard Deviations (from Table B.3, Appendix B):
Lene: Ca: 9.16-13.55mg/l; Na: 0.89-0.91mg/l; Ba: 1.43-4.55µg/l; Al: 4.76-7.17µg/l
Melvin: Ca: 1.97-3.17mg/l; Na: 1.15-1.28mg/l; Ba: 2.09-3.29µg/l; Al: 4.52-6.97µg/l

3.4.3.7 Derravaragh

Lough Derravaragh is described as a typical limestone lake with water of high hardness[26], and indeed it contained the hardest water of the 18 lakes under discussion in this report. The lake has an unusual shape, with a wide basin from which the River Inny connects as the main inflowing and outflowing river, and a long, deeper section that receives drainage from some small streams. The main inflow is approximately 16km downstream on the River Inny from Lough Sheelin. The outflowing Inny eventually joins the River Shannon.

There were two sample sites on the lake, at Donore on the wide north western end of the lake and at Faughelstown about half way along the long narrow south eastern section. Interestingly, despite the rapid replacement of water in the wide, shallow northern basin compared to the longer retention time in the deeper, more isolated, southern part of the lake[28], little difference was found in element concentration between these two sites.

3.4.3.8 Allua

This was the softest lake of all those studied, with an average calcium concentration of just 6.19mg/l. The lake is situated on very hard sandstone rock, and thus the concentrations of all the alkali and alkaline elements (both Groups I and II) are very low for all nine sample locations on the lake. In contrast, the levels of metal elements (e.g. aluminium, iron, manganese, zinc, etc…) are considerably higher than is found in the hard water lakes, and there is fluctuation in the concentrations of these elements at different locations.

3.4.4. Temporal variation in lakes over the seasons

In order to assess the temporal variation in the lakes, a mean value was calculated for each element for each month. In other words, all the January samples from each lake were averaged, and so on for February, March, etc… This summary data can be found in Appendix B. To facilitate visualisation of any trends, line plots were created for different elements on each lake. Certain elements showed more variation across the year than others. It was difficult to ascertain the trends in the very low concentration elements (e.g. cadmium, lead, cobalt, etc…).

An investigation by King and Champ on Lough Carra in 2000 found that there was a cyclic pattern displayed by many water chemistry variables.[39] They reported a maximum alkalinity between January and March, and a minimum between July and August. This could be due to an uptake of minerals and essential elements by phytoplankton, similar to that reported by Markert *et al.*[107].

A very comparable pattern was observed during this study when the annual calcium concentration trends of the various lakes were examined (Figure 3.6). The harder water lakes displayed the clearest examples of a cyclic pattern, and even lakes such as Lene and Derravaragh, which were only sampled for six months of the year, show evidence of following the same pattern. Lough Sheelin is slightly unusual from the others because the "maximum" seems to be occurring much later than that of the other lakes (June instead of March/April).

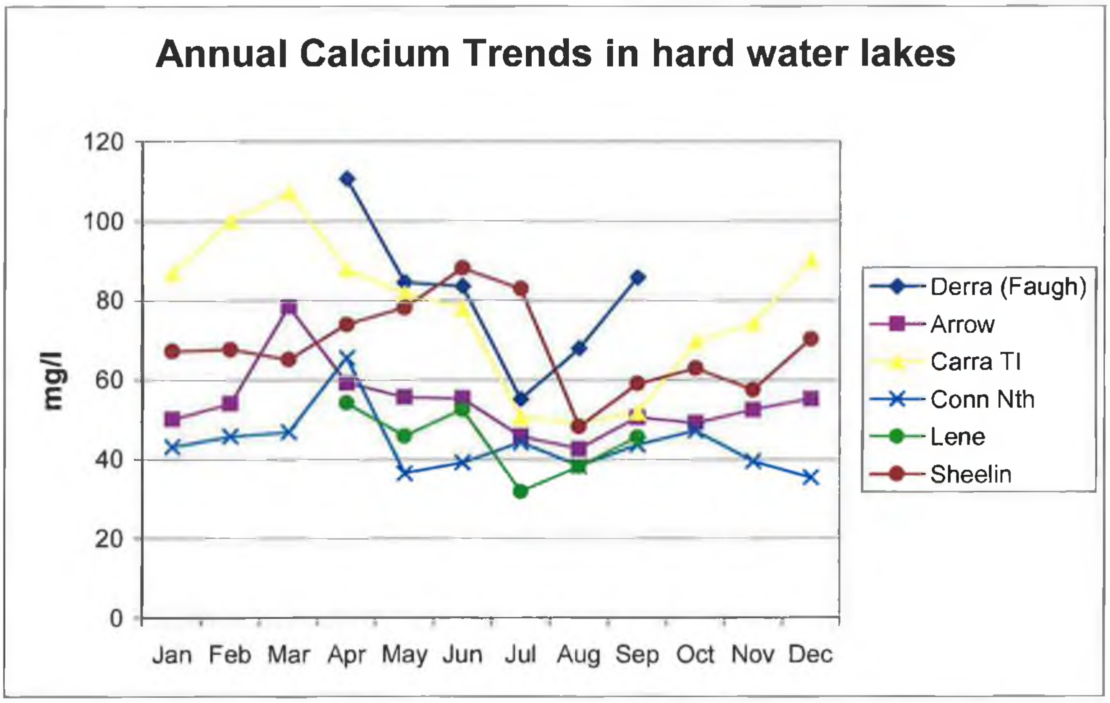

Figure 3.6: Annual calcium trends in hard water lakes

Data taken from Appendix B, Tables B.4 to B.47
Average std. dev of the mean monthly values ranged from 9.35mg/l (Conn) to 19.56mg/l (Carra)

The softest waters had a more random fluctuation in calcium during the year and it was difficult to identify a cyclic pattern similar to that found for harder waters. However, some of the soft waters seemed to have calcium "maxima" in both spring and autumn (e.g. Gowna, Naback, Lavey). In the case of magnesium, the softer waters displayed a much more distinctive pattern – with a steady rise in concentration until the autumn when the levels again decreased (Figure 3.7). The hard water lakes did not display a clear pattern for magnesium, but seemed to have a more constant concentration during the year. Again, Lough Sheelin was a notable exception, with a sharp increase in magnesium during the autumn, decreasing again by winter.

Concentrations of the other alkaline earth metals (strontium and barium) did not show any definite patterns, but had a more random fluctuation during the year. Similarly, the potassium concentration did not change significantly during the year for any of the lakes. The sodium concentration was found to be highest in the early spring for hard water lakes, and in the autumn for soft water lakes.

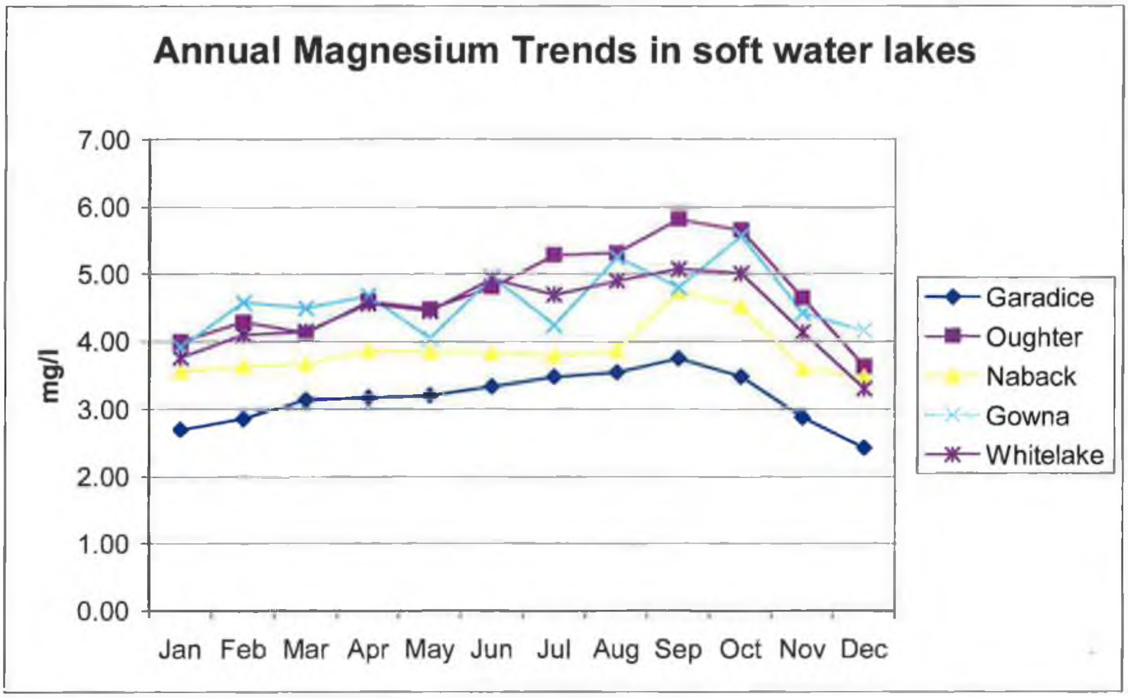

Figure 3.7: Annual magnesium trends in soft water lakes

Data taken from Appendix B, Tables B.4 to B.47
Average std. dev of the mean monthly values ranged from 0.58mg/l (Garadice) to 0.91mg/l (Whitelake)

A dramatic trend is noticeable for aluminium concentration in soft water lakes, with a sharp reduction in levels from early spring until late autumn (Figure 3.8). The reason for the decline in aluminium in summer is not known. A similar pattern in nitrogen, phosphorus and alkalinity was previously reported by King and Champ in Lough Carra, stating that subsidence of winter flooding and increased plant and animal growth were responsible for the decrease in concentrations in summer. These explanations may not apply to aluminium, however, and these soft water lakes are also not subject to acidification from forestry plantations (Section 1.5.2). A possible explanation might be a higher (more neutral) pH in summer, although this cannot be confirmed by the present study. Aluminium is known to be soluble below pH 6.0, and precipitated at higher pH values.[113] Interestingly, this aluminium trend is not seen as clearly in the hard water lakes, where levels are more constant throughout the year.

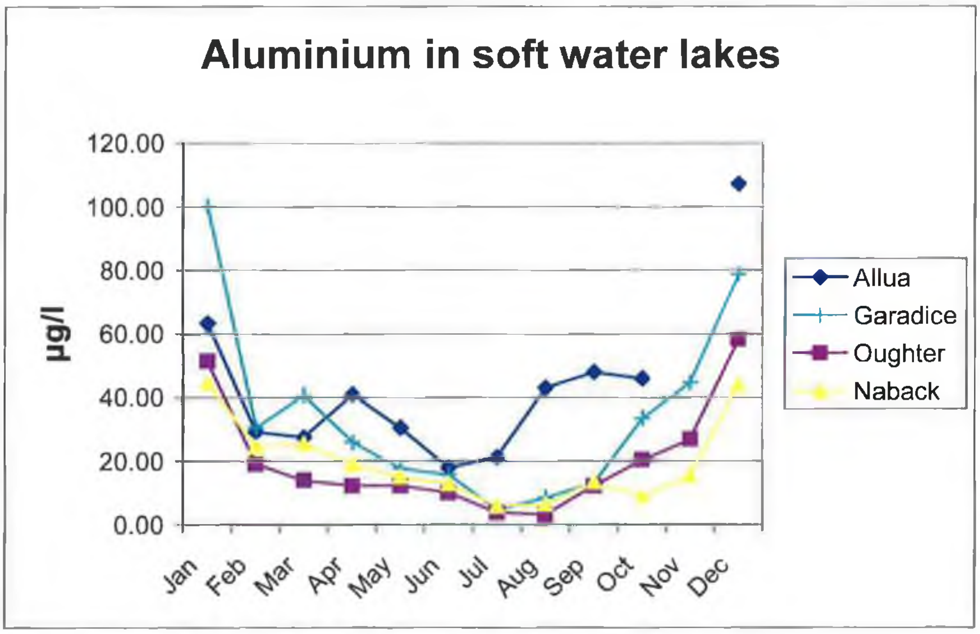

Figure 3.8: Annual aluminium trends in soft water lakes

Data taken from Appendix B, Tables B.4 to B.47
Average std. dev of the mean monthly values ranged from 6.32µg/l (Naback) to 16.12µg/l (Allua)

The trend in iron concentration is not as clear as aluminium, but there does seem to be an overall decrease in concentration during the summer months and a significant increase in levels in the late autumn/early winter. This iron trend is possibly explained by plant/animal uptake during the summer growth.

Manganese and nickel concentrations peak at different times of the year in different lakes. In harder waters there seems to be a nickel "peak" in late summer/early autumn, whereas in softer waters this peak doesn't occur until late autumn. Manganese shows a more complex pattern – in some harder waters there are two "maxima" – in spring and in autumn (Arrow, Carra). In other lakes, where the spring "maxima" is small or non-existent, there is a large "peak" towards early autumn (Conn, Corrib, Mask). Lough Sheelin again proved to be the exception, showing a large manganese peak in early summer, and a smaller peak in the autumn. The soft water lakes showed an increase in manganese from late autumn through the winter.

It was very difficult to identify trends in the other heavy metals due to their extremely low concentrations. Indeed, there seemed to be little more than random fluctuation in the results for these elements. A more in-depth study of the elements present at trace levels may reveal temporal variations, but with simple monthly averaging it was not possible to draw any further conclusions.

3.4.5. Statistical analysis and plots

3.4.5.1. Correlations

Table 3.2 (mean values for each lake) was used to carry out a simple correlation calculation in Microsoft® Excel for each element against all the others. The results are tabulated in Appendix B. Various degrees of positive and negative correlation were observed in the results. The strongest positive correlation factors were found between Periodic Table Group II elements, e.g. values of 0.80 and 0.82 respectively between Ca/Mg and Ca/Sr, and 0.82 between Ba/Mg. Ba/Ca (0.77), Ba/Sr (0.67), and Sr/Mg (0.70) were also strongly correlated.

After Group II elements, the strongest positive correlations were found between Ca/Fe (0.72), Mn/Al (0.71), K/Pb (0.64), Mg/Ni (0.66), Ba/Na (0.61) and Ca/Ni (0.60).

Negative correlations were strongest between Al and the Group II elements. For example, Ca/Al and Ba/Al each correlation factors of –0.71 and –0.70 respectively, Sr/Al had a correlation factor of –0.69 and Mg/Al a factor of –0.63. Interestingly, Mn - which was highly correlated with Al (above) - also showed a significant negative correlation with the Group II elements. There was no correlation of note observed between any of the heavy metals or transition elements.

3.4.5.2. Cross-validation

Cross-validation is a useful way to assess the discrimination between results obtained for different groups of data. It works by omitting each observation one at a time, calculating a classification function for each group using the remaining data, and then classifying the omitted observation based on this function. Only complete data sets can be used for this test (i.e. observations which contain a result for each element), so observations were omitted from the test where there was missing data.

Several cross-validation tests were carried out with the lakes data set, and a summary of the findings is given in Table 3.3, with further details of the test results outlined in Appendix B.

Table 3.3: Summary of Cross-Validation Results

Test Number	Reason for test	Number of observations	Proportion of observations correctly classified
1	Distinguish between overall lake mean values	35	97.1 %
2	Distinguish between lakes based on their max, median and min values.	132	64.4 %
3	Distinguish between a small group of closely related lakes	95	91.6 %
4	Distinguish between lakes based on Group I and II elements only	934	83.7 %
5	Distinguish between sites in the same water body	33	78.8 %

1. As a start, cross validation was carried out using the lake means, and omitting the lakes with only one sample location. This first test was carried out in order to assess the overall discrimination between the mean values of trace elements in the range of lakes studied. The results were extremely successful, showing 97.1% of lakes correctly classified. The only exception was one of the Lough Gowna sites that was classified as Lough Oughter (a lake close geographically, and from a catchment with a similar geology).
2. Cross validation was then carried out using the maximum, minimum and median values for each of the lakes. By adding these three observations for each lake it was possible to include each lake in the test (even those with only one sample location), and also to incorporate the range of values found within the results for each lake. This test was not as successful as the previous one, with only 64% of results classified correctly. The inclusion of max and min values in the test could have contributed to the misclassification by introducing a wider range of values for each element in the lakes. For example, Lough Arrow had a

calcium range of 30.08-103.93mg/l and Mask had a range of 34.42-86.96mg/l. An examination of Appendix B, Table B-3, reveals the wide range in concentrations found for each element over the course of the three years of study. Seven lakes were completely misclassified in this test – Annamakerrig, Arrow, Garadice, Mask, Na Back, Sillan and Whitelake. Only three lakes had a 100% correct classification – Lene, Derravaragh and Melvin. Interestingly, these three lakes were the only ones that were not sampled in winter – and thus the overall max/min range may have been smaller than other lakes, and therefore the classification more accurate.

3. The next test was carried out using all the observations from the eight small midland lakes in Monaghan/Cavan that contained results for every element (i.e. Gowna, Oughter, Garadice, Sillan, Whitelake, Annamakerrig, Lavey, Naback). It was found not to be possible to perform the cross-validation test for every lake and every observation in this study due to the large amount of data and the limitations of the software. These eight lakes were chosen because they are similar in catchment geology and are close geographically, and so provide a more rigorous examination of the cross-validation test. The results were very encouraging with 91.6% correct classification.
4. Cross validation was next carried out for 16 lakes using only Periodic Table Group I and Group II elements in the test. This was to determine if an even smaller number of elements could be used to discriminate between the lakes. A very large number of observations were used in this test – 934 observations in total from the 16 lakes. (Allua and Melvin were omitted in order to reduce the number of observations to a number

that was manageable by the software).

The results show a high success rate, with 83.7% correctly classified observations. Lough Lene and Derravaragh were the only two lakes where all observations were correctly classified, again raising the question if the lack of wintertime sampling has somehow increased the ability of these lakes to be distinguished from the others.

5. Finally, cross validation was carried out for eight sites in Lough Melvin using eleven elements. This test was carried out in order to determine the possibility of cross-validation as a means for distinguishing individual sites on the same lake. Eleven elements and a total of 33 observations were used in the test from eight different sites on the lake. The overall proportion of correctly classified observations was 78.8%. Four of the eight sites were correctly classified for all observations, and two more sites were correctly classified in for 80% of the cases. Of the remaining two sites one had 67% success (Site 5) and the other (Site 1) was incorrectly classified in every instance. In Section 3.4.3.6 it was noted that there was little variation in the chemical composition of Lough Melvin, so this could explain the misclassifications.

3.4.5.3. Multivariate analysis

Some simple multivariate analysis tests were carried out on the lake sample results using Minitab®. No pre-treatment was carried out on the data before it was entered into the Minitab® software. It must also be noted that many other variables not included in the dataset would also affect these plots, e.g. lake areas and residence times, weather conditions, temperature and physico-chemical parameters. However, it is still possible to ascertain some patterns and trends in the data using the data available.

3.4.5.3.1 Cluster variables

All the data collected for the lakes analysis was used to carry out a hierarchical cluster analysis of the variables (16 elements) using Minitab®. A dendogram was plotted in order to visualise the similarity between variables (Figure 3.9). The pattern that emerged from this cluster analysis was not surprising – high similarity was found between the Group II alkaline earth metals Ca, Sr, Mg and Ba. Cr and Zn also showed a high similarity. Following this, the Group I alkali metals (K, Na) were most closely related to the alkaline earth metals than to the other elements.

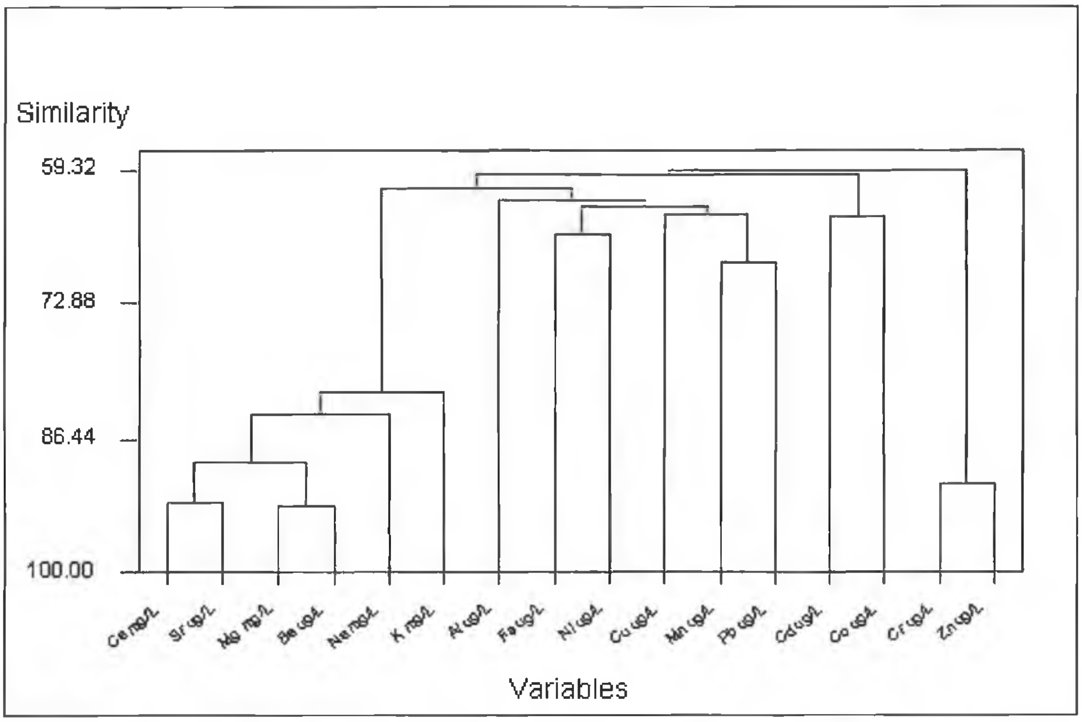

Figure 3.9: Clustering of the 16 element variables

3.4.5.3.2 Multivariate analysis of all lake data

In order to determine the level of multivariate grouping possible with the data, Principal Component Analysis was initially carried out on the full data set using Minitab®. The software automatically omitted any samples that did not have results for each of the 16-elements. The resulting plot is shown in Figure 3.10 and it represents only 187 of the total of 1,564 lake samples analysed during the course of this study. There are no obvious groupings in the plot, although the first component (x-axis) seems to be separating based on the general hardness of the water. The softest lake (Allua) is to the extreme left of the plot and the harder lakes (Derravaragh, Carra, Sheelin) are found to the right of the plot.

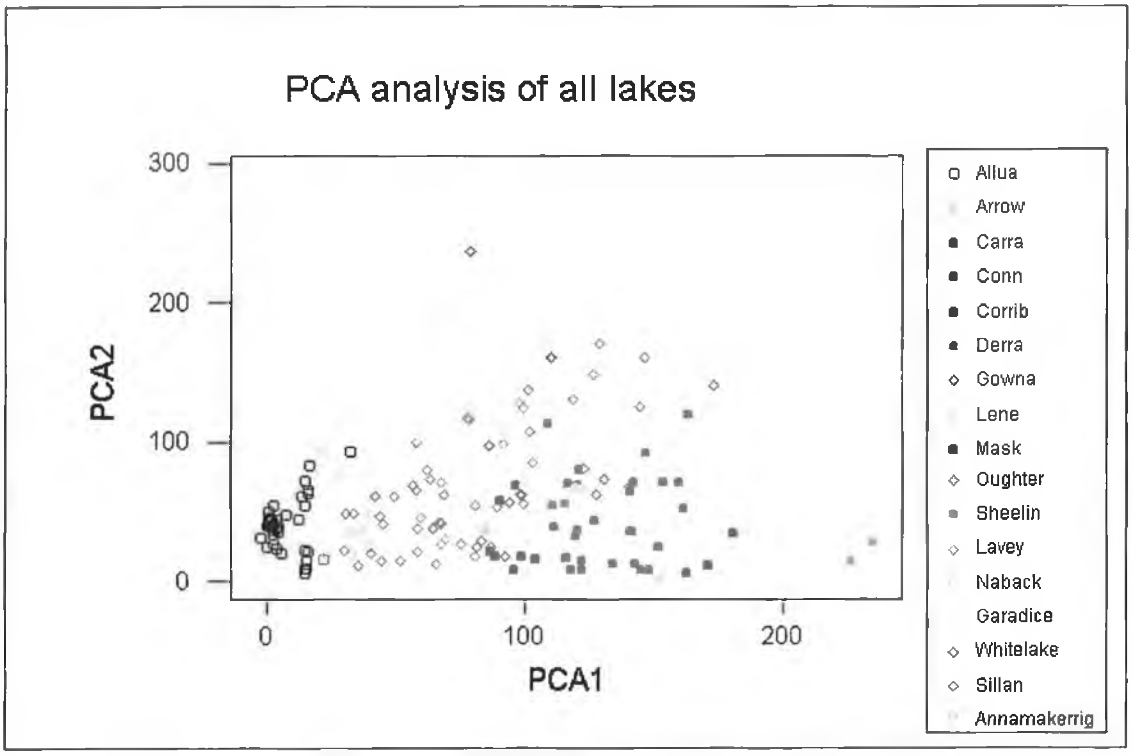

Figure 3.10: PCA Analysis of all lakes

3.4.5.3.3 Basic geological groupings

A Principal Component Analysis was carried out using only the mean values of the 16 elements at each sample location and the observations were grouped based on the geology of the lake catchment. The resultant plot (Figure 3.11) did not show any difference between first and second component separations. However, it can be seen at how samples from a bedrock of Old Red Sandstone (e.g. Lough Allua) had the most positive values in PC1 and PC2 (A) and the lakes from areas influenced by Ordovician and Silurian geologies had intermediate values (B). The lakes from a carboniferous limestone catchment (Derravaragh, Carra, Sheelin) have the most negative values in each component. Plots of subsequent components did not improve the separation. Addition of a greater number of variables may be necessary to do this.

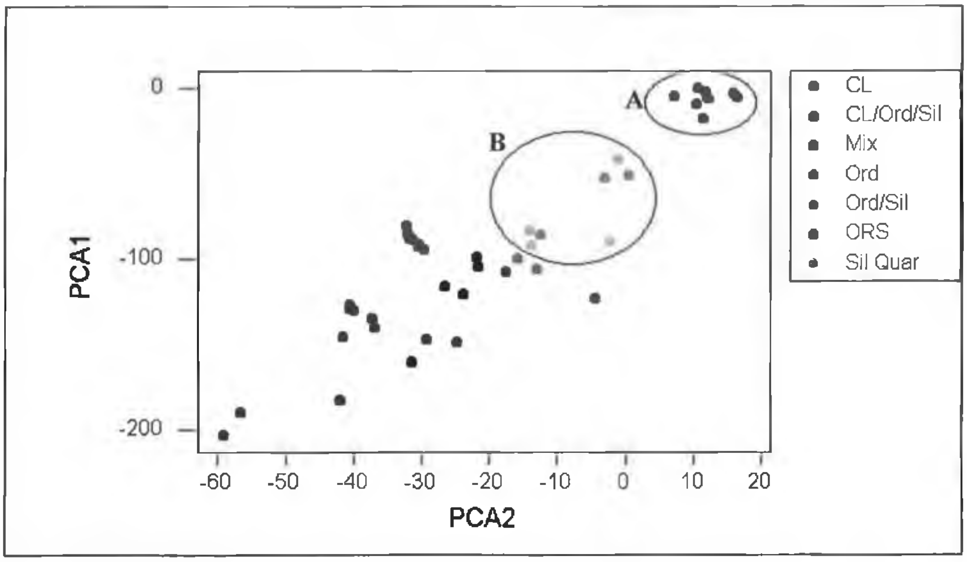

Figure 3.11: Groupings of Lake Catchment Geologies using PCA

CL= Carboniferous Limestone; CL/Ord/Sil = Carboniferous Limestone, Ordovician and Silurian; Mix = Mixed geologies; Ord = Ordovician; Ord/Sil = Ordovician and Silurian; ORS = Old Red Sandstone; Sil Quar = Silurian Quartzite

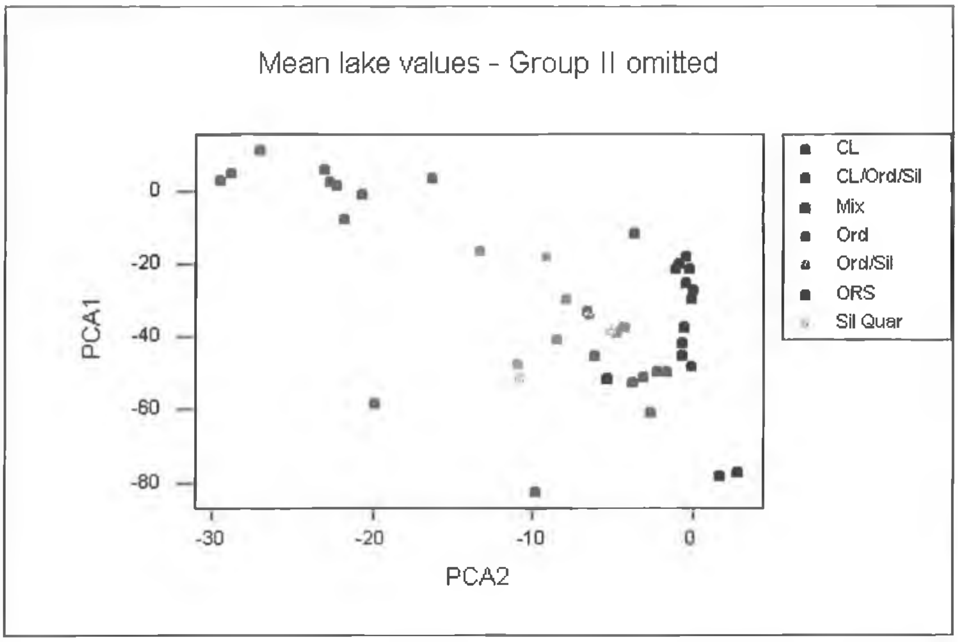

Figure 3.12: Lake Catchment Geologies PCA with Group II elements omitted

CL= Carboniferous Limestone; CL/Ord/Sil = Carboniferous Limestone, Ordovician and Silurian; Mix = Mixed geologies; Ord = Ordovician; Ord/Sil = Ordovician and Silurian; ORS = Old Red Sandstone; Sil Quar = Silurian Quartzite

When the Group II elements (Ca, Mg, Sr, Ba) were removed from the data set and another PCA carried out, there was less spread in the points, but there was still separation of the Old Red Sandstone sites (Figure 3.12).

3.5 Conclusions

As a result of the analysis described above, some useful general information was gathered which will assist in the future interpretation of Irish lake water chemistry. The first and possibly most obvious conclusion to be drawn is that the geology of a lake catchment plays an important role in the chemical composition of the lake water and with Irish lakes located in different geological catchments, this leads to a large variation in the chemical composition of their individual waters. Thus, the results of any further tests carried out can be predicted based on the overall hardness of the lake water and the type of bedrock on which the lake lies.

Calcium, magnesium and potassium (and to a lesser extent barium and strontium) were most related to geology. Geographical location (distance from the sea) was found to be the major influence on sodium concentrations. The concentrations of heavy metals are generally low in all the lakes studied. Variation in element concentrations within an individual lake is possible (for example due to the influence of a tributary river). For this reason it is important to sample at different locations in order to obtain a full knowledge of the water chemistry in the lake.

Many elements vary in concentration during the year – with discernment of trends easiest in the major elements. Hard waters displayed a cyclic pattern for many elements. For example, calcium decreased in the summer months, sodium displayed a maximum in spring and manganese seemed to have two maxima in spring and autumn for many hard water lakes. Some trends were also noticeable in soft waters, particularly for magnesium (increased in summer/autumn), sodium (increased in autumn) and aluminium and iron (both decreased in summer). Most of the heavy metals were present at concentrations too low to discern any temporal variations.

Positive correlation was very high between individual Periodic Table Group II elements, and these in turn were strongly negatively correlated with aluminium. Cross-validation showed how results could be used to classify an unknown sample with a high level of success. The most successful test was one that distinguished between lakes based on the overall mean values of each element.

Multivariate analysis illustrated some of the differences between hard and soft water lakes as the GI/GII elements were found to have the most influence on the groupings formed. However, further work would be needed in order to use multivariate models such as PCA for identification of unknowns.

The work reported in this study illustrates the dynamic nature of lake water chemistry in Ireland. There are many factors that influence the concentrations of trace elements, and so attempting to build up a 'normal' profile for any lake is a complex problem. A model that could take into account several of the varying factors would greatly improve the success of a predictive model.

CHAPTER 4

4. RIVER WATER ANALYSIS

THE LOUGH CORRIB CATCHMENT

4.1 Introduction

There are approximately 400 separate river drainage areas in Ireland, but most of these are small coastal catchments[41]. Nine river systems have a catchment area greater than 2,000km^2 and these nine systems drain approximately 50 per cent of the land area of the State (this does not include part of the Erne catchment in Northern Ireland).

Study of the trace element concentrations in rivers and streams presents a different set of challenges than study of lake water chemistry. Rivers are dynamic physical features and constantly change and shape the landscape. They are agents of erosion, continually wearing away the rock and soil in their beds and banks. Rivers collect and transport eroded material, and also any other substance that is deposited in their paths and is light enough to be carried by the current.

Rivers change in appearance throughout the year. In times of flood they can become very powerful, sweeping along much debris, silt and sediment with their elevated flows. In dry weather when the flow is very low, chemical parameters may become concentrated in the small amount of water remaining on the riverbed. Often in summer there can be an increased growth in plant and animal life around the river, which may strip the water of minerals and nutrients. River water is also very susceptible to contamination from pollutants in run-off from land or indeed from deliberate dumping into the river itself. A sudden pollution incident may cause a temporary but dramatic change in water chemistry.

For all these reasons, it is not surprising therefore, that the chemical composition of river water changes and fluctuates greatly, and as was also mentioned in Chapter 3 in regard to the lakes, this in itself presents a challenge for the correct interpretation of results obtained from analysis, especially if it is not done repeatedly over a period of time. This was illustrated well by Robson and Neal who described the variations in water quality for Eastern UK rivers[114] and also more specifically by Nea *et al.* who discussed the variations in major, minor and trace elements at three sites in the River Tweed basin[115].

4.2 Trace element concentrations in rivers

In 1973 Strumm and Bilinski investigated the difficulties in interpretation of trace metal concentrations in natural waters, stressing that information about their speciation is vital (e.g. complexes formed, stability, etc…).[116] This important fact is still relevant today, as a large percentage of metal ions in natural waters are associated with suspended and colloidal material. But interestingly, the same study by Strumm and Bilinski concluded that free trace metal ions might exist in waters as the predominant species, even when complex forming organic matter is present.

A river is a complex ecosystem composed of many different plants, animals and microscopic organisms. Trace elements are essential for all of these life forms and deficiency symptoms can occur when essential elements are present at unusually low concentrations. However, as pointed out by Strumm and Bilinski, some elements can also be toxic at certain concentrations, causing death or interference with the organism's metabolism.

The high concentration of GI/GII elements in hard waters usually provides a "buffering" capacity, which reduces the toxicity of many heavy metals. It was established by Brown in 1983 that calcium concentrations greater than 1mg/l increase the survival of brown trout in acid and aluminium rich waters.[117] Dissolved calcium in the water increases membrane stability of fish gills and reduces permeability to metal ions. However, very soft water rivers do not have this capability, and thus fluctuations in the concentrations of their trace elements are more significant.

Acid deposition and subsequent acidification of soil causes an increase in acid anions passing through the soil-solution[118] and so "acidic spates" can then occur in soft water rivers during times of increased rainfall and hence flow. These "spates" lead to a sudden decline in pH and an increase in aluminium and other metal concentrations.[119]. The extent of this increase in metal levels is critical to the survival of sensitive species and has been the subject of much investigation in recent years.
For example, in 1997 Myllynen *et al.* found mortality of lamprey roe and larvae in river water where acidification peaks resulted in low pH (below 5.0).[120] The river had high iron (1.5-3mg/l) and aluminium (0.45-0.6mg/l) concentrations, compared to the levels found in ground water at the same pH (0.002mg/l and 0.11mg/l respectively). In 1988 Weatherley *et al.* reported on the response of macroinvertebrates to experimental "acidic spates" and found that the chemical influences on benthic density during these spates was greater than the influence of increased water flow. In a laboratory simulation in 1995, Witters *et al.* demonstrated mortality and physiological disturbance in brown trout at the mixing zone of acidic, aluminium rich water with neutral, limed water.[121]

As mentioned in Chapter 1, the cause of "acidic spates" in soft water streams is often attributed to increased coniferous afforestation in upland areas with poor soils. In 1984

Stoner *et al*. concluded that chemical conditions in streams draining conifer plantations were more hostile to invertebrates than conditions in adjacent moorland streams. Work by Blackie and Newson in 1986 supported this and found that forested streams have more severe acidic spates than non-forested streams. Bowman and Bracken described the impact of acidification on fish in 1993.[55] They investigated trout survival in Irish acid-sensitive waters and found evidence of precipitation of aluminium on the gills of fish, resulting in a high rate of mortality. The river where fish mortalities occurred had a combination of low pH, high aluminium concentration and was from a forested catchment. Following this, a detailed four-part report was published in 1997 by COFORD describing the effects of water quality in forested catchments on fish and invertebrates.[45-48]

Bearing in mind the complexity of river water chemistry described above, this chapter attempts to explain the general trends and observations gathered from trace element analysis of rivers in the Lough Corrib catchment between 1998 and 2001. Detailed speciation of each individual element was beyond the scope of the present work, but it was hoped that this overall investigation would stimulate a greater understanding of the range in trace element concentrations in Irish rivers.

4.3 Lough Corrib and its catchment area

Lough Corrib is the second largest lake in Ireland, and the largest in the Republic of Ireland. It covers an area of 17,000 hectares[26] and it drains a catchment area of 3,151 square miles of the counties Galway and Mayo in Western Ireland.[122]

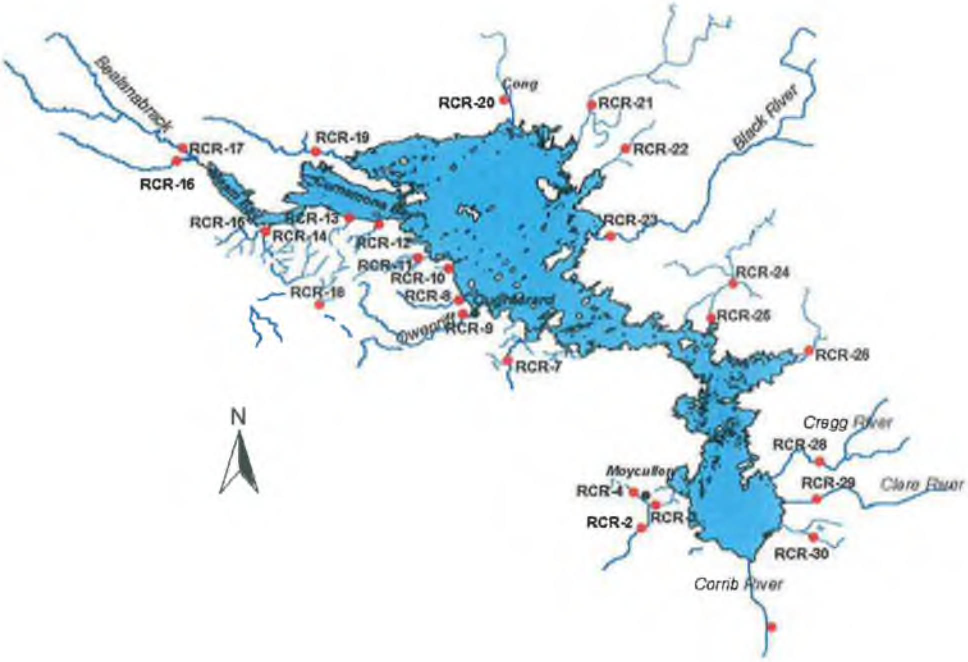

Figure 4.1: Map of Lough Corrib showing sampling locations *

The lake has two main sections. The southern (lower) basin is narrow and shallow with an average flush out time of just 10 days. The northern (upper) basin is much larger and extremely deep in places – depths up to 47m have been recorded in the northeastern corner. The flush out time in the upper basin is estimated at 173 days.[122] There is a narrow middle section joining the two basins (Figure 4.1).

The main inflowing rivers are the Clare, Cregg and Black (eastern shore), Owenriff and Bealanabrack (western shore) and Cong from Lough Mask (northern shore). The lake discharges via the Corrib River to the south, which flows through Galway city and enters Galway Bay. There are many other smaller inflowing rivers and streams around the lake, and there are also underground rivers and streams draining from Lough Mask, Nafooey and Carra to the north.

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* *Map created by author using Geographical Information System software at Central Fisheries Board*

Table 4.1: Lough Corrib Facts and Figures[122]

	Upper Basin	Lower Basin	TOTAL
Area (ha)	-	-	17,612
Length of Shoreline (km)	-	-	140
Maximum Length (km)	-	-	46
Maximum Width (km)	-	-	21
Basin Area (km^2)	129	54	-
Average Depth (m)	8.44	2.06	-
Maximum Depth (m)	47	9.3	-
Mean Daily Rainfall (mm)	4.00	3.12	-
Average Flush-out Time (days)	173	10	-
River Catchment Area (km^2)	769	1560	-

4.4 Geology in the Lough Corrib Catchment

The geological contrast within the Lough Corrib catchment provides a very unique and interesting study. Figure 4.2 illustrates the presence of six main rock categories within the area drained by the lake. These rocks span many geological ages from the most ancient igneous rock found in Ireland (granite) to more recent carboniferous limestone.

Examination of the geographical distribution of the various rock types shows the more ancient rocks to be located on the western side of the lake.[109] The majority of the high ground west of a straight line drawn from Moycullen to Oughterard is composed of either igneous granite or metamorphic schist and gneiss (rocks which may have been derived from the older igneous granite). There are also some other types of igneous rock found in small areas, all of which are intrusive igneous rock similar to granite but poor in silica. West of the long narrow Maam Bay near the Maamturk mountains there is a large area of metamorphic quartzite.

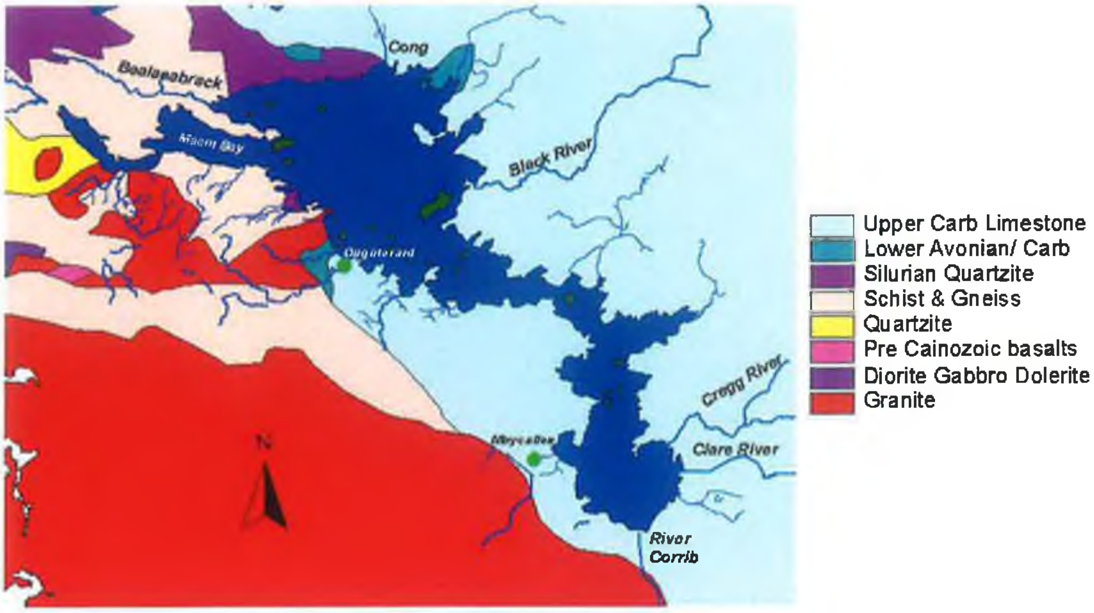

Figure 4.2: Geology map of Lough Corrib region [*]

To the north and east of the lake the bedrock is sedimentary in nature and thus more recently formed. Most of the northern shore of the lake is composed of rock formed during the Palaeozoic Era – a time when the ocean encroached upon the entire land area of what is now Ireland.[53] The rock found to the north of Lough Corrib was formed in the Silurian period – at the end of the Palaeozoic Era before the oceans retreated.

Many ages later a shallow clear-water sea returned to cover most of Ireland. Carboniferous limestone – the most important rock formation in Ireland, (occupying about half the area of the country) was formed during this period. The entire eastern shore of Lough Corrib, and also the land underlying and to the west of the lower basin and mid-lake section is composed of carboniferous limestone. Finally, there are small pockets of shales and sandstones found to the north and east of the lake at the boundaries between the carboniferous limestone and the older rocks.

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[*] *Map created by author using Geographical Information System software at Central Fisheries Board*

Table 4.2: Sample sites in the Lough Corrib catchment

River Code	River name and sampling location	Bedrock geology	Number of times analysed
RCR-1	River Corrib	Carboniferous Limestone Lake Outflow	81
RCR-2	Loughkip, Clydagh bridge	Granite	82
RCR-3	Outflow canal to Ballyquirke	Granite, Carboniferous Limestone	82
RCR-4	Inflow canal to Ballyquirke	Granite, Carboniferous Limestone	82
RCR-5	Inflow canal d/s sewage works	Granite, Carboniferous Limestone	81
RCR-7	Drimneen River, Laghtgannon bridge	Schist/Gneiss, Carboniferous Limestone	82
RCR-8	Owenriff River, Oughterard Bridge	Schist/Gneiss, Sandstone, Limestone	82
RCR-9	Derrylaura Stream, Glann Rd	Granite	82
RCR-10	Derrymoyle River	Granite	82
RCR-11	Owenkilla River, Currarevagh	Schist, Gneiss and Silurian	82
RCR-12	Owenaraha River, Lydons	Schist/Gneiss	80
RCR-13	Curraghaduff Stream	Schist/Gneiss	80
RCR-14	Owenree River, Letterkeeghaun	Schist/Gneiss	80
RCR-15	Folore River, trib of Letterkeeghaun	Granite, Schist/Gneiss	77
RCR-16	Failmore River, Tiernakill	Schist/Gneiss	80
RCR-17	Bealanabrack River, Maum Bridge	Schist/Gneiss	80
RCR-18	Letterfore River	Granite	80
RCR-19	Cornamona River, Cornamona Bridge	Schist/Gneiss	79
RCR-20	Cong River	Carboniferous Limestone L. Mask Outflow	80
RCR-21	Cross River	Carboniferous Limestone, Sandstone	81
RCR-22	Ballynalty River, Galway Road	Carboniferous Limestone	81
RCR-23	Black River, Gortbrack Bridge	Carboniferous Limestone	81
RCR-24	Cloneen Bridge, Galway Rd	Carboniferous Limestone	81
RCR-25	Cloneen River, Lisheenageeha Bridge	Carboniferous Limestone	80
RCR-26	Kilroe River, bridge Galway Rd	Carboniferous Limestone	81
RCR-28	Cregg River, bridge Galway Rd	Carboniferous Limestone	81
RCR-29	Clare River, bridge Galway Rd	Carboniferous Limestone	81
RCR-30	Carrowbrowne stream, bridge Galway Rd	Carboniferous Limestone	81

TABLE 4 3: Mean values and %RSD's for Corrib River sites

Sample ID	Ca mg/l	K mg/l	Mg mg/l	Na mg/l	Al ug/l	Ba ug/l	Cd ug/l	Co ug/l	Cr ug/l	Cu ug/l	Fe ug/l	Mn ug/l	Ni ug/l	Pb ug/l	Sr ug/l	Zn ug/l
RCR-1	**59.10** 21.55	**2.02** 0.52	**3.91** 0.64	**11.37** 2.11	**8.20** 7.75	**29.60** 10.24	**1.07** 3.99	**0.42** 0.43	**2.39** 2.36	**1.29** 0.82	**60.10** 81.63	**1.46** 1.62	**2.66** 1.71	**0.30** 0.30	**178.03** 50.96	**6.50** 8.63
RCR-2	**16.32** 8.12	**1.02** 0.27	**2.38** 0.60	**13.18** 2.87	**39.29** 22.10	**11.92** 3.65	**0.69** 2.21	**0.34** 0.48	**1.95** 1.78	**1.34** 0.87	**432.00** 237.57	**5.33** 9.70	**1.21** 1.98	**0.21** 0.15	**34.63** 14.77	**6.69** 6.73
RCR-3	**33.23** 6.97	**1.46** 0.32	**2.75** 0.42	**13.66** 2.61	**18.05** 13.13	**16.13** 3.58	**0.62** 2.06	**0.31** 0.46	**2.32** 2.08	**1.29** 0.91	**117.04** 94.83	**6.48** 10.80	**1.40** 1.71	**0.18** 0.19	**49.00** 7.61	**5.63** 8.71
RCR-4	**57.84** 13.87	**1.84** 0.41	**3.21** 0.55	**13.62** 2.52	**15.22** 9.65	**18.28** 4.20	**0.67** 2.71	**0.35** 0.63	**2.90** 2.99	**1.20** 0.73	**67.75** 57.36	**3.44** 5.81	**1.74** 1.70	**0.32** 0.82	**71.33** 11.45	**7.42** 11.75
RCR-5	**60.01** 14.57	**2.13** 0.52	**3.33** 0.55	**14.57** 2.66	**15.89** 9.09	**18.97** 7.01	**0.80** 3.12	**0.41** 0.61	**3.05** 3.04	**1.74** 0.85	**67.22** 62.84	**7.25** 33.67	**1.82** 1.89	**0.13** 0.10	**74.36** 12.24	**6.07** 6.78
RCR-7	**24.78** 12.68	**0.87** 0.24	**2.67** 0.82	**11.72** 2.46	**41.75** 23.24	**41.00** 22.66	**1.55** 8.04	**0.40** 0.73	**2.56** 2.52	**1.14** 0.94	**210.47** 129.96	**7.79** 15.01	**1.32** 2.38	**0.22** 0.22	**57.10** 25.06	**7.42** 10.45
RCR-8	**7.11** 3.17	**0.60** 0.14	**1.75** 0.40	**11.35** 2.66	**33.09** 18.56	**60.45** 22.74	**1.46** 7.36	**0.48** 0.89	**2.47** 2.33	**1.01** 0.79	**244.23** 153.20	**10.61** 18.53	**1.43** 3.47	**0.26** 0.28	**51.92** 19.71	**9.24** 17.08
RCR-9	**3.49** 1.52	**1.03** 0.29	**1.73** 0.41	**12.34** 2.65	**164.97** 56.84	**74.33** 17.66	**1.54** 7.72	**0.52** 0.94	**2.16** 2.32	**2.24** 6.85	**712.36** 445.99	**60.76** 81.26	**1.67** 3.27	**0.45** 0.43	**35.05** 10.79	**9.52** 9.31
RCR-10	**8.53** 2.84	**1.31** 0.38	**2.51** 0.59	**13.81** 2.43	**176.13** 86.09	**75.66** 15.30	**1.77** 10.13	**0.55** 0.79	**2.20** 1.84	**4.16** 23.07	**580.96** 304.88	**21.20** 51.35	**1.47** 2.21	**0.32** 0.29	**41.76** 14.22	**10.31** 17.90
RCR-11	**9.11** 4.42	**0.86** 0.30	**2.03** 0.57	**11.34** 2.70	**36.71** 25.76	**9.87** 9.59	**0.66** 1.47	**0.51** 0.75	**1.84** 1.60	**1.46** 1.19	**299.80** 211.92	**3.99** 6.99	**1.23** 1.99	**0.20** 0.17	**31.65** 10.66	**7.88** 8.05
RCR-12	**11.45** 4.87	**0.74** 0.23	**2.07** 0.49	**11.32** 2.44	**32.07** 20.91	**12.61** 7.12	**0.59** 1.45	**0.54** 0.95	**2.04** 1.65	**1.85** 1.25	**244.00** 154.84	**5.24** 7.93	**1.13** 1.55	**0.17** 0.12	**65.90** 22.05	**7.65** 9.78
RCR-13	**20.50** 9.71	**0.94** 0.34	**2.31** 0.52	**12.15** 2.41	**46.39** 30.06	**37.15** 7.21	**1.08** 5.09	**0.56** 0.95	**2.03** 1.69	**1.00** 0.68	**231.72** 128.75	**3.69** 5.80	**1.21** 2.07	**0.20** 0.12	**178.29** 70.88	**6.05** 8.62
RCR-14	**7.83** 3.90	**0.68** 0.18	**2.32** 0.58	**13.66** 2.94	**72.23** 43.23	**33.46** 6.17	**1.06** 4.82	**0.59** 1.02	**1.97** 1.52	**1.08** 0.86	**392.54** 239.03	**7.16** 15.26	**1.42** 2.62	**0.29** 0.19	**59.59** 22.80	**7.30** 9.90
RCR-15	**3.20** 2.43	**0.52** 0.16	**1.55** 0.57	**11.22** 3.53	**40.74** 23.85	**15.91** 13.18	**1.05** 4.82	**0.63** 1.11	**2.18** 1.83	**1.24** 1.82	**103.05** 96.05	**6.67** 13.25	**2.83** 4.17	**0.21** 0.22	**22.98** 18.55	**9.22** 16.12
RCR-16	**6.71** 4.03	**0.50** 0.18	**1.58** 0.63	**9.37** 3.72	**29.82** 17.09	**5.19** 3.53	**0.53** 0.70	**0.30** 0.57	**1.19** 1.43	**0.91** 0.66	**72.64** 49.63	**2.79** 4.36	**1.23** 2.09	**0.19** 0.18	**42.14** 22.26	**5.75** 6.99
RCR-17	**5.61** 2.86	**0.52** 0.15	**1.75** 0.50	**9.08** 2.59	**26.81** 23.19	**25.29** 7.35	**1.24** 5.30	**0.22** 0.26	**1.36** 1.39	**0.96** 0.59	**135.11** 107.73	**7.34** 15.38	**1.01** 0.90	**0.13** 0.10	**29.07** 8.77	**5.96** 9.17
RCR-18	**13.01** 7.73	**0.69** 0.22	**2.41** 0.76	**12.19** 2.97	**39.54** 24.29	**50.07** 18.39	**1.63** 8.38	**0.20** 0.23	**1.14** 1.14	**1.04** 0.79	**104.88** 59.19	**3.68** 7.95	**1.20** 1.83	**0.17** 0.15	**98.34** 51.54	**10.36** 23.01
RCR-19	**6.35** 2.70	**0.75** 0.22	**1.94** 0.49	**10.23** 2.71	**28.52** 23.19	**39.47** 13.32	**1.22** 5.07	**0.23** 0.36	**1.13** 0.96	**1.18** 0.97	**67.32** 58.48	**3.29** 5.95	**0.91** 0.78	**0.16** 0.20	**26.88** 7.33	**6.55** 7.77
RCR-20	**49.06** 15.46	**1.79** 0.31	**3.62** 0.58	**11.65** 2.20	**8.45** 5.54	**48.81** 12.78	**1.40** 6.56	**0.27** 0.35	**1.67** 1.28	**1.00** 0.75	**36.16** 45.13	**0.92** 0.93	**2.06** 1.10	**0.11** 0.11	**123.57** 16.69	**6.30** 7.46
RCR-21	**135.61** 54.61	**4.23** 1.13	**8.70** 1.71	**13.95** 3.76	**6.04** 4.68	**35.13** 5.91	**1.41** 6.20	**0.38** 0.41	**2.96** 2.53	**1.00** 0.65	**53.86** 115.43	**0.93** 1.53	**4.01** 1.76	**0.13** 0.14	**192.65** 30.60	**8.36** 14.87
RCR-22	**124.35** 52.24	**4.76** 1.35	**8.78** 1.54	**13.67** 3.80	**5.68** 3.92	**21.67** 3.65	**0.93** 3.87	**0.35** 0.40	**2.97** 2.38	**1.00** 0.66	**48.42** 89.97	**0.78** 0.86	**4.18** 3.10	**0.13** 0.09	**147.16** 21.08	**6.24** 9.86
RCR-23	**133.14** 50.44	**3.20** 0.91	**6.33** 1.25	**12.96** 3.36	**10.62** 9.09	**30.94** 5.94	**1.02** 4.85	**0.44** 0.48	**2.73** 2.32	**1.52** 0.95	**86.75** 101.87	**2.16** 3.79	**6.05** 3.28	**0.11** 0.10	**444.17** 82.98	**12.86** 43.40
RCR-24	**146.92** 54.59	**4.04** 1.08	**5.87** 1.07	**14.32** 3.52	**7.64** 8.00	**24.03** 4.83	**1.01** 3.75	**0.48** 0.48	**2.47** 2.11	**2.32** 4.04	**55.82** 114.54	**1.32** 1.73	**6.12** 3.39	**0.19** 0.40	**303.98** 46.19	**7.62** 11.96
RCR-25	**146.78** 58.96	**4.08** 1.28	**6.10** 1.03	**14.08** 3.90	**6.08** 4.80	**24.28** 6.31	**1.12** 4.32	**0.81** 2.80	**2.50** 2.14	**1.56** 0.75	**58.72** 112.40	**1.04** 1.23	**7.46** 14.15	**0.13** 0.16	**362.41** 62.46	**6.98** 11.56
RCR-26	**147.33** 61.77	**3.68** 1.59	**8.39** 1.86	**12.95** 3.76	**5.01** 3.93	**23.88** 8.76	**0.95** 3.52	**0.91** 3.21	**2.48** 2.11	**1.22** 0.92	**68.06** 129.64	**2.67** 14.50	**6.36** 15.24	**0.15** 0.26	**452.63** 87.63	**6.77** 9.10
RCR-28	**146.95** 59.35	**4.14** 1.73	**7.21** 1.49	**12.77** 3.61	**7.34** 7.07	**23.64** 10.88	**1.02** 3.74	**0.92** 3.27	**2.66** 2.28	**1.52** 0.96	**70.47** 110.92	**2.16** 3.28	**7.00** 18.07	**0.11** 0.16	**441.64** 73.89	**8.68** 13.87
RCR-29	**130.68** 54.04	**3.64** 1.40	**6.05** 1.40	**12.94** 3.53	**12.67** 11.27	**22.21** 4.39	**0.94** 3.22	**0.96** 3.35	**2.64** 2.47	**1.67** 1.07	**94.37** 95.38	**2.11** 3.22	**7.05** 16.21	**0.13** 0.13	**419.00** 76.83	**9.85** 23.17
RCR-30	**118.73** 47.34	**6.49** 4.09	**5.43** 1.36	**17.87** 4.09	**14.44** 15.68	**28.50** 21.92	**0.99** 3.40	**0.90** 2.48	**2.45** 1.95	**1.36** 0.94	**327.11** 622.73	**304.18** 1389.45	**5.90** 13.05	**0.15** 0.12	**219.91** 54.37	**9.84** 10.00

Details of sampling locations can be found in Table 4.2
More statistical information can be found in Appendix C, Table C-2

4.5 Sample Collection

Results obtained from analysis of twenty-eight of Lough Corrib's inflowing rivers and streams will be discussed. Staff in the Western Regional Fisheries Board collected the samples between January 1999 and July 2001. The samples were taken weekly and transported to Dublin for nutrient analysis in the Central Fisheries Board laboratory before trace element analysis by ICP-MS. All the weekly samples were tested for trace elements during 1999 and early 2000, and then trace element analysis was reduced to monthly intervals in late 2000 and 2001. Table 4.2 summarises the rivers sampled, the geological bedrock of the river and the number of times each was analysed for trace elements.

4.6 Results and Discussion

4.6.1 Initial observations

The mean concentrations calculated from the values of each element at each sample site over the duration of this study are listed in Table 4.3. A large range of concentrations can be seen, particularly for the major elements, e.g. the mean calcium concentration ranges from 3.49 – 147.33mg/l. Magnesium, potassium, sodium, barium and strontium also display a large range in values.

The metals aluminium and iron show a similar variation in concentration, although they display an opposite pattern to the GI/GII elements – e.g. in rivers where the GI/GII elements are high, these metals are low and vice versa. The other trace metals do not display such a large variation, although there is one exception – the mean concentration of manganese in the Carrowbrowne stream (RCR-30) is extremely high (304.18µg/l) compared to the values in all the other streams and rivers studied. On further examination of the raw data, this high mean value was found to be a result of six instances over the duration of the project where manganese concentrations at this location exceeded 1mg/l. In each of these instances, high levels of iron were also found on analysis. The elevated levels of both elements were possibly related to plant material present in the individual water samples submitted for analysis on those occasions.[♣]

More detailed statistics on the results for each river can be found in Appendix C. In general, on initial observation, the concentrations of elements in these samples are very acceptable and well within range of the Irish and European regulations outlined in Chapter 1 and Appendix A.

4.6.2 Spatial variation

There is a noticeable contrast between the element concentrations in rivers from the east and west sides of Lough Corrib. Clearly related to the limestone geology, rivers from the east contain high levels of calcium, potassium, magnesium, sodium, barium and strontium. Concentrations of these elements in rivers to the west are much lower in comparison. Rivers towards the north and south (i.e. at the boundaries of the limestone and the harder rock) have intermediate values (Figure 4.3). Sodium, however, does not display as much variation as the other elements, possibly due to the influence of sea spray which would affect both sides of the lake almost equally (see discussion on the relationship between sodium concentration and distance from the sea for lakes in Chapter 3).

[♣] Only the water itself was analysed, but it is possible that during transport and storage of the samples the plant material released these elements into the water.

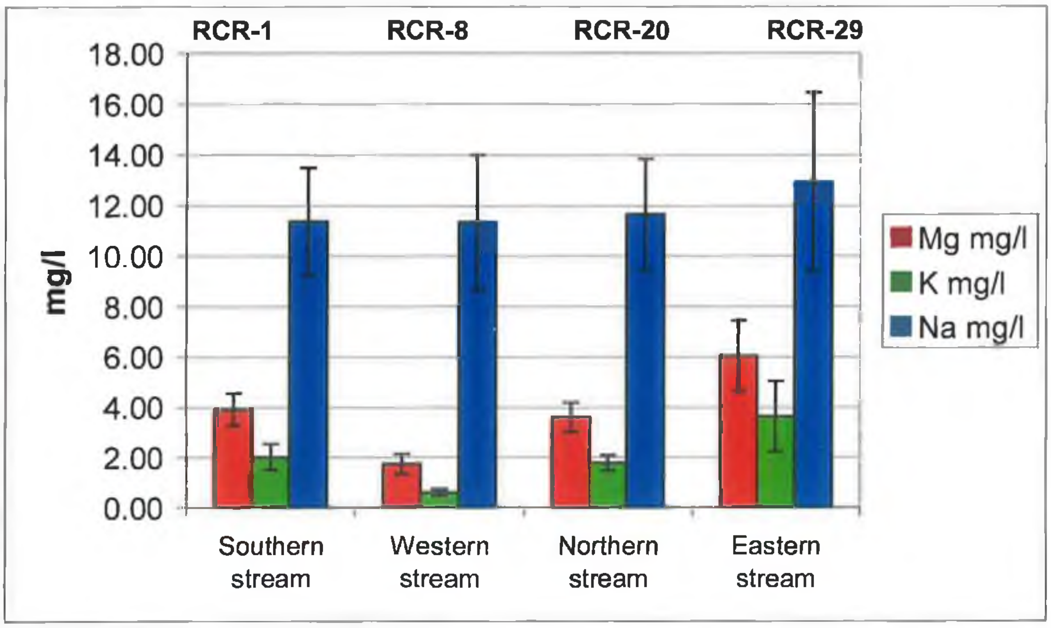

Figure 4.3: Typical GI/GII element concentrations in Lough Corrib tributaries

Data taken from Table 4.3 and Appendix C, Table C-2; Error bar is ± 1 standard deviation

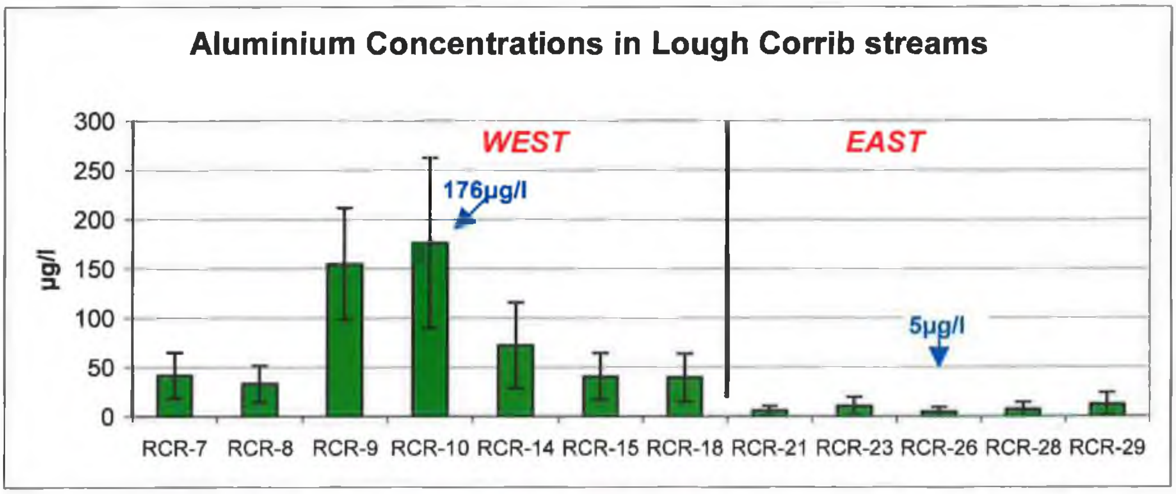

Figure 4.4: Aluminium concentrations in Lough Corrib tributaries

Data taken from Table 4.3 and Appendix C, Table C-2; Error bar is ± 1 standard deviation

In contrast to the GI/GII elements, the rivers on the western side of the lake displayed the highest concentrations of some of the metal elements, e.g. the Derrymoyle River (RCR-10) on the west had a mean aluminium concentration of 176.13µg/l compared to 5.01µg/l in the Kilroe River (RCR-26) on the east (Figure 4.4). Acidic "spates" as described in Section 4.2 may explain the high deviation in aluminium in the western streams. This pattern of high values on the west and lower values on the east is also seen with iron, manganese and lead. Other metal elements did not show an obvious spatial difference between eastern and western streams (see plots in Appendix C).

It is reasonable to presume that the Lough Corrib catchment geology discussed above is the major factor influencing the spatial distribution of all these elements. Thus, the hard rock to the western shore produces streams that have low GI/GII concentrations, are possibly acidic in nature and thus sensitive to picking up high amounts of trace metals from the rock and soil. The streams flowing from limestone rock to the east erode and dissolve high levels of calcium and other GI/GII elements, which serves to "buffer" the water and so they do not pick up high concentrations of metal elements (see Section 4.2).

Figure 4.5: The opening of Maam bay to the north west of Lough Corrib [♣]

The chemical compositions of the tributary rivers also directly influence the lake water chemistry at the points where they enter the lake. A detailed examination of the

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[♣] *Source: Central Fisheries Board – reproduced with permission* individual effects of the rivers on the chemistry of local areas of the lake is beyond the scope of this chapter, but there are several observations worthy of mention. During the course of this study, samples were also received from 29 sites around Lough Corrib itself. Analysis of these lake samples showed that despite it being one large water body, there are some local variations around Lough Corrib that are clearly a result of inflowing tributaries.

For example, in the northwestern corner of the lake there is a long narrow inlet called Maam Bay (Figure 4.5) that contains a mean calcium concentration of just 9.55mg/l (the overall lake mean was reported as 46.01-51.46mg/l in Chapter 3, Table 3.2). Similarly, nearby Cornamona bay has a mean calcium concentration of 29.77mg/l (Figure 4.6). The other GI/GII elements also have a lower than average concentration in these two bays, both of which receive inflowing water from soft water rivers on the western side of the lake, e.g. potassium, magnesium, sodium, barium and strontium. Metal elements have a higher than average concentration in these locations, e.g. aluminium, manganese and zinc (Figure 4.7). The opposite similar pattern is seen on the eastern shore, where the hard water rivers enter the lake. Lake samples taken from the Cregg River Bay, the mouth of the River Clare, and further out from the River Clare were found to have higher than average levels of calcium (i.e. 92.67mg/l, 106.48mg/l and 96.10mg/l respectively). These sites on the east also displayed a similar trend with other GI/GII elements.

Finally, the River Corrib outflow (RCR-1) to the south of the lake has mean values for each element that are comparable to the mean values reported in Chapter 3 for the lower basin of Lough Corrib (Table 3.2). This is logical, as the chemistry of an outflow should be expected to reflect the chemistry of the well-mixed lake water. Inflowing streams carry sediment that settles in the lake, and so the outflow river generally has less fluctuation in the concentrations of chemical parameters (Champ pers. com.).

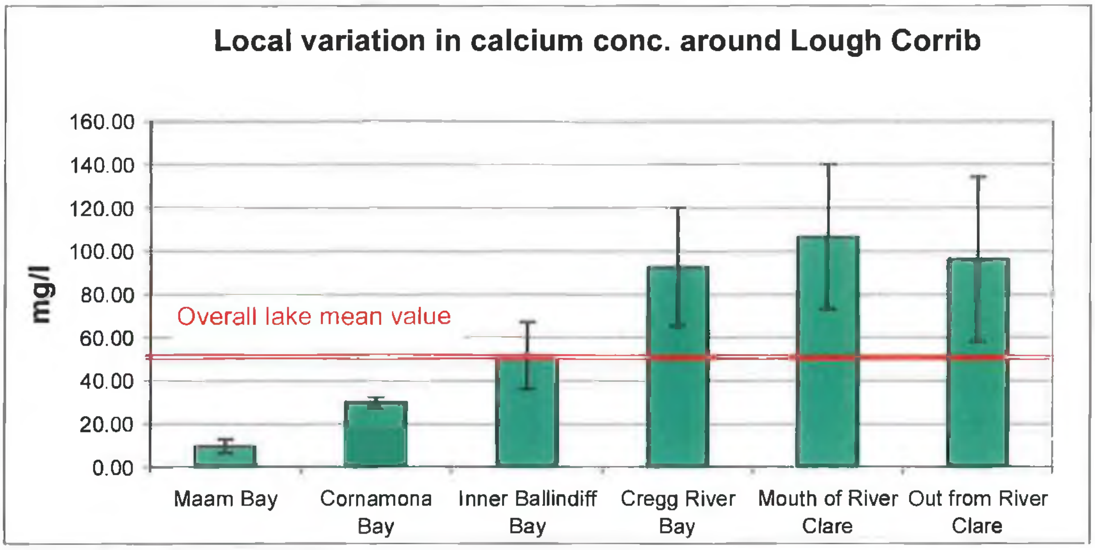

Figure 4.6: Local variation in calcium concentration in Lough Corrib

Data taken from Appendix C, Table C-43; Error bar is ± 1 standard deviation

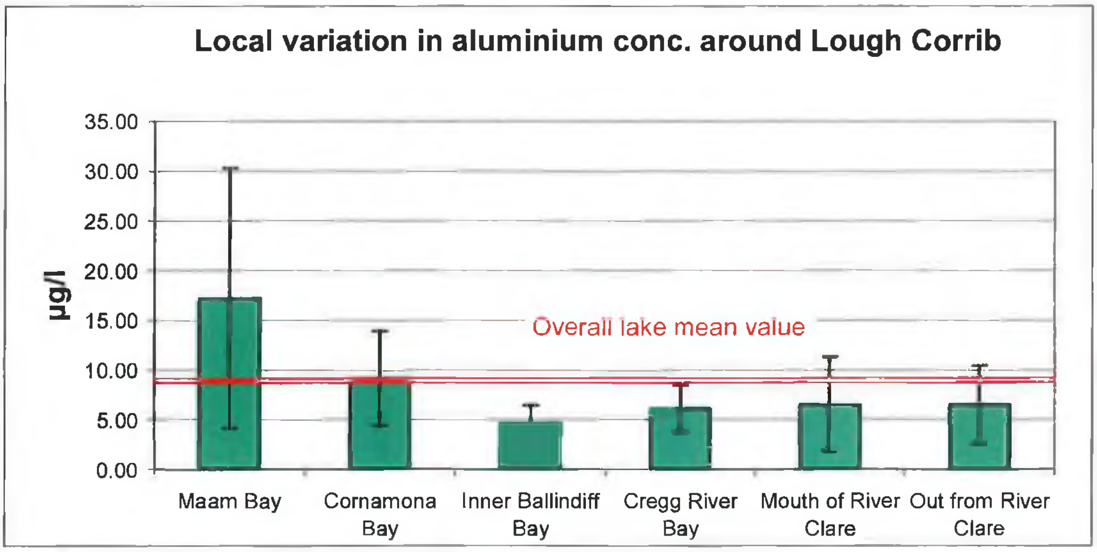

Figure 4.7: Local variation in aluminium concentration in Lough Corrib

Data taken from Appendix C, Table C-43; Error bar is ± 1 standard deviation

4.6.3 Temporal variation

The grouping and averaging of results by month revealed some interesting trends about the seasonal variation in the river water chemistry. There was a marked difference in seasonal trends between the rivers on the east and west sides of the lake.

The soft water rivers on the west, which come from areas of hard rock, showed a general increase in the GI/GII element concentrations during the summer months. Indeed, the work by Neal *et al.*[115] on the River Tweed illustrated a similar pattern – i.e. that there was an increase in alkalinity and trace elements such as barium and strontium during times of low flow. During the present work, the mean monthly results for these two elements support this finding*, particularly in the results obtained from the soft water streams to the west. Figure 4.8 illustrates this trend in annual barium and strontium concentrations for three rivers on the west side of Lough Corrib, namely the Drimneen (RCR-7), Owenriff (RCR-8) and Letterfore (RCR-18). Tables of the entire annual mean results per month can be found in Appendix C.

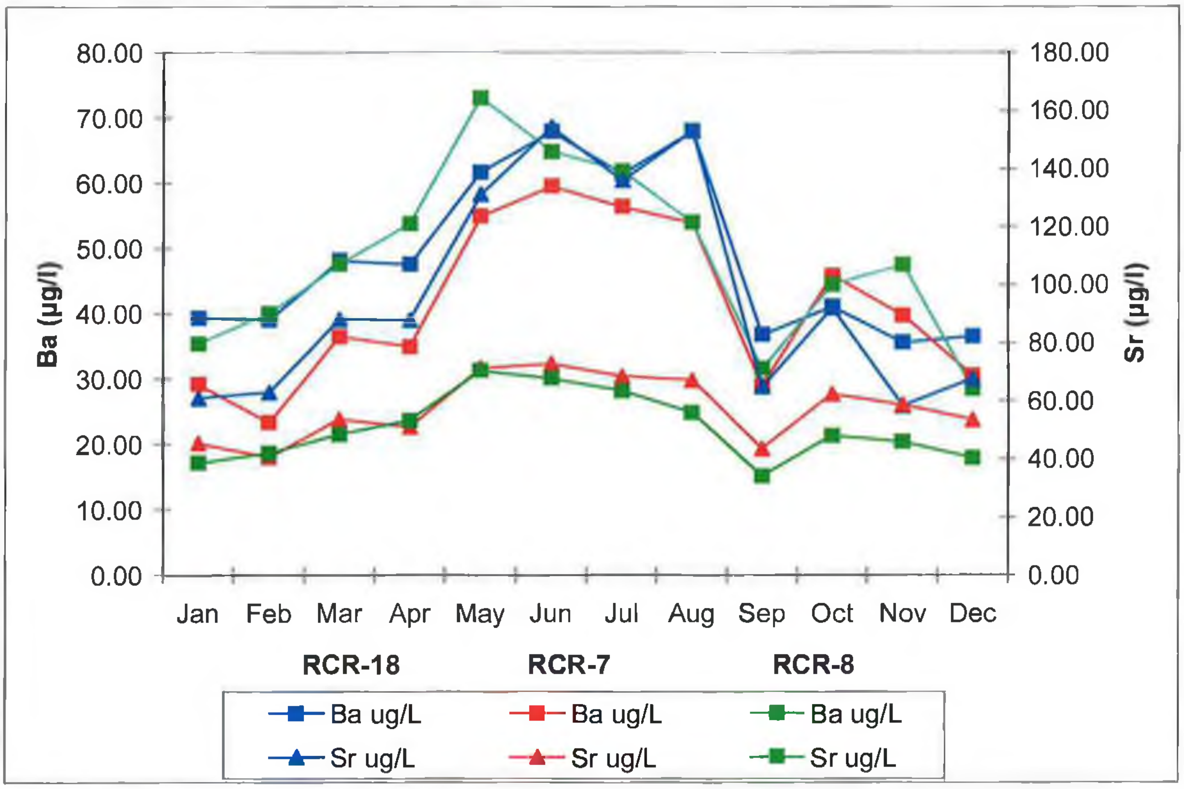

Figure 4.8: Temporal variation in barium and strontium in western Corrib streams

Data taken from Appendix C, Tables C-3 to C-30
Average monthly mean std. dev range: Ba =15-18µg/l; Sr = 16-39µg/l

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* Flow data was not available, but it is presumed for the purposes of this discussion that flow was generally higher during the winter months.

On the east side of Lough Corrib the rivers showed a decrease in the major element concentrations during the summer months, possibly due to uptake by plants and animals living in the water. Figure 4.9 illustrates the patterns for calcium in four of the rivers – two on the west side Curraghaduff (RCR-13) and Cornamona (RCR-19), one on the east side Clare (RCR-29) and the outflowing River Corrib (RCR-1) to the south. Other rivers on the east and west displayed similar patterns to these examples, and the trends also correspond to the temporal variation patterns in soft and hard water lakes discussed in Chapter 3. Interestingly, the River Corrib outflow (RCR-1) has a much smoother profile than the inflowing rivers, and the temporal pattern is similar to the calcium profile for hard water lakes (Section 3.4.4). This again shows the "mixing" effect of the lake that is reflected in the main outflow.

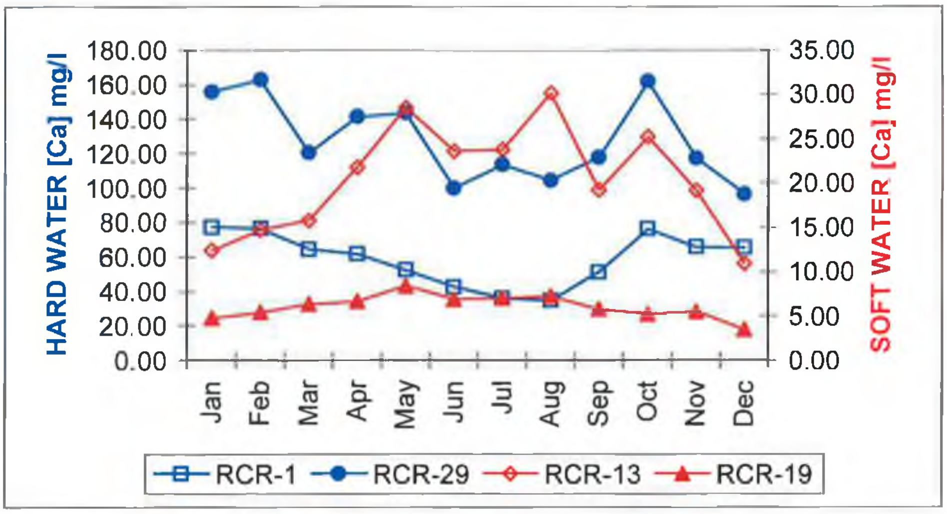

Figure 4.9: Calcium concentration in four rivers

Data taken from Table 4.3 and Appendix C, Tables C-3 to C-30
(Hard waters are coloured blue, soft waters are red)
Average monthly mean std. dev range: RCR-1 = 14.91mg/l;
RCR-29 = 46.08mg/l; RCR-13 = 8.02mg/l; RCR-19 = 2.51 mg/l

In a separate study to the previously cited, Neal *et al.* found that aluminium, iron, manganese and lead increase with increasing flow in the River Derwant in Eastern England[123] – an opposite pattern to that already discussed for the GI/GII elements. This trend was also observed during the present study, for the rivers both on the east and the west side of Lough Corrib, e.g. manganese shows a decrease in concentration in the mid/late summer for rivers both on the east and the west (Figure 4.10). Aluminium displayed a similar pattern (Figure 4.11), but iron did not – it was found to have an increasing concentration towards the late summer/early autumn in the western streams, and an erratic concentration pattern in the eastern streams. It was difficult to discern a trend with lead and other heavy metals.

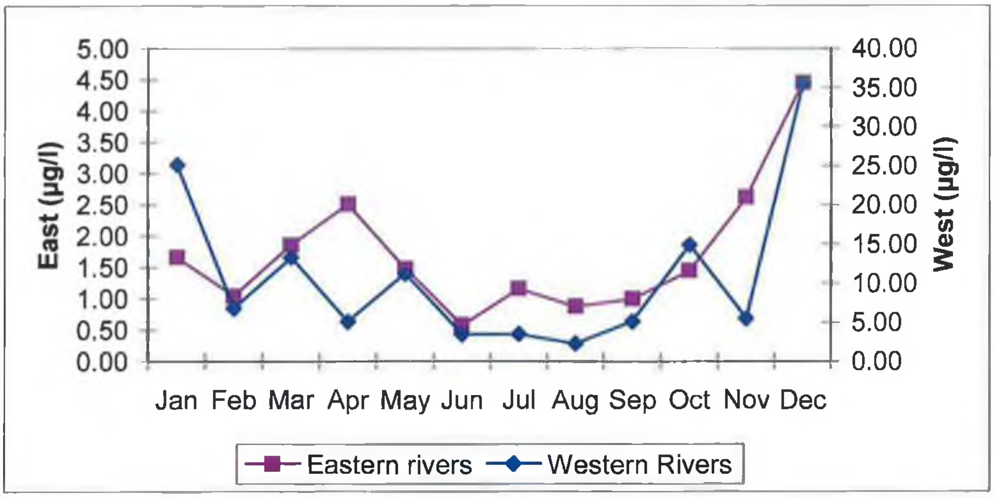

Figure 4.10: Manganese concentrations in rivers to the east and west of Lough Corrib

Data taken from Appendix C, Tables C-31 to C-32
Average monthly mean std. dev range:
Eastern Rivers = 0.59-15.02µg/l; Western Rivers = 2.78-59.67µg/l

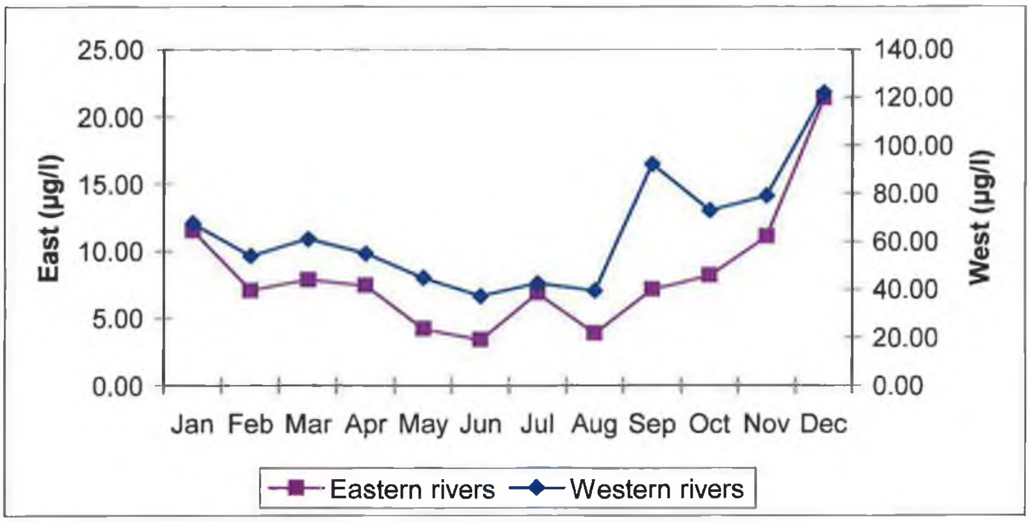

Figure 4.11: Aluminium concentrations in rivers to the east and west of Lough Corrib

Data taken from Appendix C, Tables C-31 to C-32
Average monthly mean std. dev range:
Eastern Rivers = 1.36-11.91µg/l; Western Rivers = 46.86-92.07µg/l

4.6.4 *Statistical analysis and plots*

4.6.4.1 Correlations

The first statistical tests that were carried out were simple correlation and co-variance analyses on the mean values obtained for each river (Table 4.3). A table of results can be seen in Appendix C, and as was found for the lakes (Chapter 3), a range of positive and negative correlations were found between the different elements. Again, the strongest positive correlations were found between GI/GII elements, e.g. values of 0.94, 0.92 and 0.89 for Ca/Mg, Ca/K and Ca/Sr respectively. The metal elements also showed strong correlation, e.g. Al/Fe had a correlation factor of 0.87, Al/Cu a factor of 0.67, Al/Pb a factor of 0.73 and finally Fe/Pb a factor of 0.70.

Unlike the trends seen during the lake analysis, and somewhat surprisingly, several of the GI/GII elements seemed to have a strong positive correlation with metal elements. For example, Ni was strongly correlated with Ca (0.93), K (0.86), Mg (0.83), and Sr (0.92). The reason for this is unclear, as is the high correlations of Ba with Cd (0.90) and Al (0.69) and Cr with Ca (0.63), K (0.60), Mg (0.62) and Na (0.62).

Strong negative correlations were scarce, with the highest values found between Ca/Al (-0.53) and Ca/Pb (-0.50). There was little correlation – positive or negative – between most of the heavy metals.

4.6.4.2. Cross validation

In Chapter 3, cross-validation was used to estimate the degree of variation between results obtained for different groups of data, and the ability to classify correctly observations omitted in turn. Similar work was carried out with the Lough Corrib rivers dataset and a summary of the findings is given in.

Table 4.4.

Table 4.4: Summary of Cross-Validation Results

Test Number	Reason for test	Number of observations	Proportion of observations correctly classified
1	Distinguish between rivers based on their mean, max, median and min values, using all parameters.	112	25.9%
2	Distinguish between hard water rivers based on Group I and II elements only.	599	40.6%
3	Distinguish between soft water rivers based on Group I and II elements only.	956	44.9%
4	Distinguish between rivers of intermediate hardness at the boundaries of hard and soft areas based on Group I and II elements only.	520	67.1%
5	Distinguish between rivers based on general groupings of soft, hard and intermediate hardness, using all parameters.	28	100.0%
6	Distinguish between rivers based on geology of bedrock using all parameters	228	67.5% (78.5% after reassigning sites)

1. A minimum of two observations per site is required to carry out cross-validation, so instead of just using the mean value for the first test (as done for the lakes in Chapter 3), the max, median and min values were also included. Only a quarter of the observations were correctly classified after this test, which is a poor result, considering a similar test with the lakes data gave over 60% correct classifications. There did not seem to be any pattern to the mis-classified observations here, although the spread in values (i.e. max to min) for each group, and similarity of many sites may have been responsible.
2. In the next test, the hard water rivers from the western side of the lake were taken out separately and examined based only on their GI/GII elements. This

was to determine if it was possible to distinguish between hard water rivers of very similar chemistry. Again, the results were disappointing with an average of only 40% of observations classified correctly. Indeed, only two sites had more than half their observations correctly assigned to them.

3. The previous test was repeated, this time using the soft water rivers from the west side of the lake. A similar result was obtained – with 44% of observations correctly classified. Many of the incorrectly assigned observations were attributed to another geographically close stream or river (e.g. 16 of the 74 observations for RCR-17 were attributed to RCR-16), but this was not always the case.
4. Seven rivers of intermediate hardness at the boundaries of east and west Corrib were tested in the same way as the previous two groups of data. This was a more successful test, with 67% correctly classified. The least successful classifications occurred between RCR-4 and RCR-5, two very close sites geographically, and whose misclassified observations were mostly attributed to the other. The misclassified observations in RCR-1 (lake outflow to the south) and RCR-20 (inflow coming from the Lough Mask outflow to the north) were also grouped with the other in a similar way. This is interesting because it demonstrates the similarity between the Lough Corrib and Lough Mask outflows, emphasising the mixing effect of lake outflows that was discussed in Sections 4.6.2 and 4.6.3 above.
5. Because of the obvious link in previous tests between the grouping and water hardness, for the purposes of this study it was decided to divide the sites into three general groups. These groupings are not defined in the literature or regulations, but were chosen so as to represent the range of hardness values in the set of rivers being studied. Hard water was defined as [Ca] > 120mg/l, soft

water as [Ca] < 30mg/l and those of intermediate values with [Ca] of 30-120mg/l. Details of which sites were assigned to each hardness group can be found in Appendix C. The mean values for each river site (Table 4.3) were used for the test and as expected, the cross-validation test was extremely successful, with 100% of the sites assigned to the correct group.

6. Following the success of the general water hardness cross-validation test, it was decided to group the sites based on the local geology of the river. Nine different groupings were identified with the aid of the catchment geological map and Table 4.2. Details of which sites were assigned to each geological group can be found in Appendix C. All sample observations that included a full set of results for each element were included in the test (228 observations in all). The proportion of correctly classified observations was 67.5%. The most successful classification was for the sandstone/limestone group, which had 100% success. The least successful classification was the schist/gneiss/limestone group (33% correct). A table showing detailed results of the classification can be found in Appendix C.

   Examination of the results showed that five sample sites were incorrectly classified for all observations relating to that site. These sites were RCR-2 (Loughkip), RCR-14 (Owenree), RCR-18 (Letterfore), RCR-19 (Cornamona) and RCR-22 (Ballynalty) and each was then reassigned into a different geological group. Details of the geological groups to which these sites were reassigned can be found in Appendix C. RCR-8 (Owenriff) was also reassigned because half of its observations were being classified into another specific group. The cross-validation test was repeated after the reassignments, and the results were improved with 78.5% of observations correctly classified. Indeed, two groups now had 100% correct classification (granite and sandstone/limestone). The least successful classifications were in the schist/gneiss and schist/gneiss/silurian group (47% and 50% correctly classified respectively).

Overall, the cross-validation work was much more difficult with the rivers than it was with the lakes, and it was difficult to obtain a high proportion of correctly classified observations. This is possibly due to the high degree of fluctuation and dynamism in river water chemistry compared to lakes.

4.6.4.3. Multivariate analysis

Several simple multivariate analysis tests were carried out using Minitab® in order to identify some patterns in the data and as with the lakes data, no pre-treatment was carried out on the data. It was found to be difficult to achieve successful separations, and more parameters would probably need to be added to improve the results. Some of the initial results will be presented, however, as an indication of where possible future work could be concentrated.

4.6.4.3.1 Cluster variables

The mean values for each element and sample location (Table 4.3) were used to generate a cluster variables dendogram. As was found for the lakes in Chapter 3, there was high similarity between the alkaline earth metals calcium, magnesium, and strontium – but on this occasion barium was not amongst them, but found at the opposite end of the diagram. This is unexpected and the reason for it is unclear.

As would be expected from the correlation reported in Section 4.6.4.1, iron and aluminium also show a high degree of similarity in this diagram for the Lough

Corrib Rivers. In general, there was less separation in the cluster variables for rivers than there was in the lake data.

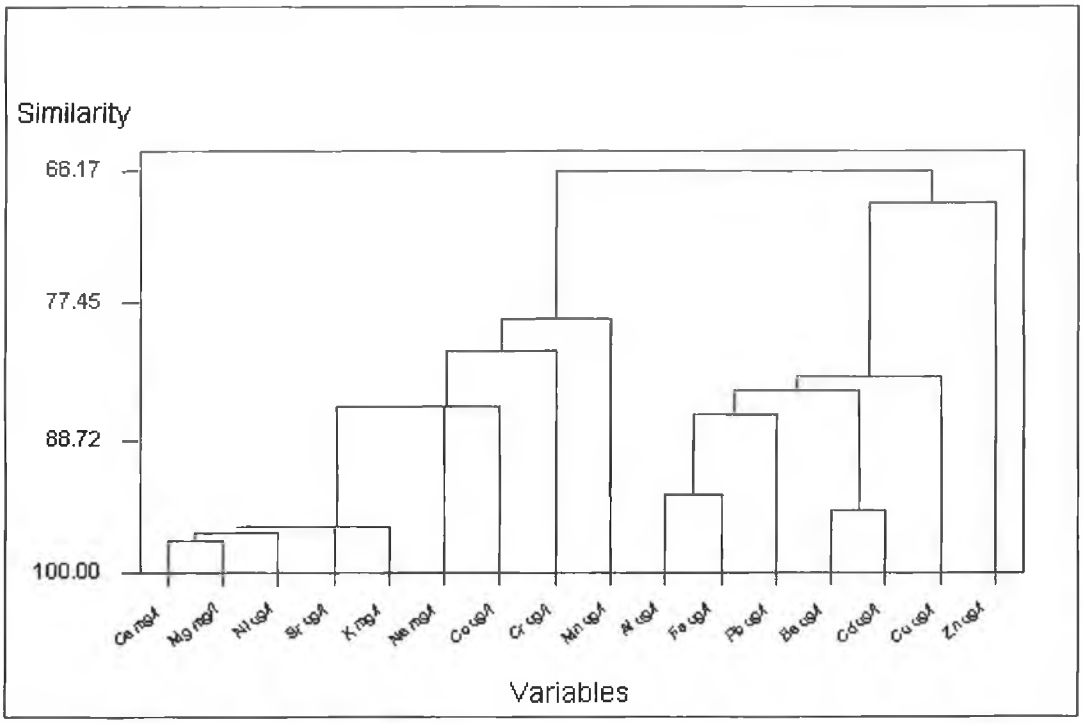

Figure 4.12: Cluster variables for the 16 element variables – Lough Corrib rivers

4.6.4.3.2 Geological groups

It has been discussed above how the unique geology of this region plays a large part in the chemistry of its rivers. The rock type over which each river or stream flows was added to the data set and used to group the data by geology. Principal Component Analysis (PCA) was carried out. Some rivers/streams had more than one type of bedrock, and these were taken into account for the groupings by giving the site a mixed geology classification. Sites at border regions between the significant geological boundaries of east and west were simply labelled "border".

There is some evidence of separation in the first component (PCA1), although it is not clearly defined (Figure 4.13). The limestone samples are mostly located at the bottom of the plot, and the granite samples at the top. The "border" samples are found between the limestone and all the others, and the sites on a schist/gneiss bedrock are grouped towards the centre of the plot. This suggests that with a larger dataset (more variables added), multivariate analysis could be used to distinguish between sites on the east and west side of the lake. Unfortunately it was not possible to extend the dataset during this work in order to achieve better separations.

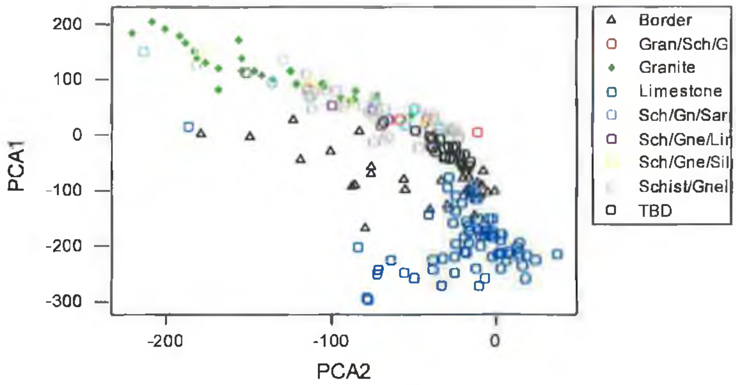

Figure 4.13: Geological influence on Corrib stream groupings

Border = Mixed geologies; Gran/Sch/G = Granite, Schist and Gneiss; Sch/Gn/San = Schist, Gneiss and Sandstone; Sch/Gne/Lim = Schist, Gneiss and Limestone; Sch/Gne/Sil = Schist, Gneiss and Silurian; Schist/Gne = Schist and Gneiss; TBD = unclassified

4.7 Conclusions

There is a large variation in the chemistry of rivers in the Lough Corrib catchment, illustrated by a wide range in concentrations of various elements. This makes the Lough Corrib catchment a very interesting and useful study area. The differences are most evident in the contrast of water chemistry in rivers to the east and west sides of the lake. These generally represent the extremes of concentrations in the catchment, with rivers to the north and south having intermediate values. Eastern rivers generally have a high GI/GII content and low metal content, with the reverse pattern in the western rivers. In some areas, particularly in sheltered bays and near the mouths of major rivers, these tributaries also have a significant local influence on the lake water chemistry in Lough Corrib. The chemistry of the lake outflow to the south reflects the mixing effect of the lake.

Calculating mean values for each element during long-term monitoring, while useful to generate an overall picture of the results, must be carried out with caution. Occasionally there may be rare elevations in certain elements that may skew the mean value. For example, the release of manganese and iron by plant matter growing in the water was found in the Carrowbrowne stream on several occasions. Thus, it is important to sample rivers regularly throughout the year under different conditions in order to gather a complete picture of the range of concentrations possible.

Local geology plays a major role in the chemical distinction (fingerprint) of rivers around the lake. GI/GII elements, in particular calcium, magnesium and strontium, were found to be the most important parameters when attempting to discriminate between rivers flowing over different geological bedrocks. This was also found to be the case with the lakes (Chapter 3) and is unsurprising as they are found in the highest concentrations and are most directly related to the geology. Metal concentrations in the Lough Corrib rivers, however, were generally higher than the values found in the lakes, with some soft water rivers flowing on hard rocks displaying particularly high values of aluminium, iron and manganese.

Temporal variation in the rivers studied showed similar trends to that found in the lakes, i.e. in soft waters there was an increase (concentration) of elements in the summer months, but in hard waters there was a decrease (depletion). Certain metal elements (e.g. aluminium, manganese) increased in concentration in the winter months and this pattern was seen in all rivers regardless of hardness. This also reflects the pattern found with the soft water lakes. With the rivers, however, it is most likely the result of winter flooding where the river carries increased sediment loads, and possibly also due to some acidic spates in the soft water rivers from the acid-sensitive areas to the west.

Statistical examination of the data for the rivers showed there was good correlation between the GI/GII elements as was the case also for the lakes. The rivers differed from the lakes in that there was also good correlation between many of the metal elements. It was more difficult to get good results for cross-validation tests for the rivers than it was for the lakes samples as there was more variation in the results for each sample site. However, there was quite a good classification of observations when the local geology was taken into consideration, and it was also found that the general level of water hardness can be distinguished very easily using this technique.

Multivariate analysis proved more difficult for the rivers than for the lakes, and a cluster dendogram showed less separation between the elements than was found for the lakes. Specific grouping and separation of individual sites was not achieved with PCA, and as with the lakes, addition of more variables would probably improve this. It seems to be possible, however, to separate groups of rivers based on the geology of their bedrock/locality.

This study of the Lough Corrib rivers illustrates the complexity of river water chemistry. This unique catchment offers a wealth of opportunity for the study of geological effects, as well as spatial and temporal variations. The trends and patterns discussed in this research are simply a beginning to the study of the dynamic nature of river water chemistry in Ireland.

CHAPTER 5

5. CANAL WATER ANALYSIS

5.1 Introduction

Canals are man-made linear networks of navigable waterway, which cut across watersheds, linking rivers, which would otherwise remain isolated. Canals also act as corridors, along which wildlife can travel, on land and in the water[124, 125]. The canal systems of Ireland were once an important means of communication and trading from their opening in the late eighteenth century, until cessation of activity in the 1950's[126]. In 1986 the canals were transferred to the Office of Public Works (OPW) and since that date, major restoration and development work has taken place, financed by the Irish State and the European Union[126]. Today the canals are under the care of Waterways Ireland and are used as important public amenities. They are enjoyed by many people for recreational pursuits such as boating, walking and fishing, and by those interested in nature, architecture and engineering.

The four most important canal systems in Ireland that were investigated in this work are the Grand Canal (Dublin to River Shannon), the Royal Canal (Dublin to Ballybrannigan), the Barrow Canal (Lowtown to Athy) and the Shannon/Erne waterway (Leitrim to River Erne). More details of the sampling locations on each canal will be discussed below.

Despite the fact that the canals cut through a variety of habitats - raised bogs, fens, eskers and solid limestone rock, they each receive water from one main feeder system, as well as several minor feeders[126]. The Grand Canal and Barrow Canal are fed from the Milltown Feeder, which originates in the Pollardstown Fen, an area abundant in springs of lime-rich alkaline waters. The Royal Canal is fed directly from Lough Owel, a lake of unique quality situated in a small carboniferous limestone catchment[28]. The Shannon/Erne system receives water from Lough Scur, a highly coloured peat-stained lake (unpublished work, Central Fisheries Board).

A report by the Environmental Protection Agency in 1999[127] discussed the water quality of Irish canals and referred to work by Caffrey and Allison[128]. The EPA report stated that this information had not previously been presented in national reports. However, the work by Caffrey and Allison concentrated mainly on nutrients and physico-chemical tests and thus before the present study began, no detailed information was available on the trace element composition of the canal systems.

Because of the unique feeder systems, it was hoped during this work that the water chemistry would be fairly consistent along the entire length of each canal, enabling a unique ‘elemental fingerprint’ to be established for each water system. The aim of this study was to therefore to establish whether each individual canal system possessed a unique inorganic chemistry, and whether this chemistry was spatially and temporally consistent.

Figure 5.1: Water sampling on the Shannon/Erne ♣

5.2 Sampling site locations

The locations of the four major canal systems in Ireland can be seen in Figure 5.2. The main line of the Grand Canal is 131km long with 43 locks, and in this study, samples were retrieved from 47 locations along its length numbered sequentially from the Grand Canal Basin in Dublin Docks (G1) to the River Shannon at Shannon Harbour (G47). The Barrow Canal runs south 45km from the summit level and intersection with the Grand Canal at Lowtown, Co. Kildare to join the River Barrow at Athy[124]. Samples were taken at 18 locations on this waterway. The main line of the Royal Canal is 145.7km long with 46 locks and it was sampled from the River Liffey in Dublin (R1) to

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♣ *Source: Central Fisheries Board – reproduced with permission*

Ballybrannigan Harbour (R44)♣. Finally, the Shannon-Erne Waterway is 62.5km long[129] and was sampled at 44 locations from the River Erne in Fermanagh (S1) to the River Shannon at Leitrim (S44). A full list of sample locations can be found in Appendix D.

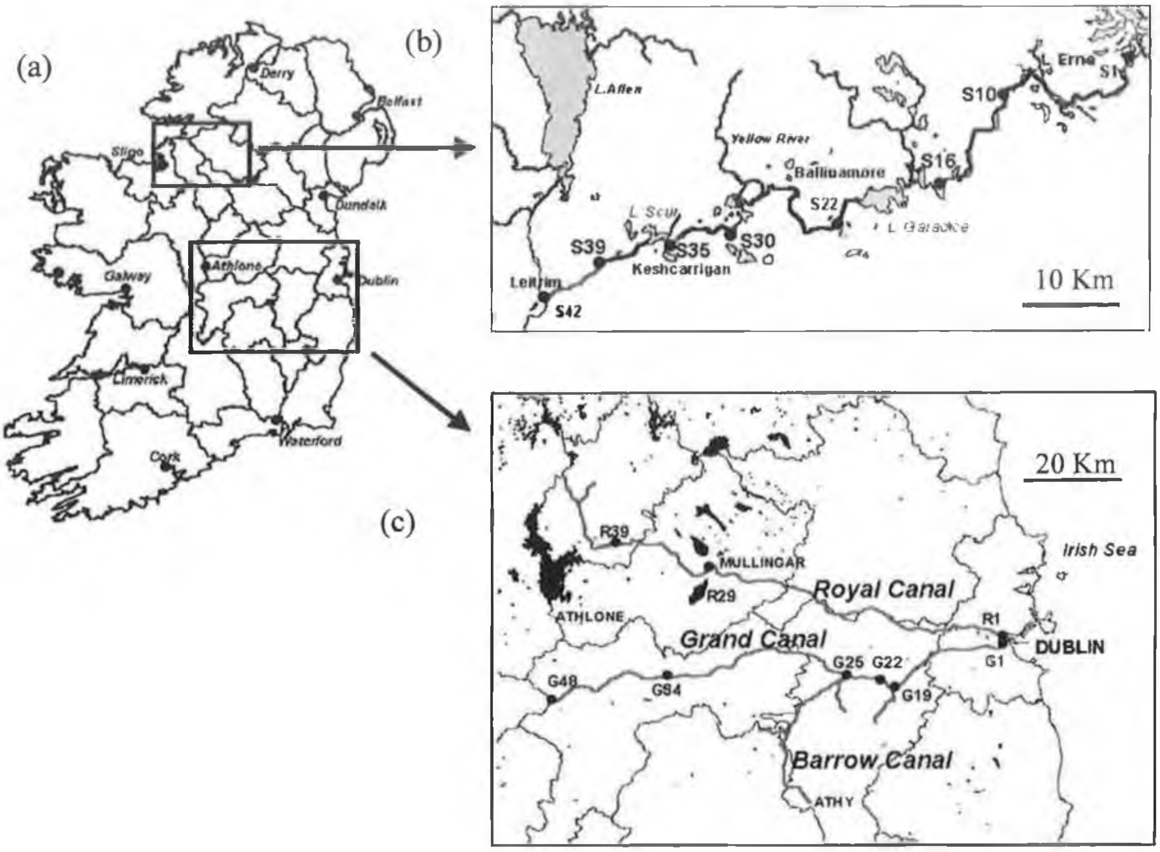

Figure 5.2: Locations of canals studied ♠

5.3 Sample collection

Sampling was carried out on a seasonal basis (i.e. spring, summer and autumn/winter) for each canal by Central Fisheries Board staff (Figure 5.1). Sample sites were spread along the entire length of each system. Sampling sites were chosen to represent the

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♣ Note: This canal has not yet been fully restored to the River Shannon[125]

♠ *Maps created by author using Geographical Information System software at Central Fisheries Board* entire canal system, i.e. at least one site in each lock system, and additional sites where the lock was particularly long or at a feeder inflow.

The complete set of samples was usually collected over the course of several weeks. Each sample was taken from the canal bank using clean, previously unused 150ml polypropylene sample bottles. In all cases the bottles were rinsed several times with the sample before filling. At some lake sites on the Shannon/Erne lakes, samples were taken from a boat. A total of 153 sampling locations were involved, and each location was visited on average three times during the year (see Appendix D). The total number of samples taken was 46, 93, 108, and 118 for the Barrow, Grand, Royal and Shannon/Erne, respectively.

Upon collection, samples were stored in large "cool-boxes" surrounded by ice-packs. Samples from the Royal, Grand and Barrow were sent to the Central Fisheries Board (CFB) laboratory in Dublin on the evening of collection and stored in a fridge overnight. Samples from the Shannon/Erne system generally arrived in Dublin on the day following collection.

5.4 Sample analysis

The samples were first analysed for nutrients and then passed to the ICP-MS laboratory where they were analysed for 16 elements. All samples were brought to room temperature before sample preparation and analysis according to the procedures outlined in Chapter 2. Five replicate measurements of each sample were made for each the 16 elements monitored to give a total of over 29,000 individual results for the canals systems – a wealth of data not previously available. The number of individual measurements for each element varies however, according to the number of sampling sites on the canal and the number of samples taken at each site.

5.5 Results and Discussion

5.5.1. Initial observations of results

In order to first identify broad patterns within the data, the mean and standard deviation of each element was calculated for each canal system. The mean results from each system, in terms of the 16 measured elements is summarised in Table 5.1. The standard deviations reported are due to spatial and temporal variation in the data and will be discussed below. The instrumental standard deviation (between the five successive replicate determinations) for each sample was extracted from the raw analysis results and a mean value calculated for each element. As expected, the elements present in higher concentrations exhibited a lower instrumental %RSD. Only four elements had an instrumental SD greater than 20% - cadmium, zinc, lead and iron. The elements cadmium, lead and zinc existed at very low concentrations in the samples measured in this study. Iron, however, displays a high instrumental SD despite its relatively higher concentrations due to the fact that it was analysed using different instrumental conditions, which results in a weaker signal at the detector and it also suffers from a greater level of spectroscopic interference (see Chapter 2). However, 15 of the 16 elements had a lower instrumental %RSD when compared to the environmental standard deviations (from spatial and temporal variation). Only cadmium showed an overall greater instrumental standard deviation than was found in the sample results.

Some broad conclusions can be drawn from these initial observations of the data. Firstly, the water of all the canal systems contains very low concentrations of heavy metals (i.e. lead, zinc, chromium, cobalt, cadmium, manganese, copper, nickel). Other elements show a larger variation in concentrations across the canals. The mean concentrations of periodic table Group II elements are lower in the Shannon/Erne than in the other three systems. However, the mean concentrations of periodic table Group I elements potassium and sodium are relatively constant across all four systems at approximately 2-3mg/L and 8.5-9.5 mg/L respectively.

The metal elements aluminium, iron and manganese display the opposite trend to the GI/GII elements, with mean concentrations relatively high in the Shannon/Erne system. Iron in particular is very high in the Shannon/Erne, with a maximum value measured at 1165µg/L, which is approximately an order of magnitude higher than the other systems.

Table 5.1: Summary data for each canal system

	Barrow n=46		Grand n = 93		Royal n = 108		Shannon/Erne n = 116	
Elements	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD
Ca (mg/L)	109	*25*	98.1	*28.1*	118	*28.1*	31.7	*39.6*
K (mg/L)	2.39	*68.3*	2.12	*43.0*	2.79	*42.6*	1.96	*47.9*
Mg (mg/L)	14.5	*13.7*	12.2	*20.2*	8.27	*20.6*	3.76	*57.1*
Na (mg/L)	9.28	*22.3*	10.3	*25.0*	10.1	*27.1*	8.39	*16.0*
Al (µg/L)	6.72	*37.2*	10.8	*93.2*	12.2	*314*	99.4	*186*
Ba (µg/L)	53.9	*23.4*	57.3	*33.5*	37.1	*62.3*	17.5	*38.5*
Cd (µg/L)	0.33	*73.7*	0.09	*130*	0.17	*120*	0.17	*95.6*
Co (µg/L)	0.42	*73.6*	0.25	*63.0*	0.36	*46.8*	0.17	*55.6*
Cr (µg/L)	2.71	*99.0*	1.38	*63.7*	2.14	*67.0*	1.22	*92.8*
Cu (µg/L)	0.79	*58.3*	1.10	*57.6*	1.47	*88.5*	2.80	*86.6*
Fe (µg/L)	24.7	*89.9*	43.6	*91.8*	27.9	*117*	317	*93.5*
Mn (µg/L)	1.14	*51.9*	8.01	*431*	5.40	*197.5*	13.7	*59.7*
Ni (µg/L)	4.75	*42.9*	2.77	*54.8*	5.24	*42.0*	4.25	*42.4*
Pb (µg/L)	0.11	*197*	0.07	*114*	0.09	*88.7*	0.45	*85.7*
Sr (µg/L)	200	*17.8*	214	*18.6*	379	*28.9*	130.5	*51.6*
Zn (µg/L)	3.86	*158*	2.33	*267*	1.45	*188*	5.00	*159*

The relative standard deviations illustrate the variation for each element is within the individual canal systems. There are two main contributors to this variability - the spatial or geographic variability and the temporal variability. For example, the mean concentration of aluminium is highest in the Shannon-Erne system (80.78 ug/L), but the variance is much higher in the Royal (%RSD=323.9 compared to 60.4), which suggests that there are places in the Royal Canal where the aluminium concentration obtained is quite different from the mean value. The differences in element concentrations between the four canal systems will now be discussed in greater detail.

5.5.2. Spatial variation between canals

Although the initial observations suggest that each water body is relatively distinct from the others, the relative standard deviations in Table 5.1 reveal that certain elements must vary considerably along the length of a particular canal system.

5.5.2.1 The Shannon/Erne Canal

The Shannon/Erne system has a much higher overall concentration of iron than the other canal systems. This was investigated in further detail by plotting the geographical distribution of the mean iron concentration from Lough Erne (S1) in the east to Leitrim (S42) at the River Shannon (Figure 5.3). Particularly high iron concentrations are found in the Yellow River (S25) and Aghascashlawn River (S32) tributaries, both of which flow from a mountainous area of shale, sandstone and coal, known locally as the "Iron Mountains" due to high iron deposits in the red/orange coloured soils. In times of flood both of these rivers discharge large brown "plumes" of material into their respective lakes. In contrast, the Group I and Group II elements potassium, sodium, calcium and magnesium show the opposite pattern to iron, with minimum values in the spatial plot corresponding to the Yellow River and Aghascashlawn River (Appendix D).

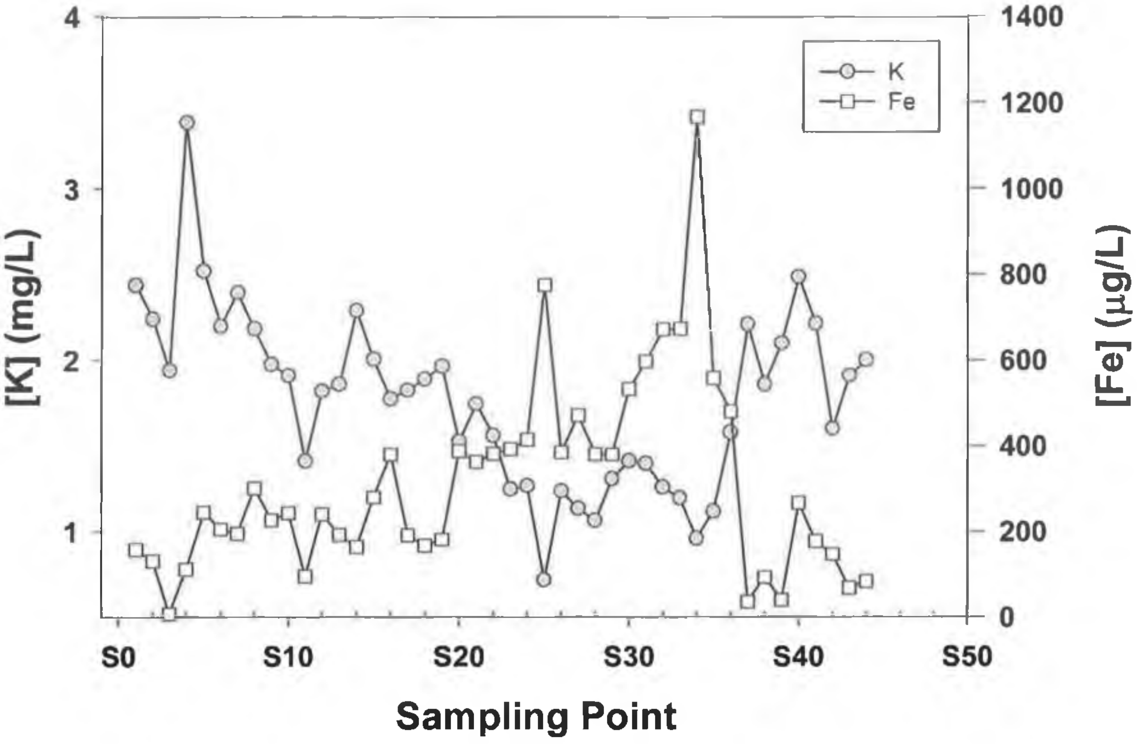

Figure 5.3: Shannon/Erne Canal [Fe, K] spatial profile

5.5.2.2 Royal Canal

The mean concentration of each element at each sampling location was plotted spatially from Dublin in the east (R1) to Ballybrannigan Harbour (R44) in the west. Again, some interesting trends were noted, particularly the sudden increase or decrease in some elemental concentrations near the main feeder from Lough Owel at Mullingar (R30). A particularly clear drop in concentration at the Owel feeder is seen for calcium, magnesium, barium, strontium, copper, iron, manganese and nickel (Figure 5.4 displays a typical profile). This is probably due to water entering the system from Lough Owel – generally regarded as being a clean lake.[130] Whereas most other elements occur in lower concentrations, sodium, potassium and zinc are present in higher concentrations in the Lough Owel Feeder than in the general water body of the canal.

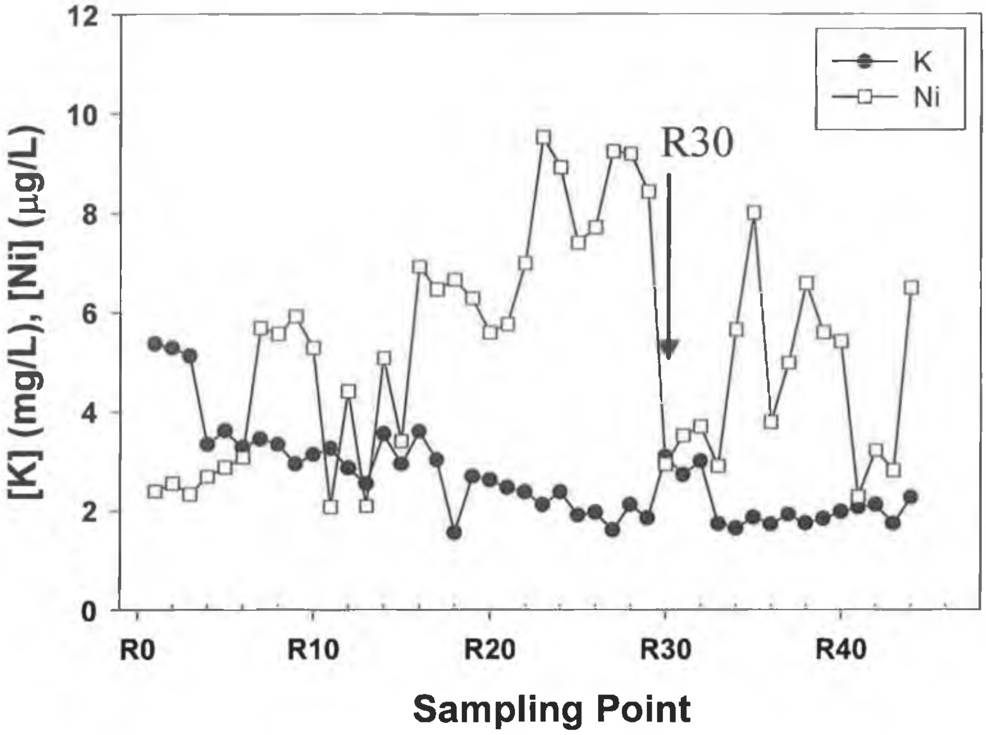

Figure 5.4: Profile of K and Ni in the Royal Canal

Another notable feature of the spatial distribution of sodium and potassium is the increase in concentration at the eastern end of the canal (R1-R3) where it joins to the salt water at the Liffey close to Dublin bay (Appendix D).

The geographical distribution of aluminium in the Royal Canal was of particular interest, given the very large relative standard deviation (Table 5.1). The levels are generally low circa 5.0 µg/L for all of its length, except in the greater Dublin region (R1-R14), where the levels reach almost 30µg/L in one case (R8). Whilst this is a factor of ten lower than the Maximum Admissible Concentration (MAC) in current drinking water regulations (Appendix A), it is interesting to note that this and many other "higher than average" results are found in samples from feeders and tributaries in the most urban section of the canal.

5.5.2.3 Grand Canal

A gradual decrease in sodium concentration westward from Dublin is seen in the spatial distribution plot for the Grand Canal (Figure 5.5 and Appendix D). There is a marked increase in the sodium concentration at the Grand Canal Basin (G1-G7) in Dublin, which would be expected due to occasional intrusions of salt-water into this area. In contrast, the magnesium concentration in this canal shows a peak at Robertstown (G22), near the Milltown Feeder, at Lowtown - the summit level of the canal - with concentrations dropping off to east and west. This trend, with a peak at the summit level is also seen for calcium and to a lesser degree for nickel. Once again, the enhancing effect of feeders due to elevated levels of some elements (e.g. sodium) and a simultaneous dilution effect on other elements (e.g. magnesium) is clearly evident at sampling sites G20 and G33. In contrast, the feeders at G20 and G31 - G33 are high in potassium and barium, and result in localised elevated levels of these elements (Figure 5.6).

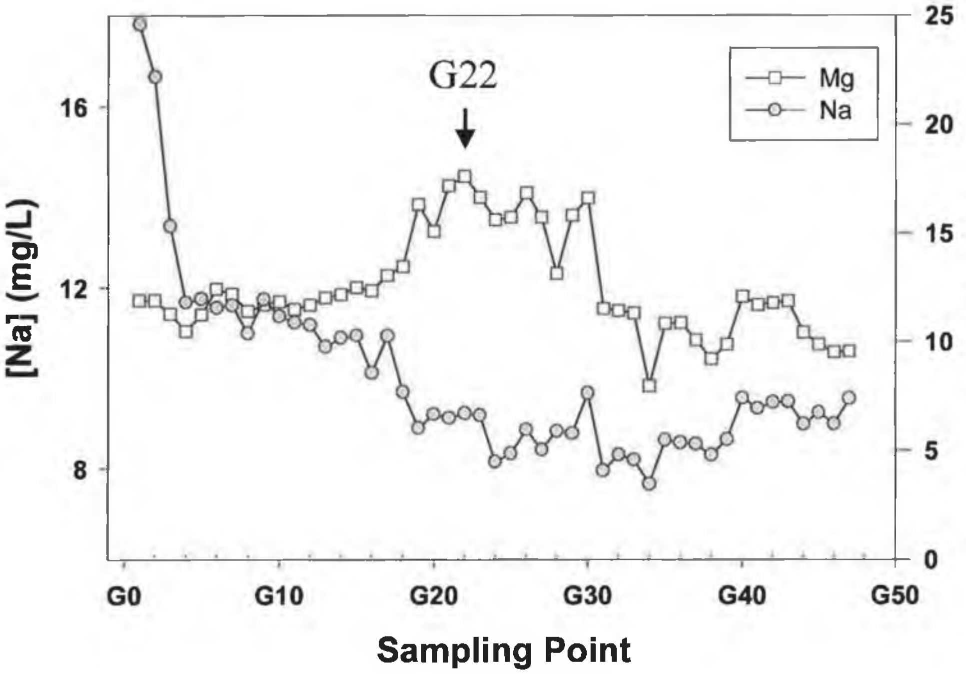

Figure 5.5: Grand canal [Mg, Na] spatial profile

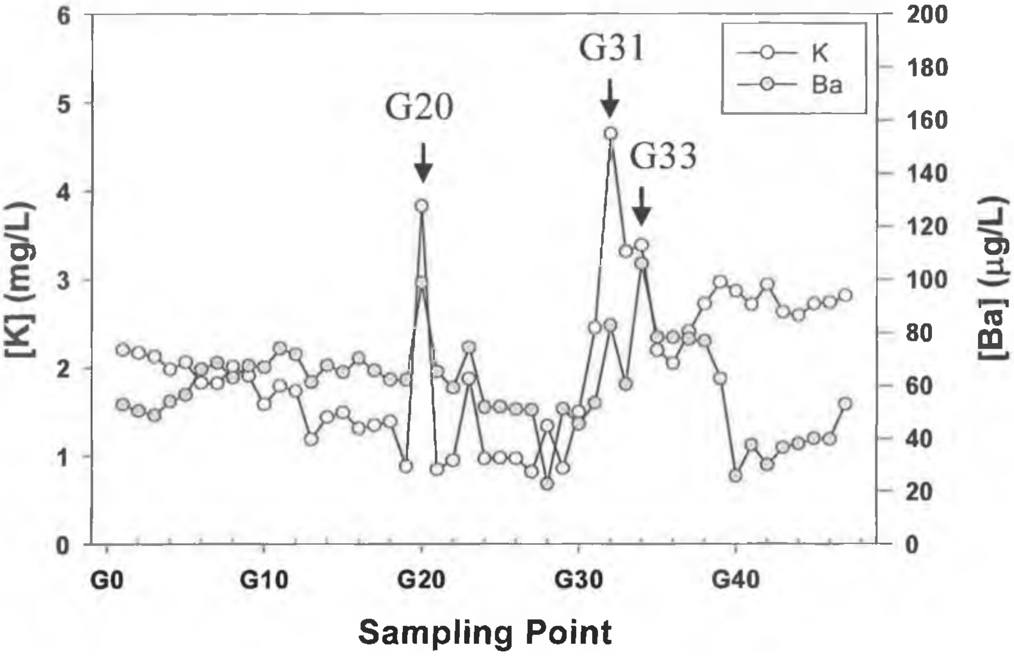

Figure 5.6: Grand canal [K, Ba] spatial profile

5.5.2.4 Barrow Canal

It can be seen that the mean concentrations of elements in the Barrow Canal are similar to those of the Grand Canal (Table 5.1). Later statistical work will illustrate the extent of the large overlap between these two systems when it was quite difficult to separate them. It is evident that the water chemistry of the Grand Canal and the Barrow Canal is very similar, which is not surprising as they arise from the same primary feeder system (the Milltown Feeder) that meets the canals at Lowtown (G25). There was no obvious common trend seen in the spatial plots of the Barrow Canal, apart from a slight rise in the levels of sodium and cobalt at the southern end, near Athy. The mean concentrations of calcium and manganese in the tributaries were found to be generally higher than the main canal channel, while those of iron and aluminium were lower. A spatial plot of the main GI/GII elements in the Barrow Canal can be seen in Appendix D.

5.5.3. Temporal variation of canals

Temporal variation proved difficult to assess in this study due to the fact that sampling was carried out at just three occasions during one specific year. These were spring, summer and autumn/winter. Nevertheless, it was interesting to note that concentrations of some elements decreased during summer, whilst others increased. E. Marengo *et al.* found that seasonally dependent species tended to be those affected by phytoplankton activity[131]. Thus, it was not expected to find much seasonal variation in the low concentration metals and transition elements. Generally, this was found to be the case, with the exception of manganese that decreased in summer. Iron, however, seemed to increase in summer.

Most interestingly, two major elements - calcium and potassium (and to a lesser extent also sodium) - showed a decrease in the summer sample. This was seen in all four canal systems and was thought to be due to biological uptake and precipitation. Indeed, Caffrey *et al.* have mentioned these two pathways in previous works on the canals where loss of nutrients in summer was observed [126,128,132]. This pattern also mirrors the trends found for hard water lakes and rivers reported in Chapters 3 and 4 respectively.

5.5.4 Statistical Analysis

5.5.4.1 Correlation

Several different correlation tests were carried out on the data. The first compared each of the four canal systems based on the mean values of the elements from Table 5.1. From observation of the results it was clear that there is always a strong similarity between the mean concentrations of elements in the Barrow and Grand Canals. The correlation coefficient between these two canals illustrates their similarity by its high value (R=0.9930), although when Group II elements and iron are omitted from the correlation test, this value drops to R=0.6486, suggesting that there are some differences that might serve as a basis for discriminating the two water bodies. The Shannon/Erne does not have a high correlation factor with any of the other three canals. Again, however, the removal of Group II elements and iron changes this and an improved correlation is seen – the highest of which is a factor of R=0.9053 with the Royal Canal (its nearest neighbour geographically). Details of all the correlation results can be seen in Appendix D.

Following these general correlations, some more detailed tests were carried out in order to investigate which particular elements displayed correlation with other elements. Tables of these results can also be seen in Appendix D. Compared to the results obtained for the lakes and rivers (Chapters 3 and 4), there was much lower correlation values found for the canals data set. (This may be due, however, to a smaller number of samples used for the comparisons). When all the data from the four canal systems was used, the highest correlations found between GI/GII elements were Ba/Mg (0.66) and Sr/Ca (0.69). There was also quite high correlation between some of the metal elements, e.g. Fe/Al (0.67), Pb/Fe (0.74) and Zn/Cu (0.64).

The data for each individual canal was then separated and a correlation test carried out. The highest correlation values were found in the calculation for the Shannon/Erne system, but in general they were not as high as the values found during the Corrib Rivers work (Chapter 4). Again, the high correlation between elements from Periodic Table Group II was noted – e.g. Sr/Ca gave a value of 0.65 in the Grand Canal samples and 0.67 in the Shannon/Erne samples. There was also high correlation between some metal elements, e.g. Zn/Cu (0.93) and Pb/Fe (0.73) in the ShannonErne. There was a very high correlation between K and Na in the Royal Canal (0.90) – this was not seen in the other canals.

In some cases, GI/GII elements had strong positive correlation with metals, e.g. Cu/Mg (0.72) and Zn/Mg (0.8) in the Shannon/Erne. (Similar observations were also made with the tests carried out on the Corrib rivers).

Although limited, this correlation work does provide a general understanding of the relationships between different elements in the canals.

5.5.4.2 Cross-validation

As was done for the lakes and rivers, cross-validation was carried out on the canals results using a variation of the "leave-one-out" method, where one result from each water body was randomly removed and the remaining data used to generate a new classification rule. The new rule was then applied to the entire data set, including those omitted, and examined for membership of the pre-determined groups. The results are illustrated in Table 5.2.

Table 5.2: Summary of Cross-Validation Results

	Royal	Grand	Barrow	Shannon/Erne
Royal	39	1	0	2
Grand	3	42	3	0
Barrow	0	3	14	0
Shannon/Erne	2	1	1	42
Total N	44	47	18	44
N Correct	39	42	14	42
Proportion	0.89	0.90	0.78	0.93

These results further illustrate the similarity between the Grand and Barrow canals. The majority of incorrectly classified measurements in each of these systems are attributed to the other. The cross-validation test also highlights the distinctive character of the Shannon/Erne system, as it has the highest proportion of correct classifications, and its two incorrectly classified samples are attributed to the Royal Canal, it's nearest neighbour geographically. This supports the results found for the correlation tests above. Because of the limited data set, more detailed cross-validation tests with sub-groups of the data - as was done for the lakes and rivers - was not carried out for the canals.

5.5.4.3. Multivariate Analysis

Principal Component Analysis (PCA) was carried out on the mean element concentrations for each sampling location on the four canal systems, and as with the lakes and river, there was no pre-treatment of the data before it was examined using Minitab®.

As expected from the high correlation between the Barrow and Grand Canals noted in section 5.5.4.1 above, a plot of PC1 Vs PC2 shows a large overlap of these two systems (Figure 5.7) and also highlights how the Shannon/Erne canal was almost perfectly discriminated from the other canals.

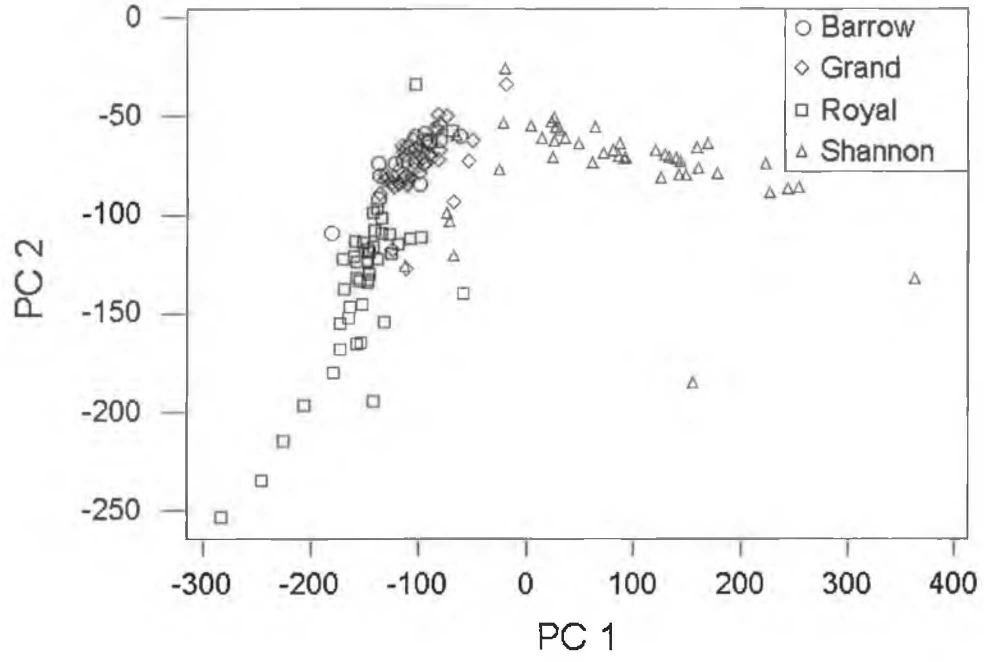

Figure 5.7: Principal Component Analysis (PCA) of canals data

A more detailed examination of Figure 5.7 reveals how the Shannon/Erne is separated well from the others in the first Principal Component, and the Royal Canal is separated in the second Principal Component. The Grand Canal displayed a certain amount of overlap with both the Barrow and Royal, due to similarities in their elemental compositions.

In order to figure out what elements were causing the discrimination and grouping in the PCA plot, Table 5.1 was examined, and it was seen that after the major elements (calcium, potassium, magnesium and sodium), strontium has the highest concentration values. This element is particularly high in the Royal Canal with a mean value of 379 μg/L and it can be assumed that this element is a major contributor to the differentiation of the Royal from the other water bodies seen in Figure 5.7.

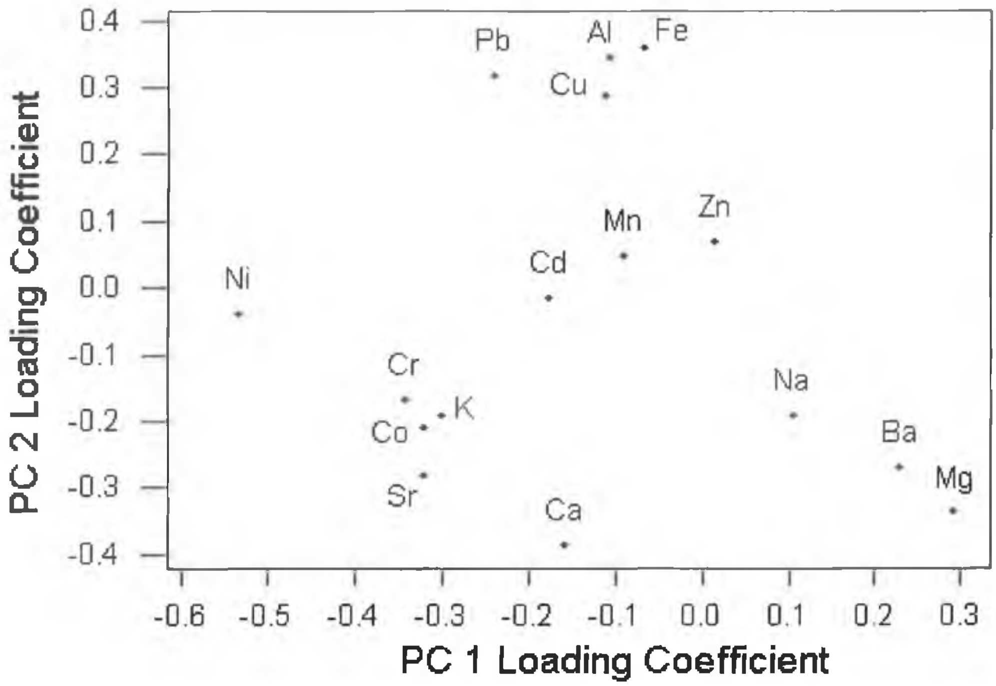

Figure 5.8: Plot of first two principal component loading coefficients

A plot was generated of the PC1 and PC2 coefficient loading values for each element (Figure 5.8). Examination of this plot shows that the PC1 coefficient is being dominated by elements such as nickel, barium and magnesium (elements with the greatest positive or negative values in PC1). The GI/GII elements in particular, are the cause of the main differentiations between the Shannon/Erne and the other three systems. Figure 5.8 also shows how PC2 is dominated by the metal elements iron, aluminium, copper and manganese to the positive side of the scale, with the GI/GII elements to the negative side of the scale. The separation in PC2 of the Royal Canal is possibly due to the different proportions of GI/GII elements in this canal compared to the Grand and Barrow (i.e. higher values for calcium and strontium, but lower values for magnesium and barium).

When periodic table Group II elements are removed from the data set, and the same PCA data exploration carried out, the discrimination between the Royal, the Barrow and the Grand is lost and the Shannon/Erne points start to diagonalise (not shown). Diagonalisation is an indication of loss of information, so it can be concluded that these elements play a particularly important role in discriminating between the four water bodies.

Although brief and sketchy, this PCA work suggests that a 'normal' profile for each canal can be defined, which could be used in the future to detect 'abnormal' or polluted conditions.

5.6 Conclusions

This investigation demonstrated that the water chemistry of Ireland's four main canal systems is distinctly different, and that using only 16 elements it is possible to differentiate between them. Results indicated how there is only slight variation in water chemistry across the length of a canal. The principal water feeder for the canal dominates the chemical content throughout each system, with localised influences from secondary feeders. The water quality in terms of the elements monitored is good, with no incidences of pollution (i.e. elements exceeding the recommendations for drinking water outlined in Appendix A).

The chemistry of the Shannon/Erne Waterway is clearly different from the other canal systems. This canal is well-separated geographically and simple observation of results show that the overall GI/GII concentration is lower in this Waterway, but the concentrations of metal elements are higher. This causes the Shannon/Erne waterway to be separated from the other systems in the statistical tests and multivariate analysis plots.

A strong correlation exists, particularly for major elements, between the results obtained for the Grand and Barrow canals, both of which receive water from the Milltown Feeder. This suggests that the major elements are derived from the main water source but minor elements have a more local origin. The Royal Canal is a separate system from both the Grand, Barrow and Shannon/Erne systems, but there are some differences in the elemental composition of this canal that allow differentiation from the others. This study demonstrates how multivariate analysis can be used to group water samples from canal systems and distinguish them from each other. It illustrates the possibility of defining a 'normal elemental profile' for these water bodies that could be used to identify 'abnormal' profiles in the future. Furthermore, geographical (spatial) plots of certain elements revealed gradual trends in concentration as well as some interesting patterns such as localised peaks and troughs. These patterns could be related to the composition of important feeders, and supports the work by Caffrey and Allison in 1998[128], which stated that nutrient concentrations declined rapidly with distance from poor quality feeders.

As an initial baseline study, this work illustrated some clear differences in the metal ion content of Irish Canal Systems. There are many possibilities for extending and improving this research by incorporating a larger suite of trace elements and considering other factors such as physico/chemical parameters, geology and human/agricultural influences. Only then will it truly be possible to create a “fingerprint” for each canal system and use this to detect environmental changes.

CHAPTER 6

6. CONCLUSIONS AND RECOMMENDATIONS

This research represents the first concentrated effort to investigate the natural concentrations of metals and trace elements occurring in a wide range of surface waters and particularly in some important fishery waters. Many hundreds of freshwater samples from rivers and lakes all over Ireland were analysed by ICP-MS in addition to the data selected for more in-depth study in this research. All the results, however, displayed similar patterns and trends. Prior to this research the most extensive study on heavy metals was carried out by the EPA and reported in 2001, but this only represented 74 individual sites.[52] The examination and interpretation of water chemistry results, which has been undertaken in this study, has provided a deeper understanding of the chemical characteristics of Irish waters that will greatly expand and compliment the information previously available. As explained at the outset, the results reported here are but a small percentage of the work carried out by the CFB during the same time period. The complete collection of results has provided a previously unavailable collection of chemical data, which will be an invaluable future reference source for the Fisheries Boards and other agencies. Data collected during this project has already contributed to the development of recent Dangerous Substances Regulations by the Department of the Environment and Local Government (DOELG).[13] The results of analyses on many previously unexamined waters was given to the DOELG and used to assess background levels in Irish rivers and lakes when the Regulations were being drafted.

Several general yet important conclusions can be drawn from this study. Firstly, as a tool for freshwater analysis, ICP-MS has proved to be excellent at measuring the very low concentrations of heavy metals found in normal natural surface waters. Its multi-element capability and speed of analysis made it a convenient tool for measurement of large numbers of parameters during regular sampling programmes. However, the ICP-MS was found to be not a particularly good instrument for measuring the higher concentration elements such as calcium, magnesium, etc… A complimentary technique such as ICP-AES or AAS should ideally be used in conjunction with ICP-MS for freshwater analysis. A possible exception to this is the analysis of acid-sensitive streams (discussed below). The ICP-MS was also found to be unsuitable for low-level iron measurements due to unavoidable interferences from argon oxide and this problem was exacerbated in hard water samples due to interference from calcium oxide.

Irish freshwaters were found to contain a wide range of different chemistries, mostly related to the geology of the bedrock. Indeed, water bodies that are quite close geographically may still have extremely different water chemistries for this reason, e.g. the rivers on the east and west of Lough Corrib. Even lakes may have variation in water chemistry at different locations due to the effects of inflowing rivers and streams, e.g. Maam Bay in Lough Corrib. Thus, it cannot be presumed that adjacent water bodies will have similar water chemistry. The canals study illustrates that even when water originates from the same source, local influences can result in changes in the chemical composition of the water body.

There is enough evidence in the results collected during this study to illustrate how water chemistry varies over the course of a year. Indeed, in cases where there was incomplete sampling across the year (e.g. canals and some of the lakes), it was difficult to interpret fully the chemistry of the water body. Where there was regular sampling across the year, it was seen how some elements increased and others decreased during the summer months. For example, calcium decreased in hard water lakes during summer, and at the same time magnesium increased in the soft water lakes. An increase in GI/GII elements in summer was also found in the soft water rivers. Aluminium and iron decreased during summer in the soft water lakes and this trend was also found for aluminium and manganese in the soft water rivers. The maxima/minima did not always occur in summer and winter – sometimes the "peaks" were found in spring or autumn (e.g. calcium in Lough Gowna).

It is clearly beneficial to carry out regular sampling over the course of a year in order to get a more accurate understanding of the range of values possible for each parameter in that water body. The temporal variation in aluminium in some lakes (Section 3.4.4) illustrates the importance of this, with values ranging from 1.00 to 143.24μg/l for Lough Garadice. This sort of annual chemical variation within a water body also highlights the danger of "once-off" sampling and putting too much reliance on the results from that one sample. A more regular sampling programme, however, can provide a very complete picture of the river/lake chemistry.

Statistical analysis can greatly aid the interpretation of large amounts of data such as was collected during this study. Indeed, the difficulty can often be in reducing the dataset to a size that is manageable for statistical analysis. Correlation tests, cross-validation analysis and principal component analysis were found to be useful tests for this type of environmental work where there is a large quantity of raw data. Interdependent elements are highlighted using correlation tests. Cross-validation provides a rigorous test of the distinctiveness of each specific sample location. Principal component analysis (following by a plotting of the scores for each site) is a good visual method to assess the grouping of different sites of similar characteristics.

Once statistical analysis has been carried out on a number of water samples, it becomes clear which samples are closely related, and which have a very different chemistry. The statistical tests such as those described above can be used to identify the expected characteristics of an unknown sample with a high degree of success.[♦] Also, the more data used to carry out the statistical tests, the more reliable the results will be. This study illustrated how broad classifications could easily be generated for Irish lakes, rivers and canals. (For example, the hard/soft water distinction in the lakes, the difference in rivers from east/west of Lough Corrib or the possibility of linking the origin of a sample to a particular canal system). Identifying sample sites on a more local level would require more input data than was available for this study.

There is potential for a much more extensive and detailed statistical study on the chemistry of Irish freshwaters.

Recommendations:

Although a large amount of information on Irish freshwater chemistry was collected over the course of this study, there is clearly an urgent need for this type or research to be expanded in order to achieve a deeper understanding of the trends and patterns in Irish water chemistry. The EPA commented in 2000 that only a minor proportion of lakes had been surveyed (Section 1.4.4).[41] The situation is the same for the many hundreds of small rivers and streams across Ireland. In the same year, the EPA also stated that a substantial survey of Irish freshwaters is required.[118] A greater understanding of water chemistry is necessary in order to assess its relationship to the

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[♦] There is always some possibility of error due to local influences that can cause changes in the chemistry of even the most similar streams.

biotic community. Water is the centre of the entire aquatic ecosystem and its condition will affect all the fauna and flora living in or near it. Whether one talks of a mountain stream or of a vast lake, the water quality still makes a vital contribution to the biotic community. (The Q-value scale takes this approach into consideration – see Section 1.4.2.2).

As much of the trace element data previously available for Irish waters was collected from once-off sampling, a more regular and widespread sampling programme would greatly improve the national database of inorganic chemical information. Whilst this would be a costly and time-consuming project for any one group to carry out, collaboration and exchange of data between universities, government and semi-state agencies and private companies would greatly add to the knowledge and understanding of Irish waters as a whole. Clearly, this co-operation between groups would need to be organised, co-ordinated and managed by an authority such as the EPA with overall responsibility for the Irish environment. The data could also be easily incorporated into the Geographical Information Systems increasingly being used by many agencies. The development of automated sampling techniques and more sensitive and reliable remote sensors for many chemical parameters could also be invaluable for helping to extend the national database of freshwater chemistry.

The difficulty in interpreting annual trends for some elements, particularly the heavy metals, shows how complex this whole subject can be. Additional physical and chemical data would help to address this problem. For example, factors which may be included into analysis of the data are: flow rates of rivers, pH values, conductivity and oxygen levels, hardness values, nutrients, amount of humic matter in the water, rainfall and temperature data, precise details of geology, bedrock and soils, information on the local area such as forestry plantations, dumps/landfills, mine ores, etc... Addition of more chemical elements would undoubtedly also assist with the interpretation of results and identification of individual sampling locations. Indeed, the very low concentration elements were sometimes overlooked during this project due to the dominance of the more common elements. Incorporation of many more trace level elements into a suite of results for each site would greatly enhance the aforementioned database. Monitoring of waters in the vicinity of new mining developments would give a greater understanding in the event of environmental impacts arising from these works (Section 1.5.3).

A detailed Irish study of the annual variation in the water chemistry of individual rivers and lakes (similar to those by Robson and Neal[114], and Nea *et al.*[115]) would also be an interesting project. Regular sampling could be followed by a calculation of the annual throughput of each element, taking account of flow rate and rainfall (as is done for the nutrients in Lough Sheelin streams by the Fisheries Boards). Each river/lake could then be given a "score" based on the ratios of different elements over different times of the year. Using these "scores" it should be possible to create a simple computer program which would store the physical and chemical "fingerprint" of each unique water body, somewhat similar to the libraries of infra-red spectra available to organic chemists to assist with identifying unknown compounds.

Should this "identification package" be designed and built on enough previously collected data, (with the capability for continuous improvement and refinement), the evidence from this research suggests that it would be reliable enough to assist in identification of unknown samples and their assignment to a probable lake or river of origin. The cross-validation work for the lakes (Section 3.4.5.2) and canals (Section 5.5.4.2) illustrates this. It should also be possible to use this "fingerprinting" software package to input known samples and assess whether the results are within normal limits for that specific system, or to perhaps determine whether the chemical results are normal for a particular time of the year. This would greatly assist management of Irish waterways, particularly as a forensic tool, but also in early identification of pollution, or in monitoring of short-term fluctuations due to human influences close to a river or lake.

It has been previously mentioned how water affects the flora and fauna that lives in or near it. Therefore, analysis of the trace element content of biological tissues can related valuable environmental and historical information about the water where growth occurred. Research in New Zealand[133], Australia[134], Sweden[135] and Peru[136] has found that analysis of calcified fish tissues can disclose much information about he life history of the fish. Otoliths (ear bones) and scales are suitable fish tissues that grow larger over the fish's lifetime and accumulate elements such as strontium in large quantities, and possibly also an elemental composition representative of the water in which the fish was living when it was growing. There are many possible methods for analysis of otoliths and one of the most useful is a laser ablation sample introduction attached to an ICP-MS which enables cross-sections of these tissues to be easily examined for many elements. Because of the range of strontium concentrations in waters of different hardness and its close association with calcium, this element has been studied previously as a possible "biomarker" for linking migrant fish to their rivers of origin.[137] The range of strontium concentrations found in Irish waters opens up the possibility of similar "biological fingerprinting" study in Ireland. Following analysis, the "fingerprinting software" suggested above for identification of waters would be an excellent tool to assist with linking the fish analysis results to the possible water body in which it was resident at various stages of its life.

Strontium isotopes have been used as "biomarkers" in North America to match fish to their rivers of origin.[137] Little difference was found between the strontium signatures of otoliths, scales and vertebrae. Similar work would be extremely useful in identifying the river of origin of fish in Lough Corrib and the other Western Lakes. Measurement of strontium in fish scales has also been suggested as a possible method of distinguishing trout that have been to sea from those that are stream resident.[138] Fish that have been to sea would have a much higher concentration of strontium in their scales than those that have remained in freshwater. Strontium analysis in otoliths has also been used in Canada to identify whether Arctic char are lake resident or anadromous (sea-run).[139]

Another possible subject for future study would be an investigation into the mixing of water within lakes of various sizes. As was described in Sections 3.4.3 and 3.4.4, lakes are dynamic systems with complex spatial and temporal variations in their trace element chemistries. It was mentioned briefly in Section 4.6.2 how lake water is affected in the vicinity of inflowing streams. A more detailed study, particularly in lakes where the tributaries have quite different chemistries, such as Lough Corrib, would greatly assist the understanding of lake mixing. Obviously, with seasonal changes in the chemistry of the tributaries, changes in the temperature of the lake water, and weather factors, this project would be complex. However, with the assistance of computer software developers, it may be possible to design a model for each lake, showing where there is greatest mixing of water, and how far from the mouth of a river its influence reaches. This sort of knowledge would be enormously beneficial for maintaining lake water quality should a specific tributary river become polluted.

Concern is increasing in Ireland about acidification of small upland streams due to the affects of forestry plantations. The availability of ICP-MS as a rapid, multi-element, low-level analysis tool is highly suited for carrying out regular monitoring of adjacent streams. Indeed, the ICP-MS is a particularly suitable tool for analysis of acid-sensitive streams, because they usually contain extremely low concentrations of GI/GII elements that may not be detectable on other analytical instruments. This is evident from the very low concentrations of calcium, magnesium and potassium reported for some of the Corrib streams in Section 4.6 and Table 4.3.

Addition of lime to streams in areas prone to acidification has been proposed in order to raise pH. In 1989 it was found that lime additions reduced mortality of invertebrates and fish in an acidic Welsh stream.[140] Extensive liming of lakes and watercourses has been carried out in Sweden since the mid 70's[141] and is related to improved reproduction of fish populations.[142] Liming of wetlands (also in Sweden) has been shown to reduce acid surges. In Norway, liming has also been carried out and has improved water quality in the River Mandal where salmon had been extinct, but have now recovered.[143] With increasing afforestation in Ireland (Section 1.5.2) and the threat of acidification mounting, there is much scope for further research in this area.

Clearly, the work carried out in this study has only provided a small insight into some of the trends and patterns of Irish freshwater chemistry. This is the first stage of what must now be a stepwise approach to increase the knowledge and understanding of the entire aquatic ecosystem. Water chemistry is not an entity on its own, but is linked to every other part of the system. Thus, it is not satisfactory to carry out water analysis after a problem has become apparent. Substances in the water may be having an impact before any obvious signs are noticed. Sub-lethal effects may never manifest (Section 1.2) but may reduce the potential of a water body. Bioaccumulation of substances in fish and plant tissues may indirectly affect organisms that are higher in the food chain. The possibilities for future research are extensive. Nevertheless, any additional knowledge such as is contained in this thesis can assist in the protection of Irish freshwater – "*a finite and vulnerable resource, essential to sustain life, development and the environment*".

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Appendix A

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CRITERIA FOR METAL LEVELS IN WATERS

(Other parameters are excluded from these lists for brevity)

A.1: DRINKING WATER QUALITY GUIDELINES

A.1.1: EUROPEAN DIRECTIVES

A.1.1.1: Directive relating to the quality of water intended for human consumption [80/778/EEC]

This Directive will be repealed on 22nd December 2003 and replaced by Council Directive [98/83/EC].

A.1.1.2: Drinking Water Directive [98/83/EC]

This Directive made significant changes to the previous 1980 Directive, and some parameters were no longer specified (e.g. metals barium, magnesium, potassium, silver, zinc and calcium). Several other metals were given more stringent values (e.g. antimony, arsenic, copper, lead, nickel and boron).

A.1.2: IRISH LEGISLATION

A.1.2.1: European Communities (Quality of Water Intended for Human Consumption) Regulations, 1988 (S.I. No. 81 of 1988)

These regulations were transposed into Irish Law on 29 April 1988 and based on EEC Directive [80/778/EEC] – see Table A-1 (below).

A.1.2.2: European Communities (Quality of Water Intended for Human Consumption) (Amendment) Regulations, 1999 (S.I. No. 350 of 1999)

This amendment made slight adjustments to the text of S.I. No. 81 of 1988 and gave further effect to EEC Directive [80/778/EEC]

A.1.2.3: European Communities (Quality of Water Intended for Human Consumption) (Amendment) Regulations, 2000 (S.I. No. 177 of 2000)

This amendment made slight adjustments to the text of S.I. No. 81 of 1988 and further effect to EEC Directive [80/778/EEC]

Table A-1: Irish Drinking Water Regulations 1988

Parameter	Parameter value	Unit
Aluminium	0.2	mg/l
Antimony	10	µg/l
Arsenic	50	µg/l
Barium	500	µg/l
Boron	2000	µg/l
Cadmium	5	µg/l
Calcium	200	mg/l
Chromium	50	µg/l
Copper	500-3000	µg/l
Iron	200	µg/l
Lead	50	µg/l
Magnesium	50	mg/l
Manganese	50	µg/l
Mercury	1	µg/l
Nickel	50	µg/l
Potassium	12	mg/l
Selenium	10	µg/l
Silver	10	µg/l
Sodium	150	mg/l
Zinc	1000-5000	µg/l

A.1.2.4: European Communities (Drinking Water) Regulations, 2000 (S.I. No 439 of 2000)

These regulations were transposed into Irish Law on 18th December 2000, and will come into force on 1st January 2004 – see Table A-2 below. They are based on EC Directive [98/83/EC]. They will revoke S.I. No. 81 of 1988 and S.I. No. 177 of 2000.

Table A-2: Irish Drinking Water Regulations 2000

Parameter	Parameter value	Unit
Aluminium	200	µg/l
Antimony	5.0	µg/l
Arsenic	10	µg/l
Boron	1.0	mg/l
Cadmium	5.0	µg/l
Chromium	50	µg/l
Copper	2.0	mg/l
Iron	200	µg/l
Lead	10	µg/l
Manganese	50	µg/l
Mercury	1.0	µg/l
Nickel	20	µg/l
Selenium	10	µg/l
Sodium	200	mg/l

A.2: FRESHWATER FISHERIES GUIDELINES

A.2.1: EUROPEAN DIRECTIVES

A.2.1.1: Directive in the quality of fresh waters needing protection or improvement in order to support fish life, 1978 [78/659/EEC]

The aim of this Directive was to protect or improve the quality of fresh waters, which support or would be capable (if pollution were reduced) of supporting fish species. Only two metals were included in the guidelines. This Directive will be integrated into the Water Framework Directive over a transitional period of 13 years.

Table A-3: EU regulations for zinc in salmonid waters 1978

Total Zinc

	Water hardness (mg/l $CaCO_3$)			
	10	**50**	**100**	**500**
Salmonid waters (mg/l Zn)	0.03	0.2	0.3	0.5
Cyprinid waters (mg/l Zn)	0.3	0.7	1.0	2.0

Table A-4: EU regulations for copper in salmonid waters 1978

Dissolved Copper

	Water hardness (mg/l $CaCO_3$)			
	10	**50**	**100**	**300**
mg/l Cu	0.005	0.022	0.04	0.112

A.2.1.2: Water Framework Directive [2000/60/EC]

This Directive which entered into force on 22nd December 2000, reforms EU water legislation by introducing a new model for water management.

A.2.2: IRISH LEGISLATION

A.2.2.1: European Communities (Quality of Salmonid Waters) Regulations, 1988 (S.I. No. 293 of 1988).

These regulations were transposed into Irish Law 18th November 1988 and based on EU Directive [78/659/EEC].

Table A-5: Irish regulations for zinc and copper in salmonid waters, 1988

Parameter	**Parameter value**	**Units**
Total Zinc	0.03-0.5 depending on water hardness	mg/l
Dissolved Copper	0.005-0.112 depending on water hardness	mg/l

A.2.3: OTHER FISHERIES & AQUATIC LIFE STANDARDS

A.2.3.1: EIFAC Recommendations

Table A-6: EIFAC Recommendations for chromium 1983

	'Soluble'	95 Percentile
Salmonid waters (µg/L)	25	100
Cyprinid waters (µg/L)	100	400

Table A-7: EIFAC Recommendations for cadmium 1977

Hardness (mg/L CaCa$_3$)	**10**	**50**	**100**	**500**
Salmonid waters (µg/L)	0.6	0.9	1	1.5
Cyprinid waters (µg/L)	20	30	38	50

Table A-8: EIFAC Aluminium recommendations

All concentrations are in µg/L

pH value	**>4.5 - <5.0**	**>5.0 - <6.0**	**>6.0**	**>6.5 - 8.0**
[Ca]<2mg/L	30	15	75	-
[Ca]>5mg/L	60	30	100	-
[Ca]>10mg/L	-	-	-	1000 (tot)

All concentrations refer to the soluble inorganic fraction of aluminium, except where indicated

A.2.3.2: US-EPA Recommendations

Table A-9: US-EPA Recommendations for iron and lead 1980

	Conc. (µg/L)	
Iron	1000	(total) for freshwater aquatic life
Lead	5	(total) for freshwater aquatic life

A.2.3.3: Miscellaneous Recommendations

Table A-10: Miscellaneous MAC's for fisheries and aquatic life

Source: *Water Quality Assessments: A Guide to the Use of Biota, Sediments and Water in Environmental Monitoring, Deborah Chapman (Editor), 1992*

	EU	Canada	Russia
Aluminium (µg/L)	-	5-100	-
Arsenic (µg/L)	-	50	-
Cadmium (µg/L)	-	0.2-1.8	5
Chromium (µg/L)	-	2-20	5-20
Cobalt (µg/L)	-	-	10
Copper (µg/L)	5-112	2-4	1
Iron (µg/L)	-	300	100
Lead (µg/L)	-	1-7	100
Manganese (µg/L)	-	-	10
Mercury (µg/L)	-	0.1	0.01
Nickel (µg/L)	-	25-150	10
Selenium (µg/L)	-	1	1.6
Zinc (µg/L)	30-2000	30	10

A.3: DANGEROUS SUBSTANCES GUIDELINES

A.3.1: EUROPEAN LEGISLATION

A.3.1.1: Dangerous Substances (discharged into the aquatic environment) Directive [76/464/EEC]

This Directive covered discharges to inland surface waters, territorial waters, inland coastal waters and ground water. Ground water was removed in 1980 under a separate Council Directive. This Directive will be integrated and eventually replaced by the Water Framework Directive over a transitional period of 13 years.

A.3.1.2: Water Framework Directive [2000/60/EC]

This Directive which entered into force on 22nd December 2000, reforms EU water legislation by introducing a new model for water management.

A.3.2: IRISH LEGISLATION

A.3.2.1: Water Quality (Dangerous Substances) Regulations, 2001 (S.I. no 12 of 2001)

These regulations were transposed into Irish Law on 1 July 2001 and gave further effect to Council Directive [76/464/EEC] and supported implementation of the Water Framework Directive [2000/60/EC].

Table A-11: Irish dangerous substances regulations 2001

Parameter	Parameter value for freshwater		Units
	Hardness < 100mg/l	Hardness > 100mg/l	
Arsenic	25	25	μg/l
Chromium	5	30	μg/l
Copper	5	30	μg/l
Lead	5	10	μg/l
Nickel	8	50	μg/l
Zinc	8-50	100	μg/l

A.4: OTHER WORLDWIDE GUIDELINES FOR METALS IN WATER

Table A-12: World Health Organisation – guidelines for drinking water quality 1996

Parameter	Guideline value	Units
Aluminium	200	μg/l
Antimony	5	μg/l
Arsenic	10	μg/l
Barium	700	μg/l
Beryllium	Not determined	
Boron	500	μg/l
Cadmium	3	μg/l
Chromium	50	μg/l
Copper	1	mg/l
Iron	300	μg/l
Lead	10	μg/l
Manganese	100	μg/l
Mercury	1	μg/l
Molybdenum	70	μg/l
Nickel	20	μg/l
Selenium	10	μg/l
Sodium	200	mg/l
Uranium	2	μg/l
Zinc	3	mg/l

Table A-13: US-EPA drinking water regulations 2002

Parameter	Guideline value	Units
Aluminium	50-200	µg/l
Antimony	6	µg/l
Arsenic	10	µg/l
Barium	2	mg/l
Beryllium	4	µg/l
Cadmium	5	µg/l
Chromium	100	µg/l
Copper	1	mg/l
Iron	300	µg/l
Lead	15	µg/l
Manganese	50	µg/l
Mercury	2	µg/l
Selenium	50	µg/l
Silver	100	µg/l
Thallium	2	µg/l
Uranium	30	µg/l
Zinc	5	mg/l

Table A-14: Miscellaneous criteria and values

Abbreviations:

DW = Drinking water
IW = Water for irrigation
MW = Marine water
FW = Surface freshwater
LW = Water for livestock

Parameter	Agency	Year	Type of water	Level/Units
Aluminium	WHO	1984	DW	0.2 mg/l
Arsenic	US EPA	1980	FW	0.440 mg/l
	US EPA	1980	DW	0.022 µg/l
		1979	DW	50 µg/l
		1979	IW	100 µg/l
	US NAS	1972	DW	0.1 mg/l
		1972	LW	0.2 mg/l
	WHO	1984	DW	0.05 mg/l
Barium	US EPA	1979	DW	1 mg/l
	US NAS	1972	DW	1 mg/l
	US NAS	1972	MW	0.5 mg/l
Beryllium	US EPA	1980	DW	0.037 µg/l
	US EPA	1979	FW	11 µg/l
	US EPA	1979	IW	100 µg/l
	US NAS	1972	MW	0.1 mg/l
Boron	US EPA	1979	IW	750 µg/l
	US NAS	1972	IW	0.75 mg/l
		1972	LW	5.0 mg/l

Parameter	**Agency**	**Year**	**Type of water**	**Level/Units**
		1979	FW	0.4 – 4.0 µg/l
		1979	MW	5.0 µg/l
	US NAS	1972	DW	10 µg/l
		1972	LW	50 µg/l
	US NAS	1977	DW	10 µg/l
	WHO	1984	DW	5 µg/l
Chromium	US EPA	1980	FW	21 µg/l
		1980	MW	1260 µg/l
		1980	DW	50 µg/l –170 mg/l (dep on valence state)
	US EPA	1979	DW	50 µg/l
		1979	FW	100 µg/l
	US NAS	1972	DW	0.05 mg/l
		1972	LW	1.0 mg/l
		1972	MW	0.01 mg/l
	WHO	1984	DW	0.05 mg/l
Cobalt	US NAS	1972	LW	1.0 mg/l
Copper	US EPA	1980	FW	12-43 µg/l (dep on hardness)
	US EPA	1980	DW	1.0 mg/l
	US NAS	1972	MW	0.01 mg/l
		1972	LW	0.5 mg/l
	US NAS	1977	DW	1.0 mg/l
	WHO	1984	DW	1.0 mg/l
Iron	US EPA	1979	DW	0.3 mg/l
		1979	FW	1.0 mg/l
	US NAS	1972	MW	0.05 mg/l
	WHO	1984	DW	0.3 mg/l
Lead	US EPA	1980	FW	0.75-20 µg/l (dep on hardness)
		1980	DW	50 µg/l
	US NAS	1972	FW	0.03 mg/l
			MW	0.01 mg/l
	US NAS	1977	DW	0.025 mg/l
Manganese	US EPA	1979	DW	50 µg/l
			MW	100 µg/l
	US NAS	1972	DW	0.05 mg/l
			MW	0.02 mg/l
	WHO	1984	DW	0.1 mg/l
Mercury	US EPA	1980	FW	1.7 ng/l
			MW	3.7 µg/l
			DW	144 ng/l
	US NAS	1972	FW/MW	0.2 µg/l
			LW	10 µg/l
	WHO	1984	DW	0.001 mg/l
Molybdenum	US NAS	1972	IW	0.01 mg/l (all soils)
			IW	0.05 mg/l (short-term)

Parameter	**Agency**	**Year**	**Type of water**	**Level/Units**
Nickel	US EPA	1980	FW	1.1-3.1 mg/l (dep on hardness)
			MW	140 µg/l
			DW	13.4 µg/l
	US NAS	1972	MW	0.002 mg/l
			IW	0.20 mg/l
			IW	2.0 mg/l
Selenium	US EPA	1980	FW	260 µg/l
			MW	410 µg/l
			DW	10 µg/l
	US NAS	1972	MW	0.005 mg/l
			LW	0.05 mg/l
	WHO	1984	DW	0.01 mg/l
Silver	US EPA	1980	FW	1.2-13 µg/l (dep. on hardness)
			MW	2.3 µg/l
			DW	50 µg/l
	US NAS	1972	MW	1 µg/l
	US NAS	1977	DW	50 µg/l
Sodium	WHO	1984	DW	200 mg/l
Thallium	US EPA	1980	DW	13 µg/l
	US NAS	1972	MW	0.05 mg/l
Uranium	US NAS	1972	MW	0.1 mg/l
Vanadium	US NAS	1972	LW	0.1 mg/l
Zinc	US EPA	1980	FW	180 –570 µg/l
			MW	170 µg/l
			DW	5 mg/l
	US NAS	1972	MW	0.02 mg/l
			LW	25 mg/l
	US NAS	1977	DW	5 mg/l
	WHO	1984	DW	5.0 mg/l

Appendix B.

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Table B.1: Sample locations on lakes with multiple sampling sites

Sample Code	Lake Name	Sampling Site Location
Melvin 1	Melvin	Off Crannog
Melvin 2	Melvin	Lareen Bay - level with Rosfriar point
Melvin 3	Melvin	West of Rusheen Point
Melvin 4	Melvin	Off Stracummer
Melvin 5	Melvin	Mid lake
Melvin 6	Melvin	Off Roosky point
Melvin 7	Melvin	Off lakeshore plantation
Melvin 8	Melvin	Off Ross point
Allua 1	Allua	Lough Allua - Inlet to Cages
Allua 2	Allua	Lough Allua - Cages
Allua 3	Allua	Lough Allua - Cages
Allua 4	Allua	Lough Allua - Cages
Allua 5	Allua	Lough Allua - 50m d/s of cages
Allua 6	Allua	Lough Allua - 50m d/s of cages
Allua 7	Allua	Lough Allua - 50m d/s of cages
Allua 8	Allua	Lough Allua - Upper Lakes
Allua 9	Allua	Lough Allua - 1st bay d/s of cages
Carra CC	Carra	Castlecarra
Carra TI	Carra	Twin Islands
Corrib Lwr	Corrib	Mid-lower basin
Corrib Upr	Corrib	Mid-upper basin
Corrib Dp	Corrib	At the deepest location of the upper basin
Conn N	Conn	North basin
Conn S	Conn	South basin
Conn Cbay	Conn	Cloghan's bay
Conn Tbay	Conn	Tolans bay
Lene 1	Lene	The exact sampling locations are unknown for this lake
Lene 2	Lene	The exact sampling locations are unknown for this lake
Lene 3	Lene	The exact sampling locations are unknown for this lake
Derra D	Derravaragh	Donore
Derra F	Derravaragh	Faughelstown
Gowna Nth	Gowna	Dernaferst North
Gowna Sth	Gowna	Dernaferst South
Oughter Eon	Oughter	Eonish
Oughter Cha	Oughter	Chalets

Table B.2: Summary of all data collected for 44 sites on 18 lakes

	AVERAGE	MAX	MIN	Std Dev	N
Ca mg/L	33.26	166.58	1.77	23.58	1364
K mg/L	2.22	11.63	0.14	1.50	1344
Mg mg/L	3.84	45.68	0.78	2.53	1525
Na mg/L	9.05	28.08	4.75	2.80	1353
Al ug/L	21.58	551.67	0.01	30.81	1376
Ba ug/L	22.58	89.78	0.03	14.15	1535
Cd ug/L	0.52	5.79	0.01	0.51	799
Co ug/L	0.43	3.44	0.01	0.49	1205
Cr ug/L	2.48	71.03	0.01	4.19	1124
Cu ug/L	1.85	46.50	0.01	2.34	1388
Fe ug/L	113.97	1143.24	0.30	135.70	1095
Mn ug/L	11.51	912.26	0.02	34.70	1469
Ni ug/L	3.09	78.36	0.03	4.89	1144
Pb ug/L	0.55	27.37	0.01	1.92	935
Sr ug/L	119.29	440.91	6.11	82.98	1549
Zn ug/L	6.99	1291.40	0.01	41.23	1172

Table B.3: Statistics for individual lake sites

A detailed table of statistics follows on the next four pages, with information on the maximum, minimum and standard deviation of each element in each lake site. This information is supplementary to the mean values for each lake reported in Table 3.2 (Chapter 3 of the main text).

Table B.3: Statistics for individual lake sites

Sample	Stat	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Allua 1	Max	13.45	1.33	3.95	10.39	249.78	5.01	1.96	1.36	4.02	1.74	195.43	160.97	3.33	0.64	26.70	27.28
	Min	2.83	0.14	0.90	5.09	4.44	1.09	0.02	0.01	0.09	0.02	3.32	0.14	0.10	0.03	6.11	0.02
	Std Dev	2.54	0.22	0.53	1.40	44.09	0.90	0.49	0.37	1.08	0.45	49.28	32.27	0.93	0.18	4.38	5.75
Allua 2	Max	11.08	1.20	2.70	10.35	234.40	4.33	1.99	1.23	35.25	5.30	258.79	60.58	14.17	0.47	18.96	1291.40
	Min	3.00	0.58	0.92	4.99	5.02	1.30	0.10	0.01	0.10	0.02	0.54	0.63	0.10	0.01	6.78	0.10
	Std Dev	1.98	0.16	0.34	1.35	41.87	0.82	0.47	0.31	9.35	1.23	72.98	17.17	4.29	0.17	3.29	239.01
Allua 3	Max	10.23	1.15	2.21	10.33	230.12	5.05	1.95	1.30	2.15	3.10	133.72	194.54	1.36	0.70	20.52	94.24
	Min	1.77	0.21	0.90	4.84	3.59	0.13	0.01	0.01	0.01	0.06	0.62	0.46	0.07	0.04	6.11	0.10
	Std Dev	1.97	0.19	0.30	1.33	41.61	0.99	0.49	0.38	0.72	0.65	35.67	35.64	0.37	0.19	3.50	16.54
Allua 4	Max	9.93	1.16	1.95	10.16	215.11	24.52	1.94	1.64	66.33	25.06	202.46	443.07	42.40	8.59	131.76	162.94
	Min	3.00	0.17	0.88	4.92	2.92	0.64	0.01	0.01	0.03	0.38	4.38	0.96	0.10	0.01	6.47	0.01
	Std Dev	1.96	0.18	0.27	1.32	39.97	3.77	0.46	0.46	13.87	4.72	43.77	74.13	8.72	1.69	19.29	31.79
Allua 5	Max	10.55	1.24	1.77	10.28	196.56	38.85	1.98	2.31	71.03	46.50	259.47	94.42	38.79	13.57	160.57	99.15
	Min	2.00	0.24	0.87	5.04	0.62	1.14	0.02	0.04	0.05	0.05	2.37	0.42	0.10	0.04	6.63	0.10
	Std Dev	2.23	0.19	0.27	1.29	37.41	6.07	0.46	0.55	15.30	8.07	54.50	18.85	9.29	3.07	23.86	18.81
Allua 6	Max	10.60	1.21	1.83	10.27	210.93	12.02	1.95	2.33	41.96	11.83	122.00	200.68	25.55	3.18	52.55	51.77
	Min	2.00	0.56	0.78	4.79	0.43	0.03	0.01	0.02	0.06	0.04	16.23	0.79	0.10	0.04	6.61	0.06
	Std Dev	2.14	0.17	0.27	1.37	39.95	1.85	0.49	0.64	8.79	1.93	29.02	34.48	5.58	0.68	7.07	13.05
Allua 7	Max	10.73	1.34	1.95	10.23	206.37	11.44	1.95	1.59	44.15	17.77	153.03	241.39	17.65	5.40	70.98	157.48
	Min	2.99	0.54	0.82	4.75	3.37	0.69	0.02	0.02	0.04	0.12	3.67	0.68	0.09	0.04	6.55	0.01
	Std Dev	1.90	0.18	0.26	1.36	36.08	2.08	0.60	0.40	9.43	2.97	32.56	51.20	4.51	1.32	9.84	39.00
Allua 8	Max	18.19	1.42	2.09	12.64	122.85	8.94	1.12	2.37	3.96	4.93	273.57	285.48	7.53	0.46	42.95	359.78
	Min	3.34	0.51	0.98	5.55	1.00	1.75	0.08	0.06	0.10	0.34	11.88	0.84	0.05	0.02	11.39	0.10
	Std Dev	4.23	0.25	0.31	1.67	27.99	1.78	0.28	0.61	1.31	1.06	74.24	48.07	2.30	0.13	6.96	72.92
Allua 9	Max	10.24	1.12	1.74	10.38	92.56	5.14	1.40	2.33	3.09	4.82	122.37	49.31	3.05	0.52	21.33	75.06
	Min	3.16	0.55	0.93	5.00	2.74	0.97	0.01	0.03	0.10	0.22	11.13	0.49	0.03	0.05	8.76	0.10
	Std Dev	1.77	0.15	0.22	1.30	23.97	0.97	0.35	0.61	0.84	1.09	33.00	11.22	0.85	0.15	2.62	14.89
Arrow	Max	103.93	3.46	8.94	14.40	20.18	54.05	2.68	2.33	8.48	4.13	481.08	32.08	15.01	0.82	169.48	23.63
	Min	30.08	0.97	2.78	7.09	0.26	19.68	0.01	0.03	0.06	0.22	5.43	0.28	0.04	0.01	64.91	0.10
	Std Dev	13.05	0.46	0.97	1.72	4.74	5.43	0.57	0.54	2.54	0.95	145.53	7.28	2.65	0.23	18.17	5.10
Carra CC	Max	123.34	5.75	5.82	28.08	15.92	30.41	1.76	1.26	16.02	24.45	1143.24	2.99	15.13	3.15	323.49	24.59
	Min	33.85	1.97	1.83	7.99	0.88	11.49	0.05	0.01	0.55	0.19	3.64	0.19	0.28	0.01	73.46	0.12
	Std Dev	22.90	0.69	0.84	3.58	3.24	3.18	0.50	0.30	3.22	4.00	285.62	0.78	2.66	0.90	45.93	5.27
Carra TI	Max	127.77	5.60	6.73	27.56	89.66	35.11	1.85	0.89	18.54	13.20	1116.09	10.27	17.90	8.81	348.39	73.95
	Min	36.00	1.88	2.36	8.02	0.67	12.18	0.01	0.01	0.30	0.08	1.86	0.13	0.35	0.01	123.41	0.20
	Std Dev	25.43	0.69	0.92	3.51	15.41	4.07	0.56	0.23	3.55	2.91		1.86	2.97	1.71	36.98	13.48

Table B.3: Statistics for individual lake sites

Sample	Stat	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Corrib Lwr	Max	166.58	3.47	5.80	15.91	23.72	36.45	1.55	1.04	13.00	5.37	831.76	9.12	18.26	1.19	440.91	36.18
	Min	11.87	1.27	1.33	8.09	0.40	8.42	0.01	0.02	0.28	0.01	3.54	0.43	0.04	0.02	35.88	0.10
	Std Dev	30.88	0.47	0.82	1.88	5.46	6.15	0.47	0.28	2.99	1.13	179.18	2.31	3.34	0.31	71.40	8.07
Corrib Upr	Max	108.52	2.49	4.23	15.58	33.23	41.85	1.31	1.35	9.34	2.54	489.72	26.97	13.84	0.46	164.71	40.72
	Min	30.13	1.08	1.34	5.60	1.26	15.39	0.01	0.01	0.08	0.08	0.68	0.51	0.20	0.02	34.59	0.15
	Std Dev	14.50	0.32	0.54	1.96	5.61	5.02	0.38	0.38	1.94	0.60	115.05	5.04	2.52	0.13	20.85	8.01
Corrib Dp	Max	103.55	2.56	5.22	16.04	16.02	64.59	1.38	1.48	9.55	16.10	765.56	54.26	14.69	1.72	239.42	24.23
	Min	31.86	1.18	1.34	7.45	0.14	15.09	0.04	0.02	0.07	0.07	6.17	0.16	0.03	0.02	32.24	0.03
	Std Dev	13.44	0.34	0.64	1.92	3.34	7.19	0.42	0.38	2.35	2.54	167.73	8.56	2.91	0.43	28.83	6.53
Conn N	Max	84.85	2.40	5.40	21.60	78.83	41.86	1.94	1.71	7.54	11.12	562.42	34.18	13.70	1.58	262.83	114.51
	Min	29.00	1.17	2.70	7.49	0.04	20.54	0.03	0.01	0.02	0.03	6.38	0.47	0.61	0.03	158.96	0.14
	Std Dev	11.66	0.29	0.63	2.77	14.45	3.74	0.52	0.45	2.09	1.88	129.47	6.87	2.38	0.34	24.38	19.48
Conn S	Max	82.07	2.24	5.78	20.20	30.31	42.59	1.95	1.43	7.57	8.85	565.49	9.88	14.13	2.07	273.65	43.69
	Min	30.07	1.22	2.56	8.34	2.41	19.05	0.04	0.01	0.36	0.01	9.28	0.02	0.05	0.01	120.71	0.02
	Std Dev	10.81	0.30	0.68	2.51	6.05	3.81	0.50	0.29	1.85	1.36	124.93	2.51	2.43	0.43	27.86	10.03
Conn Cl B	Max	88.98	2.26	5.84	19.77	294.56	86.89	1.94	1.72	7.73	9.65	557.54	91.24	13.02	0.81	323.58	52.25
	Min	30.27	1.22	3.05	7.44	3.83	18.19	0.01	0.01	0.28	0.04	1.00	0.11	0.42	0.01	179.68	0.04
	Std Dev	11.87	0.30	0.67	2.57	45.74	9.36	0.45	0.35	2.04	1.74	136.39	17.56	2.74	0.18	31.71	9.61
Conn To B	Max	89.97	2.80	6.32	22.28	551.67	89.78	1.92	2.23	8.59	16.07	666.16	912.26	19.88	2.29	292.41	35.17
	Min	25.49	1.14	2.76	7.68	4.78	18.90	0.02	0.02	0.18	0.01	20.01	0.11	0.31	0.01	137.68	0.11
	Std Dev	12.32	0.33	0.79	2.73	82.66	9.63	0.44	0.50	2.54	2.56	164.50	139.46	3.88	0.46	34.68	8.45
Mel-1	Max	29.45	1.37	3.71	11.80	19.10	25.32	0.65	0.71	1.16	9.27	107.65	2.41	1.51	0.29	170.33	7.44
	Min	22.42	1.01	2.57	8.58	1.07	18.01	0.11	0.05	0.33	0.36	26.71	0.38	0.37	0.06	98.88	1.50
	Std Dev	2.31	0.11	0.34	1.12	6.38	2.09	0.22	0.26	0.37	3.31	29.10	0.67	0.57	0.09	21.18	2.75
Mel-2	Max	27.95	1.37	3.58	11.56	22.38	25.58	0.54	0.59	1.68	7.91	99.34	1.93	1.44	0.42	166.98	136.35
	Min	21.63	0.95	2.46	8.28	1.13	16.52	0.17	0.04	0.63	0.28	5.28	0.06	0.89	0.03	97.09	0.82
	Std Dev	1.97	0.13	0.30	1.19	6.54	2.57	0.18	0.14	0.33	3.10	32.36	0.73	0.21	0.19	21.18	49.72
Mel-3	Max	29.03	1.40	3.56	11.49	15.28	26.13	0.83	0.72	3.87	6.87	110.40	1.80	1.78	0.28	164.44	6.80
	Min	21.67	0.98	2.47	8.34	3.37	17.55	0.19	0.03	0.03	0.25	59.51	0.17	0.85	0.03	97.90	1.43
	Std Dev	2.42	0.12	0.31	1.22	4.52	2.42	0.37	0.19	1.60	2.54	23.62	0.61	0.37	0.11	20.06	2.60
Mel-4	Max	31.11	1.38	3.54	11.43	19.57	25.08	0.19	0.75	3.73	7.40	112.13	1.27	1.73	0.24	164.69	4.45
	Min	20.52	1.06	2.65	8.79	1.74	17.68	0.05	0.19	0.95	0.56	3.10	0.32	0.03	0.05	97.36	0.32
	Std Dev	3.17	0.11	0.26	1.16	6.23	2.19	0.06	0.19	1.23	2.59	36.50	0.40	0.74	0.07	20.46	1.92
Mel-5	Max	27.76	1.35	3.45	11.39	20.37	26.96	0.44	0.55	3.01	6.84	117.71	1.99	1.95	0.30	164.11	4.76
	Min	21.45	0.96	2.40	8.05	1.05	17.34	0.44	0.01	0.60	0.68	29.61	0.08	0.43	0.01	95.54	1.39
	Std Dev	2.15	0.12	0.30	1.20	6.97	2.82	#DIV/0!	0.21	0.79	2.35	30.54	0.74	0.71	0.11	20.89	1.53

Table B.3: Statistics for individual lake sites

Sample	Stat	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Mel-6	Max	28.77	1.43	3.67	11.88	20.10	27.44	1.22	1.00	3.83	15.75	123.86	2.17	1.75	0.51	164.59	15.37
	Min	21.13	1.00	2.42	8.07	3.83	16.77	0.01	0.13	0.24	0.39	2.25	0.52	0.84	0.01	98.66	0.76
	Std Dev	2.58	0.14	0.33	1.28	5.76	3.28	0.46	0.25	1.30	6.08	46.57	0.68	0.39	0.24	20.27	6.80
Mel-7	Max	28.12	1.66	3.50	11.79	19.52	26.26	1.38	1.03	3.28	8.08	155.16	1.89	3.47	0.29	167.46	7.19
	Min	21.02	1.03	2.46	8.24	3.84	17.88	0.03	0.05	1.68	0.37	5.44	0.04	0.24	0.09	98.05	1.20
	Std Dev	2.54	0.20	0.29	1.15	6.42	2.46	0.64	0.29	0.81	2.79	51.88	0.65	1.21	0.09	21.05	2.56
Mel-8	Max	29.09	1.46	3.55	11.99	19.06	27.46	2.06	1.16	3.93	7.85	101.70	1.74	2.04	0.32	165.46	7.15
	Min	20.35	0.98	2.50	8.13	0.99	16.71	0.07	0.07	0.46	0.65	8.20	0.19	0.35	0.25	98.48	0.26
	Std Dev	2.87	0.15	0.29	1.16	6.26	3.29	0.98	0.35	1.10	3.11	30.96	0.59	0.59	0.04	20.29	3.08
Mask	Max	86.96	3.09	5.03	17.85	95.93	58.85	1.39	1.08	10.81	12.53	831.23	38.80	16.41	5.12	252.83	63.11
	Min	34.42	1.33	1.38	6.28	0.58	19.97	0.01	0.04	0.19	0.19	1.92	0.10	0.26	0.01	60.93	0.06
	Std Dev	13.42	0.45	0.70	2.27	15.58	6.79	0.44	0.29	2.39	2.74	198.08	6.82	2.93	1.51	29.09	13.58
Sheelin	Max	142.13	4.39	12.25	10.41	16.92	58.28	1.07	2.53	6.52	3.18	486.81	19.12	6.58	2.90	183.93	48.78
	Min	36.00	2.82	7.71	6.82	1.36	45.02	0.12	0.01	0.02	0.08	14.03	0.11	0.05	0.01	151.07	0.54
	Std Dev	20.72	0.40	1.07	0.91	5.14	3.40	0.38	0.60	1.90	0.79	152.39	4.76	1.59	0.95	9.22	18.62
Gowna N	Max	24.29	4.38	4.76	10.53	26.45	20.28	5.79	1.08	3.35	4.32	197.56	64.63	76.71	9.15	80.05	32.90
	Min	7.04	2.38	2.35	5.68	0.78	6.92	0.10	0.02	0.03	0.68	0.43	0.32	0.10	0.04	38.53	0.10
	Std Dev	3.89	0.55	0.58	1.41	5.70	3.25	1.15	0.25	1.00	0.84	51.51	15.51	11.81	1.57	11.09	5.43
Lavey	Max	61.46	4.93	8.72	10.96	35.88	59.30	1.42	2.82	7.49	3.00	402.85	59.61	9.20	11.77	156.26	40.64
	Min	16.50	2.51	3.87	5.98	0.10	21.54	0.02	0.07	0.10	0.34	3.90	0.71	0.10	0.03	80.00	0.10
	Std Dev	10.37	0.58	1.11	1.31	7.58	7.66	0.37	0.69	1.58	0.72	118.35	12.79	1.52	2.07	18.74	6.93
Naback	Max	27.72	3.46	5.40	8.96	57.10	34.02	1.85	3.44	6.75	5.15	340.25	23.89	14.08	15.91	169.15	65.27
	Min	7.15	1.46	2.65	4.87	2.76	8.36	0.02	0.06	0.10	0.20	9.45	0.91	0.10	0.02	28.99	0.10
	Std Dev	5.32	0.52	0.73	1.32	12.83	4.69	0.54	0.71	1.53	0.89	83.08	6.95	2.26	2.87	31.69	10.58
Gowna S	Max	42.44	4.21	6.70	11.30	53.00	33.64	1.33	1.56	3.69	6.87	350.72	39.14	78.36	15.24	170.75	45.43
	Min	9.00	2.27	3.22	5.90	0.38	6.98	0.10	0.02	0.10	0.45	2.39	0.08	0.10	0.01	46.06	0.10
	Std Dev	7.53	0.54	0.84	1.41	11.06	5.60	0.35	0.36	0.99	1.22	101.44	9.83	11.75	2.71	27.11	7.57
Garadice	Max	42.49	2.17	4.25	10.12	143.24	20.39	1.45	1.89	4.02	13.07	765.40	51.57	37.92	12.68	194.99	50.42
	Min	7.83	1.14	2.12	5.10	1.00	8.56	0.02	0.03	0.10	0.40	2.04	0.50	0.15	0.01	31.81	0.09
	Std Dev	8.04	0.29	0.56	1.41	28.07	2.66	0.40	0.43	1.18	2.09	174.94	8.96	5.54	2.60	29.07	9.19
Ought Eon	Max	50.92	5.35	6.70	15.71	66.80	41.94	1.59	2.56	5.26	6.56	423.87	58.17	29.28	11.12	193.45	21.72
	Min	11.21	2.68	2.94	6.84	0.74	25.17	0.04	0.01	0.04	0.52	5.52	0.79	0.13	0.02	83.00	0.04
	Std Dev	8.05	0.73	0.90	2.41	15.07	4.36	0.35	0.57	1.33	1.18	108.27	13.87	4.24	2.22	29.69	3.76
Ought Cha	Max	53.02	5.28	7.12	19.16	79.05	44.99	2.09	2.34	6.81	4.94	450.10	112.02	33.95	16.69	239.14	33.89
	Min	11.84	2.64	3.03	6.27	0.10	24.53	0.01	0.01	0.06	0.63	7.10	0.42	0.26	0.01	78.89	0.10
	Std Dev	8.60	0.77	0.93	3.11	17.55	4.35	0.59	0.54	1.58	1.04	119.29	24.82	4.84	2.80	32.82	5.49

Table B.3: Statistics for individual lake sites

Sample	Stat	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Whitelake	Max	47.97	9.60	6.69	14.82	52.22	32.69	1.63	2.67	6.46	4.90	486.44	184.43	32.35	21.75	127.65	61.12
	Min	11.34	3.67	2.54	6.09	0.01	10.82	0.02	0.04	0.10	0.49	4.38	0.42	1.75	0.01	33.03	0.10
	Std Dev	8.94	1.32	0.90	2.09	14.79	4.43	0.40	0.66	1.37	1.12	129.00	29.92	4.43	3.81	19.80	12.31
Sillan	Max	47.01	11.63	5.62	11.76	26.14	28.49	2.11	2.77	4.63	4.05	226.51	241.07	18.49	13.91	105.91	27.78
	Min	6.34	2.94	2.76	5.70	0.10	17.06	0.05	0.07	0.10	0.11	2.24	0.39	0.10	0.02	55.16	0.10
	Std Dev	7.75	1.79	0.76	1.70	6.36	3.39	0.55	0.74	1.13	0.83	58.31	55.30	2.85	3.09	15.53	4.56
Annamak	Max	68.85	7.35	5.47	12.03	27.88	32.63	1.90	2.80	8.13	3.38	386.34	25.43	10.92	27.37	140.16	24.17
	Min	16.50	4.60	2.87	5.95	0.88	17.31	0.10	0.01	0.10	0.04	0.43	0.03	0.05	-0.07	61.86	0.10
	Std Dev	10.59	0.89	0.67	1.64	4.84	3.68	0.47	0.71	1.80	0.67	119.91	6.61	2.01	4.97	17.00	6.07
Lene 1	Max	80.03	1.43	5.24	8.00	27.00	13.88	1.22	1.01	8.74	1.51	190.13	48.56	15.61	0.39	308.41	8.46
	Min	27.35	0.87	3.21	5.25	0.82	8.22	0.05	0.05	0.13	0.01	0.30	0.23	0.92	0.01	203.51	0.10
	Std Dev	13.55	0.17	0.64	0.91	7.17	1.43	0.38	0.34	2.51	0.42	78.31	12.54	3.31	0.14	30.75	2.73
Lene 2	Max	66.30	1.46	5.11	7.99	22.75	18.38	2.18	1.34	8.32	1.12	193.41	35.98	14.20	0.46	299.00	7.96
	Min	29.44	0.86	3.35	5.33	1.27	9.01	0.05	0.02	0.33	0.03	8.67	0.19	0.63	0.02	197.68	0.09
	Std Dev	9.26	0.17	0.54	0.91	5.95	2.01	0.72	0.40	2.81	0.30	67.31	9.72	3.09	0.16	27.16	2.51
Lene 3	Max	64.81	1.47	5.06	8.04	14.50	31.27	1.16	1.74	8.43	1.29	198.95	31.68	14.44	0.53	281.50	6.80
	Min	28.81	0.88	3.36	5.31	0.21	9.29	0.04	0.04	0.58	0.15	6.28	1.19	0.05	0.01	191.28	0.28
	Std Dev	9.16	0.18	0.53	0.89	4.76	4.55	0.32	0.54	2.86	0.38	80.35	8.42	3.21	0.17	26.39	2.19
Derra D	Max	125.01	3.32	11.40	10.18	15.65	64.55	1.29	1.55	15.78	3.55	366.29	25.38	31.28	0.28	364.22	85.35
	Min	52.62	1.91	7.46	6.95	0.48	35.33	0.01	0.05	0.73	0.06	1.42	0.23	0.46	0.01	244.65	0.38
	Std Dev	18.78	0.41	1.03	0.96	4.10	6.37	0.47	0.45	4.33	0.76	141.39	6.26	6.67	0.09	36.35	19.50
Derra F	Max	129.52	3.24	10.58	9.98	22.10	54.49	1.23	1.42	16.95	2.82	394.39	17.44	32.79	0.39	402.62	24.53
	Min	41.76	1.93	7.34	6.85	0.57	36.33	0.03	0.02	0.48	0.14	5.04	0.06	0.73	0.02	267.61	0.11
	Std Dev	20.92	0.42	0.99	1.05	4.94	5.03	0.31	0.39	4.55	0.72	151.37	4.88	7.46	0.14	38.01	6.02

SPATIAL VARIATION

The following plots are related to the discussion in Section 3.4.2 and represent visually the spatial variation for each element within the lakes studied, and a brief discussion of the trends that are observed. The mean values reported in Table 3.2 were used to generate these plots. Standard deviations are as reported in Table B.3 above.

Calcium

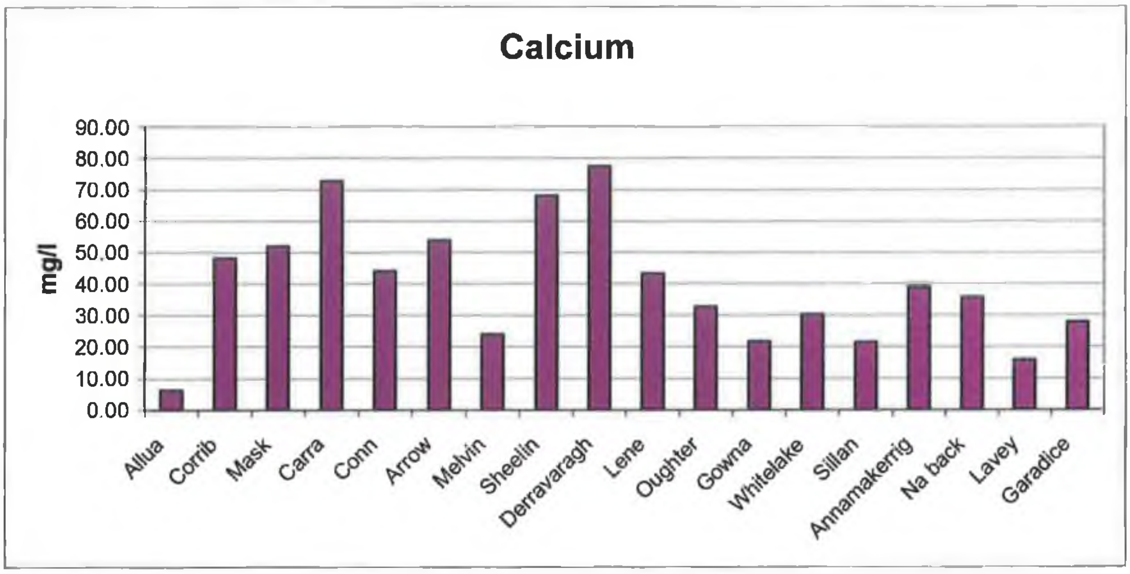

Figure B.1: Spatial variation in total mean calcium conc. in the 18 lakes

Lough Derravaragh and Lough Carra have the highest concentrations of the 18 lakes measured (>70mg/L), with Lough Sheelin just slightly less than this.
After these, the Western lakes follow with high concentrations – Arrow and Mask (>50mg/L), Corrib, Conn and also Lene (a close neighbour of Derravaragh) all >40mg/L. The remaining lakes all have concentrations less than 40mg/L. Melvin, Lavey and Allua have the lowest concentrations of calcium.

Potassium

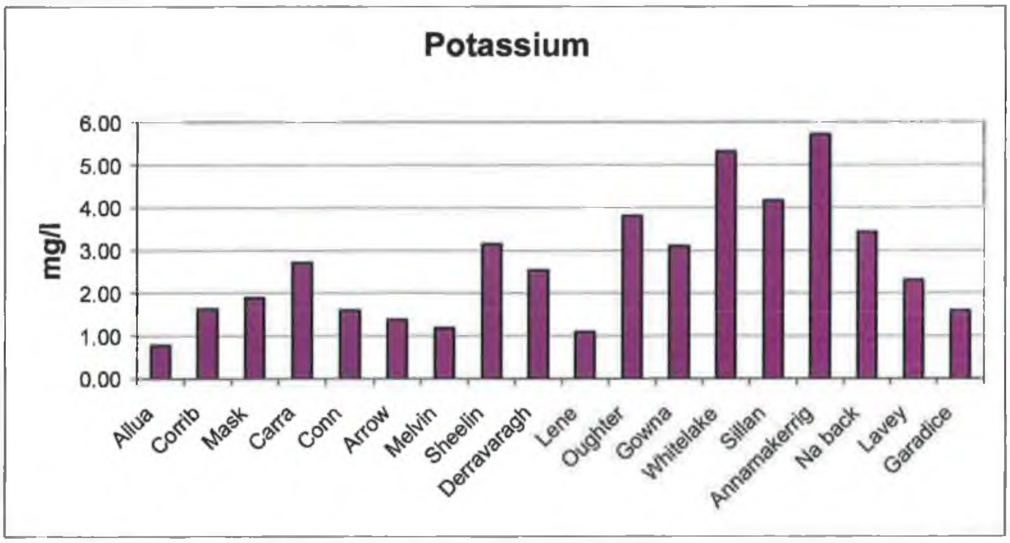

Figure B.2: Spatial variation in total mean potassium conc. in the 18 lakes

The Cavan/Monaghan lakes showed the highest concentrations of this element, particularly Annamakerrig and Whitelake (>5mg/L), closely followed by Sillan (>4mg/L). Sheelin, Oughter, Gowna and Naback also showed high levels of potassium. Of the western lakes, Carra had the highest concentration of potassium, the other lakes all had values <2mg/L. The lowest levels were found in Allua, Lene and Melvin.

Magnesium

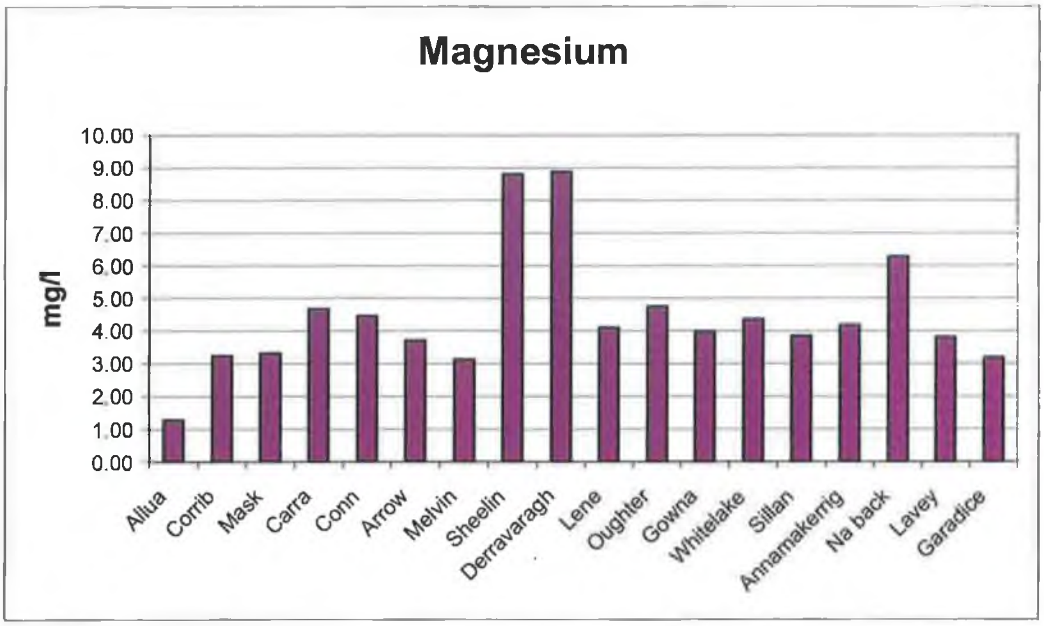

Figure B.3: Spatial variation in total mean magnesium conc. in the 18 lakes

Sheelin and Derravaragh had by far the greatest values for magnesium (>8mg/L), at more than twice the concentrations found in most of the other lakes. Lough na back also had quite a high value (>6mg/L). All the remaining lakes had a magnesium level between 3-5mg/L, with the exception of Allua which had the lowest value >1mg/L.

Sodium

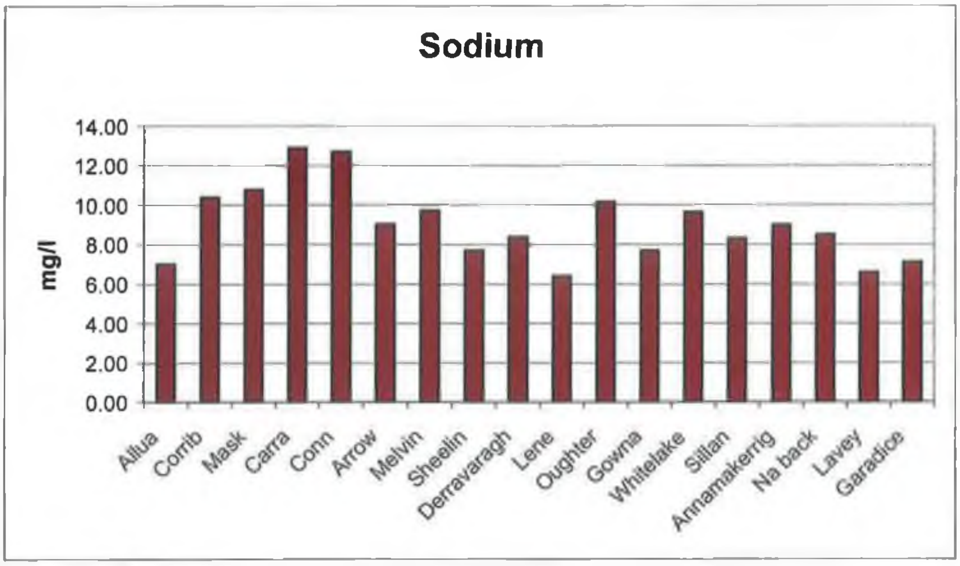

Figure B.4: Spatial variation in total mean sodium conc. in the 18 lakes

The highest levels of sodium were found in the Mayo lakes Conn and Carra (>12mg/L), closely followed by the other two main western lakes Corrib and Mask (>10mg/L). Oughter also had a value marginally >10mg/L.
The lowest concentration was found in Lene, which along with Garadice, Lavey, Allua, Sheelin and Gowna all had values <8mg/L.

Aluminium

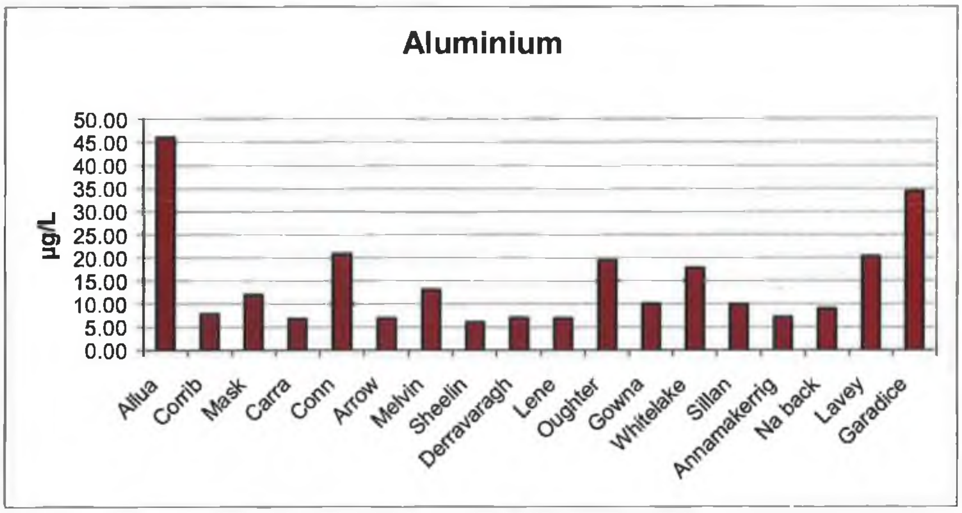

Figure B.5: Spatial variation in total mean aluminium conc. in the 18 lakes

Lough Allua had by far the greatest concentration of aluminium and >45μg/L. Garadice was the second highest, with a value >30μg/L. Conn, Oughter, Whitelake and Lavey all had intermediate values >15μg/L, and Melvin and Mask had values >10μg/L. All the other lakes had low aluminium <10μg/L.

Barium

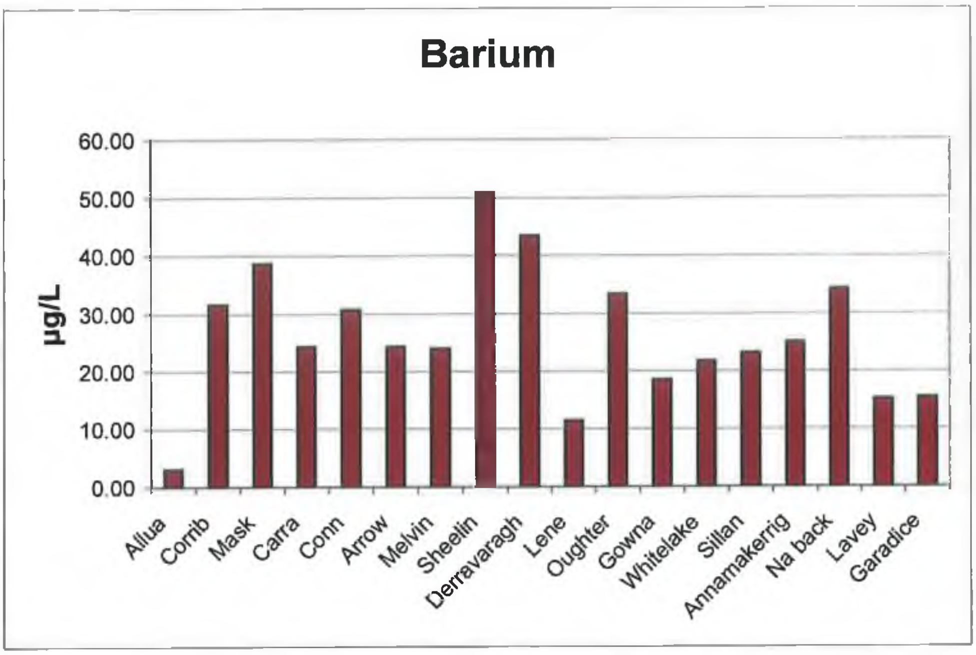

Figure B.6: Spatial variation in total mean barium conc. in the 18 lakes

Sheelin and Derravaragh had the greatest values for barium (>40µg/L), and then the western lakes Corrib, Mask and Conn along with the midland lakes Oughter and Na back (all >30µg/L).
The lowest concentrations were found in Allua (<10µg/L), Lene, Lavey, Garadice and Gowna (all <20µg/L).

Cadmium

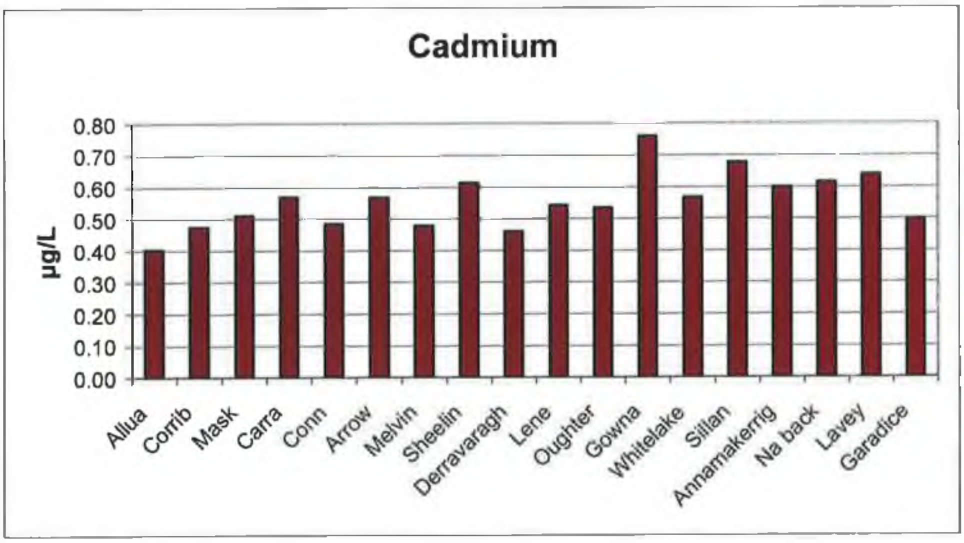

Figure B.7: Spatial variation in total mean cadmium conc. in the 18 lakes

There was little variation in the cadmium concentrations. All the mean values ranged between 0.4 and 0.8 µg/L. However, the lower values seem to be found in the western lakes and also the lakes with the hardest water, with the exception of Lough Allua which had the lowest concentration of cadmium in all the lakes studied.

Cobalt

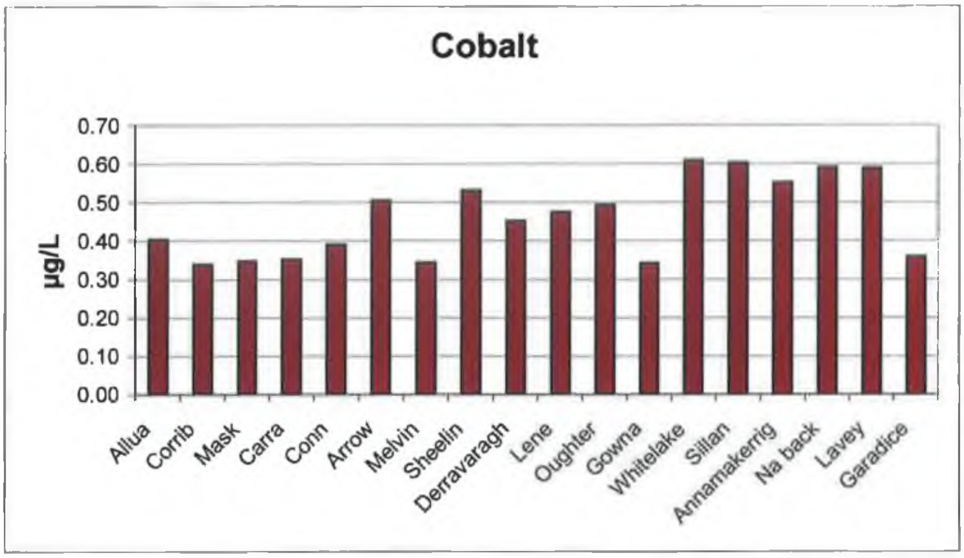

Figure B.8: Spatial variation in total mean cobalt conc. in the 18 lakes

There was little variation in the cobalt concentrations. All the mean values ranged between 0.3 and 0.7 µg/L. Similar to cadmium, lower values were found in the western lakes, but unlike cadmium the softer water lakes have the lowest values (e.g. Garadice, Gowna, Melvin). Again, Lough Allua is an exception to this pattern with a cobalt value >0.4µg/L.

Chromium

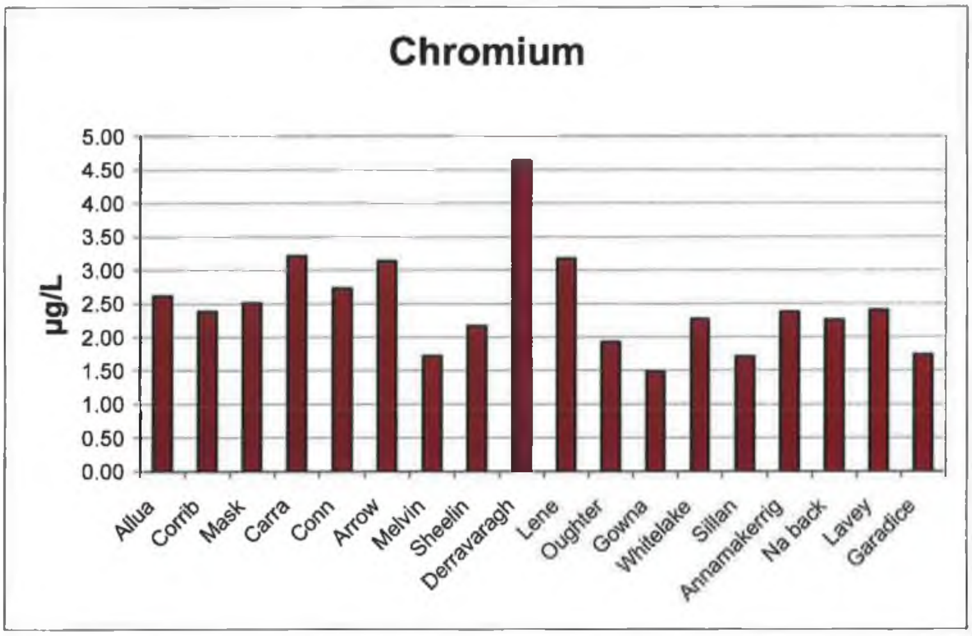

Figure B.9: Spatial variation in total mean chromium conc. in the 18 lakes

The highest values of chromium are found in the hard water lakes such as Derravaragh, Arrow, Lene and Carra (all >3µg/L). The lowest values are found in the softer waters of Melvin, Oughter, Gowna, Sillan and Garadice (all <2µg/L). However, the softest water lake – Lough Allua – is an exception to this rule with a value >2.5µg/L.

Copper

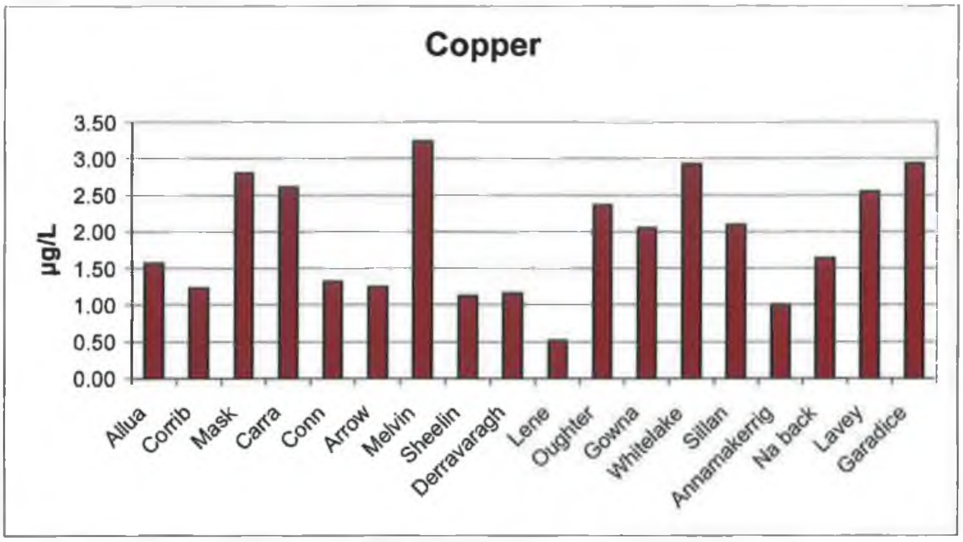

Figure B.10: Spatial variation in total mean copper conc. in the 18 lakes

This element has an unusual distribution across the lakes, with no clear pattern emerging. Values range from 0.5-3.5µg/L, and both high and low values are found in waters of both high and low hardness.
The lowest concentration of copper was found in Lough Lene (<1.0ppn), and the highest in Lough Melvin (>3µg/L). Mask, Carra, Whitelake, Lavey and Garadice also had high values (>2.5µg/L).

Iron

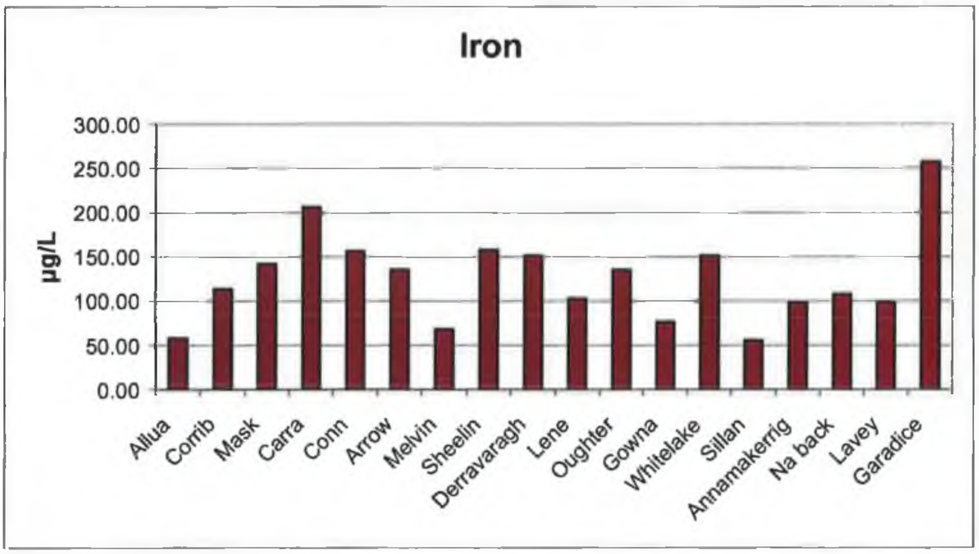

Figure B.11: Spatial variation in total mean iron conc. in the 18 lakes

The lowest values for iron were found in the softest water lakes – Allua, Melvin, Gowna, Sillan, Annamakerrig and Lavey (all with Fe <100µg/L). The exception to this was Lough Garadice – a soft water lake, but that which contained the highest iron concentration (>250µg/L). This is discussed in the main text as being due to its location close to an area rich in iron mineral deposits.
Lough Carra also had quite high concentrations of iron. The reason for this is unclear as the other western lakes had much lower values.

Manganese

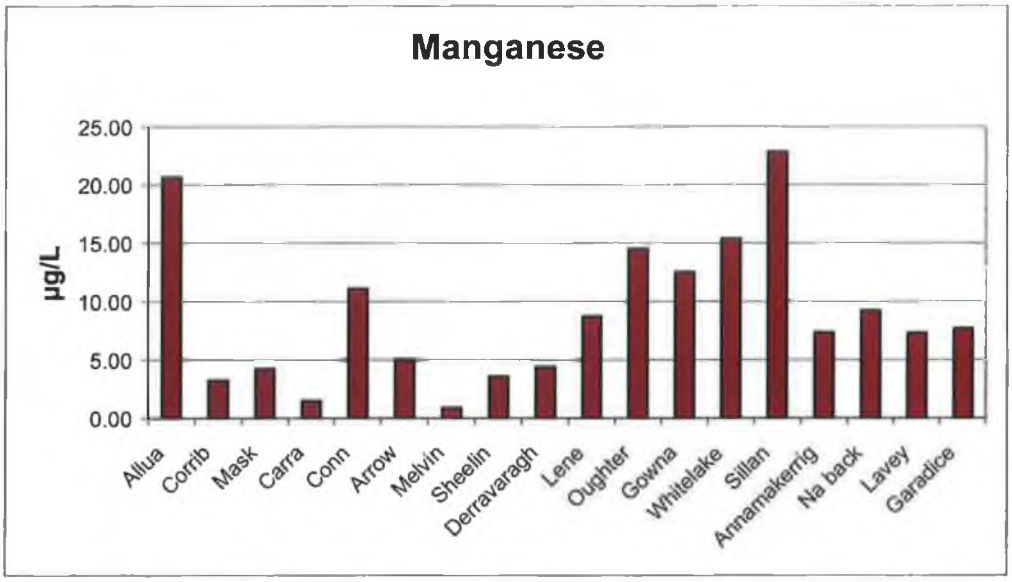

Figure B.12: Spatial variation in total mean manganese conc. in the 18 lakes

The highest values for manganese were found in Lough Allua and Lough Sillan (both with means >20µg/L). Several other Cavan/Monaghan lakes had reasonably high values also. The lowest values were found in the western lakes and hardest midland lakes, all which had a value <5µg/L, with the exception of Lough Conn which had a relatively high value (>10µg/L).

Nickel

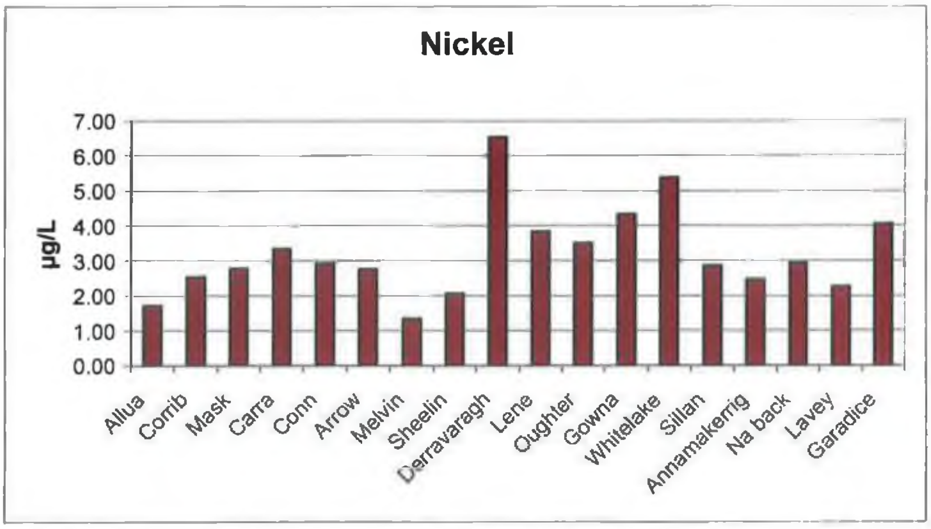

Figure B.13: Spatial variation in total mean nickel conc. in the 18 lakes

Lough Derravaragh reported the highest value for nickel (>6µg/L) followed by Whitelake (>5µg/L), Gowna and Garadice (both >4µg/L). All the other lakes had values less than 4µg/L. The two softest water lakes (Allua and Melvin) reported the lowest nickel results.

Lead

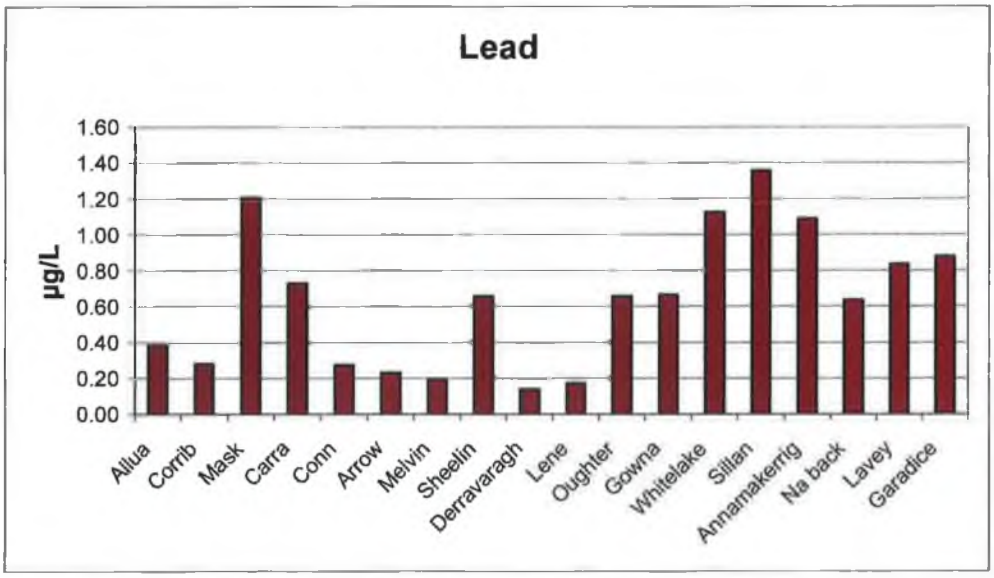

Figure B.14: Spatial variation in total mean lead conc. in the 18 lakes

The results for lead in all the lakes were low, with every lake reporting a mean value less than 1.4µg/L. Because of the very low concentrations, detailed examination of the results is not worthwhile. There does not seem to be any relationship between lead concentration and water hardness in the lake as some hard water lakes report the highest results (e.g. Mask has a value >1.2µg/L) and other hard water lakes report low results (e.g. Derravaragh has a value <0.2µg/L). The same pattern is true for the soft water lakes.

Strontium

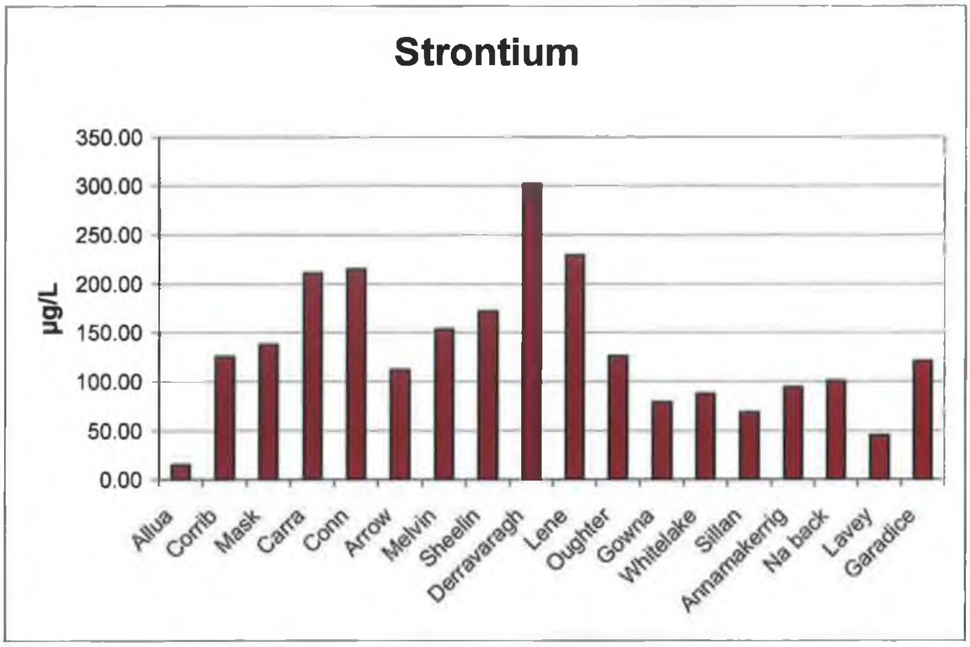

Figure B.15: Spatial variation in total mean strontium conc. in the 18 lakes

The highest concentration of strontium was found in Lough Derravaragh (>300µg/L) - the lake with the highest concentrations of calcium and magnesium also. Lough's Lene, Carra and Conn – other hard water lakes – also had high concentrations of strontium (>200µg/L).
Allua and Lavey have the lowest concentrations of strontium (<50µg/L), and the other inland lakes of Cavan/Monaghan have low concentrations also.

Zinc

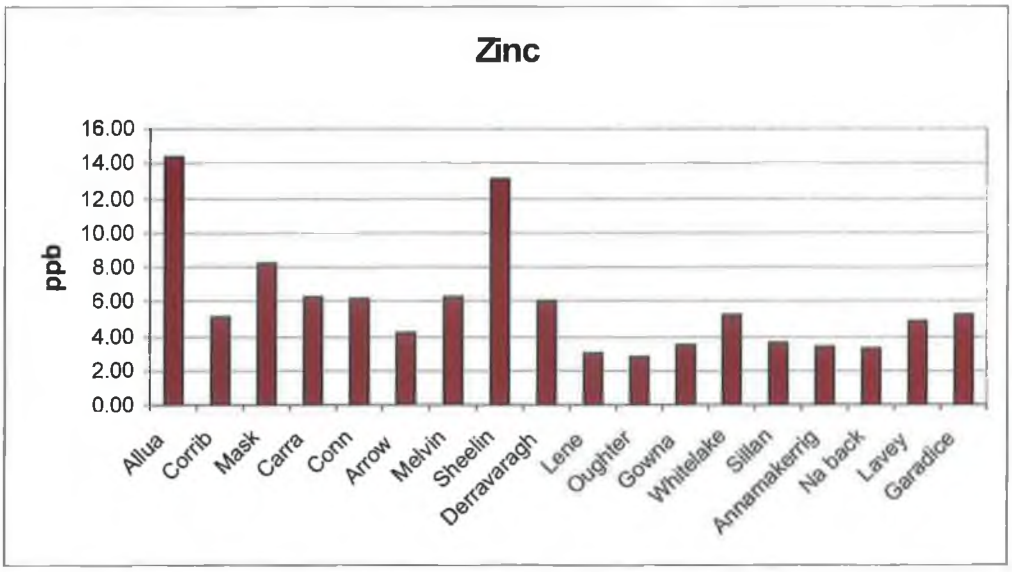

Figure B.16: Spatial variation in total mean zinc conc. in the 18 lakes

Lough Allua and Lough Sheelin had the highest concentrations of zinc (both >12µg/L), which is interesting because these lakes have completely different hardness values. All the other lakes had values <10µg/L. The lowest values were found in the midland lakes, particularly Oughter and Lene.

TEMPORAL VARIATION

The tables on the following pages were generated by calculating a mean value from the element results at each lake site during each of the calendar months over the three years of this study. Blank values in the tables indicate that no data is available for that month.

Table B.4: Mean monthly values, Lough Allua Site 1

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.61	0.92	1.38	7.49	48.48	3.28	0.23	0.76	0.14	0.94	38.65	57.88	0.39	0.18	14.90	1.54
Feb	8.50	0.92	1.45	8.47	27.74	3.96	0.68	0.29	0.98	0.87	54.23	10.88		0.38	17.20	4.05
Mar	6.50	0.78	1.28	7.70	28.71	2.75		0.13	0.95	0.55	18.34	33.24	0.22	0.19	13.94	
Apr	4.12	0.60	0.99	6.22	47.88	2.44		0.30	1.27	0.45	43.52	5.51			9.64	0.70
May	7.44	0.75	1.31	7.06	23.32	2.33	0.25	0.03	0.78	0.89	47.55	31.59	1.44	0.35	15.68	2.48
June	7.45	0.61	1.39	6.90	12.91	1.95	0.35	0.15	0.77	0.63	19.24	12.42	0.46	0.28	16.98	2.31
Jul	5.15	0.58	1.14	6.38	18.79	2.46	1.26	0.75	2.95	1.23	60.93	1.45	3.33	0.09	13.30	0.93
Aug	4.55	0.59	0.98	5.09	27.17	2.28	0.10	0.01	0.10	0.19	31.93	6.86	0.10	0.03	12.30	0.02
Sep	5.65	0.72	1.22	6.49	76.31	2.71	0.25	0.43	0.21	1.13	195.43	25.40		0.34	13.07	0.10
Oct	5.88	0.87	1.28	7.40	52.99	3.17	0.47	0.76	0.36	1.09	75.61	3.81	0.69	0.46	11.63	8.13
Nov																
Dec	7.02	0.75	1.04	6.32	96.56	3.53	0.28	0.40	0.10	1.05	50.53	11.95	1.25	0.18	14.16	7.20

Table B.5: Mean monthly values, Lough Allua Site 2

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.07	0.83	1.18	7.15	68.02	2.74		0.38	0.16	0.86	41.36	23.42	0.41	0.12	11.65	2.09
Feb	8.07	0.94	1.43	8.63	28.36	4.33	1.09	0.27	2.75	0.54	18.98	11.03		0.38	15.73	2.58
Mar	6.00	0.80	1.29	7.70	23.80	2.80	1.23	0.21	1.78	0.63	13.09	20.92	0.21	0.05	13.36	
Apr	4.08	0.64	1.02	6.29	44.31	2.26	0.35	0.43	0.79	0.94	21.08	7.33			10.51	2.11
May	6.55	0.74	1.25	6.95	26.44	1.95	0.20	0.09	0.57	0.72	28.71	13.72	0.55	0.34	14.05	2.01
Jun	6.85	0.80	1.41	7.05	28.96	2.95	0.63	0.16	23.96	4.14	179.30	11.57	9.69	0.32	16.32	433.46
Jul	5.71	0.79	1.27	6.78	16.45	1.68	0.40	0.56	1.15	3.56	127.84	0.90	1.78	0.08	14.04	9.35
Aug	4.37	0.58	0.93	4.99	34.16	2.50	0.10	0.01	0.10	1.40	39.43	3.28	0.60	0.11	10.96	0.63
Sep	5.46	0.85	1.22	6.49	69.40	2.23		0.18	1.75	1.33	177.63	33.90		0.03	12.73	1.70
Oct	5.27	0.87	1.28	6.96	48.30	2.13	0.62	0.71	0.56	1.04	47.44	7.63	0.17	0.25	11.83	6.99
Nov																
Dec	8.08	0.75	0.99	6.08	102.18	2.97	0.31	0.41	0.71	1.37	82.45	9.50	1.85	0.26	12.52	6.23

Table B.6: Mean monthly values, Lough Allua Site 3

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.25	0.84	1.23	7.21	66.59	3.25	0.01	0.35		0.99	43.52	35.05	0.31	0.07	12.17	33.27
Feb	7.32	0.90	1.44	8.77	35.07	3.59	0.14	0.20	1.76	0.98	32.99	12.39		0.17	15.42	9.23
Mar	5.84	0.76	1.28	7.38	28.52	3.06		0.27	0.34	0.27	63.90	28.62	0.19	0.04	13.50	
Apr	2.74	0.67	1.06	6.45	43.46	2.57	0.99	0.41	1.30	0.98	49.08	7.04			10.71	2.96
May	6.50	0.72	1.27	6.94	28.35	2.10		0.06		1.27	27.73	29.53	0.73	0.48	14.15	7.01
Jun	6.44	0.62	1.34	6.87	13.20	2.21	0.10	0.04	1.87	0.46	10.80	12.40	0.10	0.20	15.31	1.44
Jul	5.44	0.70	1.26	6.80	14.55	2.79	0.61	0.59	1.62	1.00	48.83	0.82	1.17		14.01	5.12
Aug	4.15	0.57	0.90	4.84	43.17	2.82	0.10	0.01	0.01	1.57	56.23	8.96	0.10	0.09	11.10	1.08
Sep	5.63	0.89	1.22	6.68	41.47	2.76	0.27	0.04		1.51	90.50	20.69		0.12	12.14	3.81
Oct	6.37	0.88	1.29	7.09	45.90	2.25	0.57	0.69	0.86	0.87	87.02	7.16	0.46	0.16	12.03	4.65
Nov																
Dec	6.87	0.75	1.03	6.10	103.46	3.48	0.23	0.39	0.66	1.61	52.97	9.75	0.52	0.11	13.00	9.80

Table B.7: Mean monthly values, Lough Allua Site 4

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.57	0.83	1.19	7.18	63.51	2.86	0.02	0.25	0.03	1.01	29.91	26.96	0.42	0.10	11.97	5.83
Feb	8.80	0.89	1.37	8.53	29.30	3.54	0.09	0.11		0.75	24.22	9.02	0.36		13.25	1.58
Mar	5.65	0.79	1.29	7.62	27.64	3.11		0.01	1.61	0.73	43.16	14.84	0.57	0.07	13.56	2.56
Apr	4.07	0.67	1.07	6.39	40.96	2.21		0.31	1.09	0.68	58.77	4.56	0.50	0.06	10.74	1.21
May	6.14	0.71	1.19	6.81	30.52	2.05	0.15	0.18	0.08	1.37	34.31	40.62	0.67	0.50	13.39	2.57
Jun	6.38	0.62	1.31	6.74	17.99	1.98	0.24	0.07	3.44	0.83	58.04	12.51	0.15	0.22	15.02	54.98
Jul	6.36	0.75	1.25	6.85	21.36	2.14	0.48	0.76	3.85	7.63	120.19	2.43	1.53	0.22	14.03	2.15
Aug	4.03	0.60	0.91	4.92	43.15	2.03	0.10	0.06	0.10	1.20	68.01	7.82	0.10	0.05	10.34	0.01
Sep	5.63	0.81	1.21	6.52	48.11	2.76	0.23	0.09		1.07	153.19	44.03	0.49	0.23	12.66	2.94
Oct	6.33	0.88	1.31	7.16	46.03	2.69	0.52	0.88	1.85	0.97	62.11	8.69	0.85	0.33	12.46	5.12
Nov																
Dec	4.62	0.76	0.90	6.39	107.22	3.75	0.22	0.32	0.45	1.28	64.30	10.21	1.96	0.01	13.12	19.75

Table B.8: Mean monthly values, Lough Allua Site 5

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	3.45	0.79	1.23	7.02	67.18	2.94	0.02	0.25		0.65	29.05	24.90	0.25	0.08	11.81	1.59
Feb	8.92	0.92	1.36	8.62	25.49	2.93	0.47	0.38		0.82	42.28	7.31		0.17	14.52	1.43
Mar	5.40	0.74	1.25	7.60	24.79	2.74		0.11	1.10	0.45	38.54	12.22	0.26		12.88	
Apr	4.51	0.61	0.99	6.28	49.23	2.62		0.19	0.12	0.82	42.44	7.16			9.63	2.20
May	6.76	0.80	1.28	7.14	27.37	2.20		0.17	0.10	0.93	26.24	12.48		0.51	14.25	2.29
Jun	6.57	0.62	1.32	6.91	13.14	2.46	0.24	0.17	2.25	0.86	259.47	14.72	0.10	0.17	14.84	0.26
Jul	5.44	0.70	1.23	6.69	14.31	2.45	0.57	0.46	2.26	2.35	50.77	1.02	1.54	0.08	14.76	1.08
Aug	4.62	0.59	0.91	5.04	37.09	2.92	0.10	0.10	0.10	0.76	54.42	22.36	0.10	0.11	12.28	0.72
Sep	5.50	0.79	1.23	6.47	41.29	2.73		0.12		0.72	146.15	21.63		1.69	11.87	0.44
Oct	5.69	0.87	1.21	7.06	55.17	3.09	0.50	1.25	1.65	1.25	49.37	8.41	0.57	0.26	12.13	4.12
Nov																
	3.96	0.75	0.94	6.28	96.47	3.51	0.29	0.40	0.40	1.61	44.72	8.14	1.31	0.10	13.20	6.46

Table B.9: Mean monthly values, Lough Allua Site 6

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.17	0.84	1.17	7.15	61.64	2.93	0.01	0.31	0.06	0.74	39.62	28.98	0.45	0.06	12.98	2.64
Feb	6.46	0.92	1.35	8.71	27.81	3.58	0.29	0.11		0.22	32.00	10.34			13.88	1.76
Mar	5.49	0.77	1.28	7.67	29.04	2.60	0.05	0.09	1.72	0.49	38.47	10.04	1.00		13.39	0.78
Apr	3.93	0.65	1.04	6.51	44.65	2.33		0.55	0.14	0.73	46.15	6.95	0.58		10.52	1.39
May	6.57	0.74	1.27	6.96	29.38	1.87	0.17	0.48	0.63	1.25	44.80	23.23	1.72	0.50	13.99	3.13
Jun	6.92	0.72	1.30	6.87	13.83	1.72	0.22	0.30	0.90	1.36	39.96	4.16	0.10	0.19	14.73	0.45
Jul	5.53	0.71	1.25	6.74	13.71	1.77	0.38	0.65	2.39	1.95	68.35	0.98	1.67	0.13	14.06	1.73
Aug	4.28	0.56	0.89	4.79	48.06	2.21	0.10	0.02	0.10	0.77	57.20	24.55	0.10	0.09	10.86	0.75
Sep	5.32	0.79	1.19	6.40	39.30	1.85	0.27	0.12		1.06	118.29	21.09		0.22	11.85	2.91
Oct	5.78	0.89	1.29	7.26	54.04	2.86	0.56	1.32	2.37	1.09	58.73	8.20	0.47	0.22	12.87	5.13
Nov																
Dec	7.42	0.74	0.82	6.37	105.23	3.78	0.08	0.35	0.44	1.28	61.10	10.75	0.77	0.14	12.94	31.62

Table B.10: Mean monthly values, Lough Allua Site 7

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	3.98	0.89	1.22	7.11	63.49	3.20	0.02	0.21		0.85	42.23	37.92	0.16	0.09	12.60	2.76
Feb	7.30	0.93	1.36	8.62	28.38	3.49	0.08	0.15		0.39	21.60	7.28		0.05	13.70	1.59
Mar	5.62	0.75	1.28	7.76	33.05	3.37	1.16	0.04	1.29	0.46	46.23	21.31	1.05		12.58	1.09
Apr	3.85	0.65	1.05	6.52	39.38	2.72	0.49	0.27	0.04	1.31	39.77	2.79			10.47	0.71
May	6.36	0.73	1.23	6.97	29.04	2.89	0.05	0.29	1.06	1.38	52.84	30.76	2.57	2.58	13.48	3.71
Jun	6.74	0.70	1.27	6.71	18.69	1.85	0.29	0.27	0.81	1.31	50.27	72.05	0.10	0.22	13.98	0.95
Jul	5.96	0.77	1.27	6.99	17.40	1.46	1.23	0.41	2.67	3.43	81.18	3.57	1.88	0.18	15.40	105.98
Aug	3.88	0.58	0.88	4.75	43.91	2.42	0.10	0.10	0.10	1.64	61.42	4.89	0.24	0.10	11.20	0.01
Sep	5.42	0.77	1.16	6.36	40.35	3.00		0.35	1.12	1.03	83.01	20.38		0.05	11.30	8.61
Oct	5.93	0.89	1.28	7.23	48.59	2.90	1.45	0.93	1.35	0.65	69.23	11.31	0.41	0.30	11.64	7.12
Nov																
Dec	5.17	0.74	0.85	6.26	91.87	3.84	0.09	0.42	0.53	1.68	56.05	8.98	4.57	0.11	13.21	5.77

Table B.11: Mean monthly values, Lough Allua Site 8

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	8.39	0.99	1.45	8.71	44.27	5.50		0.25		0.63	40.32	24.76	0.60	0.10	23.65	1.91
Feb	11.02	0.98	1.55	9.11	23.19	3.78	0.25	0.33		0.82	24.36	5.58			17.17	4.45
Mar	8.29	0.86	1.41	8.34	28.27	2.97		0.28	2.62	0.74	41.03	16.09	0.28		17.06	
Apr	5.53	0.66	1.10	6.63	40.96	2.62	0.08	0.56	0.33	0.98	41.56	5.14			12.44	4.98
May	9.35	0.71	1.38	7.51	18.61	3.92	0.22	0.30	1.03	1.16	72.97	7.68	2.52	0.31	19.55	1.47
Jun	10.73	0.63	1.46	7.65	16.13	2.87	0.35	0.09	1.30	0.88	47.95	14.64	0.10	0.14	21.46	1.59
Jul	9.96	0.76	1.50	8.04	14.58	1.90		0.61	3.30	1.03	91.23	2.45	0.81	0.12	19.95	3.86
Aug	6.94	0.72	1.07	5.64	28.08	3.07	0.10	0.15	0.10	1.40	139.76	29.65	0.10	0.08	15.36	1.27
Sep	10.74	0.99	1.58	8.06	41.08	5.38	0.08	0.29		2.81	201.94	31.57	7.53	0.19	21.38	359.78
Oct	10.88	1.21	1.49	7.90	35.12	5.65	0.20	1.40	1.32	0.91	89.54	17.96	0.87	0.22	20.31	9.07
Nov																
Dec	12.21	0.64	1.35	7.49	96.33	4.97	0.35	0.48	0.37	2.65	62.67	88.35	1.85		23.53	15.92

Table B.12: Mean monthly values, Lough Allua Site 9

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.29	0.80	1.41	7.88	63.84	3.53	0.01	0.28	0.11	1.12	23.93	23.80	0.47	0.08	14.66	2.54
Feb	6.45	0.88	1.34	8.80	29.89	3.52	0.60	0.59	1.49	0.81	35.75	6.36	0.40		16.31	1.53
Mar	5.52	0.76	1.28	7.76	33.08	2.93	0.38	0.08	1.20	0.60	59.20	27.12			13.26	
Apr	4.72	0.71	1.14	6.71	36.81	2.18	0.32	0.42		1.13	29.54	3.71			11.76	4.76
May	6.08	0.71	1.20	6.95	31.50	1.94	0.14	0.46	0.68	1.78	31.46	2.61	2.11	0.52	12.90	3.55
Jun	6.90	0.71	1.31	6.79	13.96	2.14	0.28	0.32	2.15	0.86	29.78	12.50	0.10	0.13	14.47	37.58
Jul	5.95	0.72	1.30	7.07	14.27	2.13	0.93	0.72	1.86	3.55	50.94	2.73	1.52	0.14	14.60	2.33
Aug	4.56	0.69	0.93	5.00	44.87	3.38	0.10	0.11	0.10	0.86	26.02	11.07	0.03	0.05	11.63	1.88
Sep	5.36	0.76	1.22	6.47	56.59	1.83	0.24	0.21	0.66	1.31	80.08	18.76	0.48		12.17	2.02
Oct	6.24	0.91	1.23	6.80	49.14	2.22	0.54	1.23	1.90	0.90	50.96	15.06	0.91	0.15	12.51	6.15
Nov																
Dec	7.13	0.73	1.08	6.54	81.72	3.27	0.86	0.49	0.52	2.09	39.65	10.46	1.33	0.07	14.29	8.73

Table B.13: Mean monthlv values. Lough Arrow

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	50.14	1.42	3.27	8.47	9.25	23.42	0.51	0.53	1.35	1.80	98.38	2.76	2.31	0.82	111.03	4.65
Feb	54.03	1.59	3.66	10.63	6.79	23.26	0.19	0.13	0.28	0.87	68.22	2.45	1.51	0.09	108.73	1.22
Mar	78.50	1.28	4.91	9.06	10.89	31.53	0.55	0.49	3.32	0.86	34.55	3.91	3.38	0.13	121.82	1.25
Apr	59.23	1.26	3.36	8.84	10.73	23.90	0.46	0.61	4.04	1.46	67.49	3.18	2.65	0.32	112.03	4.65
May	55.65	1.27	3.84	9.01	5.90	26.92	1.88	0.53	6.06	4.13	41.24	2.64	3.16	0.17	117.26	13.94
Jun	55.33	1.44	4.02	10.42	5.54	21.90	0.43	2.11	1.72	0.79	106.44	9.92	1.02		111.19	5.42
Jul	45.81	1.10	3.45	8.40	3.32	22.02	0.29	0.50	3.53	0.65	198.55	9.65	3.65	0.04	109.24	1.31
Aug	42.67	1.25	3.54	8.98	5.41	25.15	0.15	0.38	4.29	0.74	145.90	0.83	5.52	0.16	121.53	1.38
Sep	50.56	1.40	3.74	9.95	3.27	22.13	0.88	0.42	4.34	0.45		1.40	2.38	0.06	88.95	3.15
Oct	49.15	1.68	3.53	8.27	3.96	23.36	0.57	0.18	1.18	1.52	325.63	9.31	1.13	0.25	109.26	3.67
Nov	52.47	1.22	3.36	8.55	7.55	22.67	0.31	0.48	3.40	2.30	219.37	6.82	3.41	0.07	105.73	3.32
Dec	55.22	1.25	3.65	8.73	9.66	22.92		0.27		1.20	51.65	3.73	1.49		127.10	9.01

Table B.14: Mean monthly values. Lough Carra. Castlecarra

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	68.77	2.95	3.79	12.32	5.84	23.84	0.20	0.33	1.90	1.72	214.55	0.73	1.89	0.54	174.64	4.92
Feb	102.88	3.70	4.93	18.31	9.66	23.96	0.97	0.20	0.67	1.11	215.67	0.64	2.85	0.19	212.13	1.44
Mar	87.71	2.81	4.38	14.84	3.37	23.11	0.06	0.22	3.29	1.46	13.19	1.18	3.46	0.01	170.39	4.65
Apr	74.81	2.50	4.24	12.73	3.74	25.74	0.67	0.25	7.35	1.85	139.96	2.31	2.47	1.11	179.37	2.20
May	66.07	2.48	4.34	12.38	5.42	26.45		0.85	3.27	3.07	205.64	2.32	2.93	2.99	169.50	4.65
Jun	77.58	2.36	4.67	12.26	5.93	23.61	0.26	0.44	0.85	2.45	76.75	0.77	3.34		194.81	6.66
Jul	50.02	2.36	4.63	12.09	5.52	24.57	0.36	0.07	2.27	1.62	87.73	1.10	8.22	0.88	176.08	3.77
Aug	43.58	2.53	4.91	12.42	2.94	23.84			4.79	0.88	104.29	0.48	2.71	0.32	186.58	11.34
Sep	42.11	2.50	4.69	13.06	9.23	23.11	0.72	0.58	3.30	3.17	170.39	1.42	3.61	0.16	162.79	3.80
Oct	54.56	2.50	4.18	12.48	7.37	19.67	0.69	0.51	3.43	9.37	238.05	1.88	2.05	1.02	179.83	4.34
Nov	69.55	2.33	4.17	10.36	2.63	25.12	0.52	0.57	3.90	1.39	402.75	1.51	3.98	0.25	234.61	3.97
Dec	71.31	2.42	4.02	11.19	6.18	25.61	1.44	0.53	2.28	2.52	436.93	1.01	2.07	0.60	197.26	9.85

Table B.15: Mean monthlv values. Lough Carra. Twin Islands

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	87.04	3.18	4.11	12.10	5.26	25.42	0.09	0.15	3.38	2.51	146.78	0.77	2.56	1.42	212.88	8.90
Feb	100.13	3.64	5.41	17.60	6.48	25.42	0.18	0.18	0.62	3.70	137.43	0.56	3.17	0.23	240.89	2.71
Mar	107.22	3.05	4.84	15.04	5.36	22.78	0.02	0.29	3.30	2.08	37.49	1.38	3.74	0.08	212.80	4.98
Apr	87.75	2.64	4.65	12.70	5.08	25.98	0.31	0.32	7.33	1.96	175.04	1.55	3.53	0.67	229.81	3.42
May	81.85	2.69	5.31	12.66	4.21	25.42		0.58	3.16	0.33	243.72	4.65	2.59	0.17	249.48	1.84
Jun	78.00	2.44	5.08	12.33	4.73	22.42	0.17	0.34	1.12	2.61	192.32	0.72	6.94	0.04	242.47	4.72
Jul	50.72	2.39	5.21	12.22	7.20	24.78	0.29	0.29	1.97	1.73	92.74	1.09	6.48	0.40	231.93	2.91
Aug	48.96	2.59	5.44	12.08	6.83	23.54	0.68		4.87	1.73	116.09	0.84	2.01	0.14	249.65	12.85
Sep	51.87	2.96	5.51	13.27	5.83	24.32	0.97	0.33	2.79	7.43	81.90	3.46	2.17	0.28	223.82	26.62
Oct	69.72	2.74	4.61	12.67	6.77	20.69	0.48	0.37	3.21	3.07	345.52	2.11	3.23	3.41	222.02	5.02
Nov	74.26	2.38	4.45	10.49	4.02	23.97	0.73	0.29	5.96	1.62	345.87	1.65	2.56	0.46	247.41	2.94
Dec	90.14	2.72	4.71	10.94	26.98	28.58	1.53	0.26	2.85	3.77	605.31	2.35	2.24	1.89	269.93	10.36

Table B.16: Mean monthly values, Lough Conn, North Basin

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	43.17	1.83	4.39	11.97	23.72	26.77	0.54	0.25	2.67	0.82	145.36	3.27	2.05	0.37	204.71	0.74
Feb	45.81	1.86	4.22	15.13	18.44	27.31	0.62	0.50	1.59	1.80	172.90	3.97	2.53	0.43	200.99	7.08
Mar	46.88	1.61	4.23	13.31	14.64	28.36	0.08	0.18	2.79	0.66	118.06	3.50	2.44	0.34	206.51	10.01
Apr	65.56	1.57	4.35	13.04	14.35	30.97	0.69	0.53	2.72	4.57	115.51	2.04	3.82	0.93	211.39	43.86
May	36.48	1.48	4.24	12.12	27.35	30.78	0.24	0.10	5.04	0.96	99.19	8.63	3.46	0.21	211.18	3.02
Jun	39.20	1.38	4.51	11.96	12.02	31.79		0.66	2.89	0.73	84.87	2.13	1.65	0.21	214.89	3.54
Jul	44.23	1.49	4.59	12.19	5.04	34.10	0.30	0.93	3.79	0.71	193.83	5.06	6.01	0.25	220.19	1.32
Aug	38.27	1.59	4.52	12.79	23.05	33.38	0.35	1.23	4.81	2.20	96.13	13.58	3.53	0.16	210.95	3.18
Sep	43.66	1.58	4.66	12.96	6.72	31.70	0.82	0.42	2.53	0.56	76.24	5.57	3.16	0.44	202.17	1.63
Oct	47.26	1.65	4.62	13.06	9.34	27.33	1.94	0.15	0.02	0.84	105.57	1.75	2.01	0.24	198.84	16.39
Nov	39.47	1.46	4.00	11.26	14.52	30.10	0.34	0.60	1.64	0.99	293.16	2.68	2.82	0.05	205.33	4.32
Dec	35.48	1.55	3.65	11.51	28.96	26.85	0.64	0.29	2.64	1.11	281.22	3.34	1.07	0.20	201.45	5.22

Table B.17: Mean monthly values, Lough Conn, South Basin

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	46.19	1.93	4.39	12.21	18.53	27.52	0.33	0.20	1.92	0.80	119.96	3.09	1.27	0.13	224.22	1.28
Feb	43.17	1.84	4.30	14.96	15.99	27.80	0.62	0.21	1.90	1.27	143.39	3.18	1.28	0.88	194.62	6.38
Mar	47.45	1.68	4.10	13.29	11.74	26.56	0.12	0.08	2.33	1.13	105.56	1.77	1.50	0.26	180.73	12.93
Apr	59.53	1.54	4.31	12.88	8.32	30.37		0.59	2.14	0.91	72.53	1.76	4.15	1.20	193.81	2.08
May	35.21	1.49	4.12	12.19	11.81	29.24	0.59	0.12	3.58	1.03	85.58	3.89	2.57	0.10	184.78	2.62
Jun	37.95	1.45	4.49	12.27	12.91	31.05	1.17	0.20	1.16	1.06	82.95	0.98	2.15	0.12	197.30	1.47
Jul	41.76	1.41	4.69	11.94	5.72	32.84	0.15	0.35	4.96	0.64	101.99	2.53	5.30	0.19	211.52	3.34
Aug	38.11	1.54	4.61	12.62	4.76	31.90	0.29	0.83	1.95	2.95	78.11	3.43	3.02	0.31	198.49	17.57
Sep	43.67	1.63	4.74	13.45	6.42	29.82	0.56	0.43	3.26	0.70	137.72	3.12	2.84	0.08	188.57	2.01
Oct	50.04	1.79	4.70	13.81	8.50	27.23	1.11	0.34	2.28	1.45	113.00	1.93	1.57	0.05	195.92	19.22
Nov	39.93	1.49	4.24	11.98	7.74	31.56	0.64	0.28	1.19	0.59	328.90	2.74	3.70	0.01	198.90	4.72
Dec	39.00	1.48	4.10	11.34	15.53	30.28	0.39	0.17	2.26	0.88	227.30	2.53	1.23	0.12	207.04	2.84

Table B.18: Mean monthly values, Lough Conn, Cloghans Bay

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	48.27	1.98	4.49	12.12	21.26	27.51	0.42	0.27	2.83	0.97	118.05	5.55	2.03	0.15	235.06	0.90
Feb	43.75	1.82	4.33	14.44	17.37	26.26	0.67	0.29	2.36	1.40	144.92	4.61	3.46	0.23	213.14	2.07
Mar	46.87	1.65	4.65	13.52	28.52	30.97	0.44	0.25	2.87	0.80	85.99	23.89	2.48	0.48	226.62	5.59
Apr	67.79	1.59	4.58	13.03	9.58	29.66	0.20	0.77	3.04	1.74	64.46	1.29	4.23	0.47	233.33	3.81
May	40.65	1.64	4.68	13.36	11.88	30.93	0.20	0.19	2.70	1.15	144.32	2.56	2.64	0.11	239.23	3.24
Jun	37.11	1.41	4.97	12.63	13.29	28.64		0.30	2.29	0.80	88.07	3.97	1.79	0.19	239.12	2.17
Jul	39.66	1.42	4.80	12.05	17.85	29.71	0.35	0.49	3.66	5.53	93.86	5.03	6.55	0.05	238.73	3.92
Aug	36.16	1.45	4.68	12.46	102.14	44.92	0.49	0.73	7.73	0.84	125.17	17.24	3.24	0.11	243.12	0.92
Sep	42.38	1.60	4.93	13.30	7.95	31.66	0.44	0.48	2.59	1.84	95.76	6.50	3.11	0.10	223.55	1.60
Oct	52.94	1.78	4.94	13.53	6.37	27.15	1.20	0.40	0.72	0.79	92.63	1.15	1.12	0.04	237.04	26.37
Nov	44.44	1.61	4.38	11.66	21.32	32.98	0.23	0.32	1.64	1.60	291.90	11.26	4.97	0.09	249.42	9.92
Dec	42.83	1.65	4.06	12.26	20.56	28.66	0.32	0.06	2.55	1.60	270.13	2.82	2.84	0.30	234.94	4.14

Table B.19: Mean monthly values, Lough Conn, Tolans Bay

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	45.26	1.89	4.52	13.04	21.05	27.32	0.31	0.25	2.40	0.66	102.29	3.11	1.79	0.32	212.69	0.43
Feb	47.22	1.97	4.35	15.50	20.23	27.08	0.08	0.54	2.30	1.01	241.55	7.80	1.88	0.35	213.76	4.52
Mar	47.44	1.58	4.53	13.55	33.42	32.56	0.19	0.24	2.94	1.18	180.14	29.93	2.68	0.23	236.33	5.97
Apr	65.45	1.40	4.34	13.11	16.58	33.37		1.19	3.50	1.45	252.71	1.94	3.86	0.39	226.79	4.06
May	38.52	1.51	4.30	12.59	12.65	29.71	0.41	0.07	4.23	0.62	117.64	3.71	2.69	0.09	206.52	2.86
Jun	40.51	1.46	4.47	12.79	18.30	30.97		0.38	2.17	1.14	95.87	2.96	0.87	0.14	207.49	2.76
Jul	44.60	1.44	4.68	12.09	5.53	33.58	0.32	0.65	3.55	0.87	115.36	4.85	4.55	0.36	223.84	1.11
Aug	35.30	1.59	4.75	12.06	196.25	45.01	0.26	0.91	4.32	4.63	142.01	229.81	4.97	0.66	223.02	8.96
Sep	46.89	1.58	4.80	12.92	8.29	33.29	0.81	0.41	6.65	0.63	118.06	6.83	3.34	0.15	217.79	1.56
Oct	46.82	1.87	4.42	13.29	17.43	27.92	0.93	0.27		0.88	222.50	2.16	1.23	1.02	193.62	13.72
Nov	42.71	1.52	4.15	11.65	44.52	32.59	0.21	0.29	1.31	1.51	394.95	21.20	7.59	0.24	226.10	10.82
Dec	40.12	1.61	3.65	10.61	33.07	29.08	0.51	0.29	3.69	1.14	364.67	3.25	1.07	0.19	224.99	3.34

Table B.20: Mean monthly values, Lough Corrib, Lower Basin

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	49.48	1.74	3.12	10.28	10.11	30.09	0.77	0.30	2.18	2.21	44.66	1.56	2.96		133.55	4.49
Feb	61.41	2.21	3.83	12.77	9.34	31.70	0.09	0.11	0.62	1.21	101.66	1.60	3.13	0.10	162.63	1.45
Mar	94.05	2.48	3.80	11.28	9.25	24.79	0.03	0.18	3.20	2.09	24.18	2.89	3.69	0.18	219.68	3.52
Apr	52.89	1.69	3.43	10.67	9.05	31.51	0.95	0.22	5.63	1.08	114.91	2.23	2.17	0.24	149.13	7.30
May	46.90	1.68	3.84	11.24	8.69	26.67		0.33	1.87	1.39		3.29	1.84	0.28	118.92	3.21
Jun	48.63	1.44	4.01	10.50	7.52	24.54	0.01	0.35		1.01	67.99	4.26	2.78	0.04	198.06	4.51
Jul	23.71	1.37	3.52	9.94	4.74	23.04	0.12	1.04	2.88	0.88	72.62	5.30	5.25	0.19	134.45	3.58
Aug	32.07	1.68	3.56	10.91	4.66	28.60	0.26	0.02		0.61	115.49	9.12	0.34	0.24	131.80	2.93
Sep	41.03	1.78	3.50	10.83	4.47	29.06	1.22	0.36	2.56	0.30	130.13	2.54	1.49	0.15	130.24	0.97
Oct	83.24	1.70	2.89	10.60	14.00	25.43	0.75	0.70	4.43	0.46	81.89	2.68	1.95	0.18	115.71	3.37
Nov	50.25	1.62	3.22	9.44	7.80	29.70	1.55	0.38	0.93	1.04	197.23	1.89	2.97	0.39	131.87	3.19
Dec	43.01	1.31	2.71	8.34	10.07	25.68		0.37		1.34	445.97	3.18	1.31		109.31	10.87

Table B.21: Mean monthly values, Lough Corrib, Upper Basin

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	45.95	1.89	3.09	10.11	7.25	32.26	0.08	0.14	1.86	1.19	125.95	1.61	1.72	0.07	122.64	3.52
Feb	51.89	1.99	3.52	12.74	6.83	32.61	0.14	0.16	0.49	0.56	74.06	1.00	2.19	0.12	122.18	0.48
Mar	49.48	1.63	3.49	10.93	5.45	37.54		0.25	1.63	1.27	33.22	1.58	2.39	0.11	127.22	3.50
Apr	47.86	1.56	3.07	10.32	7.67	34.37	0.13	0.23	4.89	0.71	100.09	1.90	1.27	0.18	117.42	4.76
May	44.19	1.59	3.25	10.49	8.34	32.18	0.12	0.63	1.35	0.62	133.88	1.47	2.19	0.06	107.92	4.68
Jun	51.14	1.43	3.11	9.91	7.62	34.96	0.18	0.61	0.61	1.10	87.59	1.92	2.31		116.30	7.22
Jul	42.75	1.36	3.07	9.31	7.34	35.97	0.67	1.10	2.79	1.09	39.49	2.89	8.06	0.31	119.31	3.57
Aug	39.66	1.57	3.31	10.68	5.66	33.37	0.58	0.11	0.61	1.22	80.09	1.10	1.62	0.20	112.74	2.05
Sep	38.21	1.47	3.07	9.86	6.67	34.47	1.20	0.49	2.37	1.03	86.61	7.01	2.41	0.11	103.23	1.11
Oct	62.39	1.53	2.70	10.33	15.51	27.32	0.62	0.36	2.81	0.71	74.39	2.87	1.24	0.26	95.02	3.78
Nov	42.65	1.37	2.76	8.88	4.55	33.21	0.30	0.11	1.50	1.04	262.50	7.60	1.00	0.46	111.77	3.47
Dec	40.24	1.34	2.78	8.51	11.35	34.86	0.23	0.13	1.71	1.21	188.74	2.96	1.26	0.03	132.81	7.63

Table B.22: Mean monthly values, Lough Corrib, Upper Basin Deep

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	47.41	1.95	3.12	10.02	8.26	32.68	0.15	0.21	1.33	1.70	125.93	1.55	1.66	0.77	127.64	5.04
Feb	49.17	1.99	3.53	12.54	5.35	34.29	0.30	0.13	0.54	0.56	96.60	0.63	1.44	0.65	125.45	0.34
Mar	48.90	1.66	3.48	11.03	6.79	35.35		0.29	2.09	0.73	30.42	1.61	1.63	0.16	120.79	5.14
Apr	48.87	1.62	3.13	10.58	8.67	35.32	0.37	0.18	4.91	1.09	106.55	2.11	2.01	0.49	118.34	1.98
May	46.19	1.69	3.35	11.07	8.66	31.83		0.68	1.96	1.27	82.35	1.76	2.04	0.17	110.04	2.88
Jun	52.37	1.46	3.63	10.06	6.91	40.83	0.51	0.38	1.18	0.81	61.74	2.53	3.16	0.34	144.32	3.89
Jul	42.93	1.46	3.24	9.68	5.79	36.22	0.19	0.64	2.14	1.58	49.09	3.05	6.87	0.47	122.77	2.10
Aug	41.95	1.60	3.25	10.49	4.99	35.92	0.49	0.06	5.57	1.43	107.73	2.35	3.03	0.24	112.05	13.51
Sep	38.69	1.53	3.13	10.13	5.04	33.51	0.77	0.51	2.25	5.53	102.32	16.02	8.11	0.24	103.24	7.70
Oct	61.44	1.53	2.72	10.37	6.70	27.34	0.86	0.36	3.17	0.86	64.55	2.53	1.63	0.38	94.72	2.76
Nov	44.53	1.44	2.77	9.05	5.91	32.22	0.80	0.27	0.88	0.71	201.69	4.66	2.32	0.19	115.59	6.05
Dec	42.75	1.46	2.91	9.26	10.05	33.19		0.05	0.24	2.40	296.40	2.90	0.92	0.95	124.10	7.85

Table B.23: Mean monthly values, Lough Derravaragh, Donore

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr	105.13	2.82	9.22	8.88	4.74	46.59	0.38	0.09	1.84	1.28	176.78	4.78	7.06	0.15	319.13	5.85
May	81.69	2.68	8.99	8.66	5.99	46.56	0.11	0.21	6.24	1.23	187.98	5.28	5.48	0.04	308.13	3.01
Jun	77.23	2.26	8.34	8.09	7.83	42.03	0.01	0.45	2.45	1.30	60.41	3.99	6.37	0.12	302.44	1.17
Jul	55.45	2.16	9.22	7.82	3.96	44.62	0.69	0.42	7.28	0.69	158.42	7.22	12.09	0.05	290.44	2.25
Aug	63.12	2.45	9.06	8.23	9.25	42.26	0.15	0.48	3.81	0.86	154.86	6.49	4.94	0.12	290.38	46.28
Sep	80.27	2.79	8.91	8.57	9.40	39.95	0.84	0.71	7.34	1.69	150.45	1.53	4.69	0.21	265.48	2.85
Oct																
Nov																
Dec																

Table B.24: Mean monthly values, Lough Derravaragh, Faughelstown

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr	110.72	3.00	9.45	9.21	6.07	50.05	0.63	0.67	0.86	2.29	209.37	9.65	9.29	0.27	342.55	3.83
May	84.52	2.75	9.14	8.89	5.60	45.55	0.18	0.25	6.95	1.40	138.89	3.57	5.18	0.08	322.82	2.85
Jun	83.54	2.33	8.50	8.07	8.94	44.55	0.17	0.24	2.51	1.38	67.51	2.71	6.67	0.39	318.03	0.93
Jul	55.14	2.19	8.70	7.77	4.81	42.45	0.50	0.33	5.24	0.63	172.36	5.22	11.89	0.04	312.01	2.45
Aug	67.94	2.43	8.78	8.36	6.52	41.92	0.43	0.30	3.23	1.00	200.87	3.97	4.42	0.17	290.35	15.63
Sep	85.77	2.67	8.85	8.63	9.95	39.58	0.71	0.94	5.86	0.99	311.43	1.68	4.79	0.15	292.52	3.14
Oct																
Nov																
Dec																

Table B.25: Mean monthly values, Lough Lene, Site 1

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr	54.20	1.16	4.24	6.71	3.56	12.31	0.81	0.09	0.83	0.11	69.12	1.03	4.46	0.39	250.16	4.47
May	45.84	1.12	3.93	6.46	7.57	10.79	0.34	0.15	5.63	0.62	190.13	7.62	2.26	0.07	237.18	3.68
Jun	52.47	1.02	4.11	6.07	5.95	10.59		0.36	1.22	0.34	32.06	9.64	3.60	0.11	238.70	0.87
Jul	31.79	0.96	4.13	5.97	4.71	11.32	0.54	0.39	2.71	1.24	165.85	14.24	7.02	0.32	231.13	1.99
Aug	38.13	1.04	4.21	6.36	2.41	11.89	0.67	0.78	2.78	0.68	91.02	14.74	3.92	0.10	223.11	5.61
Sep	45.56	1.11	3.88	6.46	16.04	10.38	0.68	0.68	6.07	0.14	176.80	8.15	3.72	0.21	216.44	2.32
Oct																
Nov																
Dec																

Table B.26: Mean monthly values, Lough Lene, Site 2

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr	53.10	1.21	4.25	6.84	3.00	11.05	1.62	0.04		0.24	76.84	2.14	3.90	0.25	254.03	5.45
May	47.97	1.16	4.07	6.79	5.81	10.88	0.05	0.07	3.14	0.35	193.41	7.27	2.13	0.07	233.39	4.02
Jun	43.51	1.10	4.25	6.51	5.78	10.28		0.29	2.83	0.43	45.03	8.20	3.54	0.22	237.85	0.37
Jul	32.42	0.96	4.09	5.93	7.03	10.34	0.34	0.55	4.05	0.77	157.89	10.79	5.17	0.10	227.89	2.23
Aug	37.20	1.04	3.96	6.35	2.68	10.44	0.25	0.44	1.96	0.31	107.85	10.19	3.37	0.11	209.16	4.73
Sep	46.40	1.13	3.97	6.54	13.68	13.32	1.18	0.66	3.64	0.45	168.44	5.53	4.28	0.19	219.56	1.98
Oct																
Nov																
Dec																

Table B.27: Mean monthly values, Lough Lene, Site 3

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr	51.66	1.20	4.24	6.77	2.33	12.97				0.22	71.21	2.55	4.30	0.27	250.83	5.24
May	46.89	1.15	4.02	6.68	5.64	10.72	0.15	0.15	3.55	0.67	175.15	8.11	2.27	0.03	235.82	3.53
Jun	41.89	1.06	4.11	6.28	5.01	11.11	0.04	0.45	2.40	0.59	43.52	8.05	3.40	0.07	233.31	0.85
Jul	32.41	0.99	4.12	6.02	7.23	11.25	0.30	0.46	4.01	0.83	166.17	11.31	4.43	0.10	225.56	2.78
Aug	38.58	1.08	4.18	6.52	2.97	10.93	0.45	0.43	1.57	0.28	102.93	9.88	2.35	0.28	219.23	6.12
Sep	47.06	1.14	4.13	6.54	11.28	16.12	0.55	1.14	4.28	0.67	167.49	3.64	3.65	0.31	214.35	2.14
Oct																
Nov																
Dec																

Table B.28: Mean monthly values, Lough Mask

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	57.17	2.17	3.00	10.12	13.77	38.13	0.25	0.41	1.98	3.98	154.56	3.92	2.09	0.94	146.86	7.34
Feb	42.81	2.29	3.58	13.18	95.93	37.73	0.18	0.14	0.29	1.25	101.21	1.76	1.41	0.63	137.94	4.86
Mar	66.23	2.23	3.53	12.73	11.41	35.99	0.11	0.18	1.59	3.24	52.68	5.04	2.61	3.80	137.09	9.70
Apr	60.66	2.11	3.58	11.97	8.90	39.81	0.05	0.21	7.16	3.34	146.01	5.30	2.98	2.57	138.56	3.73
May	52.10	1.88	3.73	10.94	7.09	38.85		0.70	2.15	1.31	101.43	3.46	2.02	2.64	147.23	4.00
Jun	57.71	1.69	3.57	10.40	7.36	41.30	0.23	0.63	1.03	1.62	78.10	1.24	4.18	1.03	147.48	3.81
Jul	48.87	1.61	3.38	9.88	6.15	39.26	0.50	0.13	2.31	1.64	58.22	2.90	6.18	0.19	137.12	22.45
Aug	47.84	1.82	3.47	10.80	16.26	31.59	0.36		2.33	6.38	84.05	1.47	2.49	0.11	143.04	3.37
Sep	44.72	1.80	3.39	10.81	7.65	40.82	1.17	0.47	2.49	4.45	97.36	10.42	4.38	1.22	119.82	14.62
Oct	50.67	1.72	2.84	10.44	6.89	34.29	0.72	0.54	2.48	2.07	194.34	1.41	1.89	1.00	111.58	3.73
Nov	43.96	1.49	2.75	8.70	6.20	40.68	0.75	0.31	4.21	1.64	236.47	5.93	2.30	0.28	131.02	4.11
Dec	55.38	1.85	3.16	9.75	14.73	41.66	0.98	0.35	3.22	3.39	306.23	5.48	1.55	0.77	157.56	18.14

Table B.29: Mean monthly values, Lough Melvin, Site 1

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr																
May	25.67	1.34	3.44	11.18	19.10	18.01	0.11	0.11	1.16	0.92	107.65	2.41	0.37	0.13	98.88	
Jun	29.45	1.01	2.57	8.58	1.07	23.30		0.36	0.33	0.92	47.03	0.38		0.13	143.94	
Jul	22.86	1.19	3.17	10.28	9.11	23.52	0.65	0.69	1.14	5.19	66.58	0.55	1.00	0.18	155.02	7.44
Aug	25.44	1.27	3.60	10.76	14.27	24.36		0.08		1.27	37.77	1.40	1.33	0.14	164.92	1.50
Sep	23.12	1.17	3.10	9.15	17.74	24.33	0.43	0.42	0.58	3.25	100.05	1.32			166.56	3.07
Oct																
Nov																
Dec																

Table B.30: Mean monthly values, Lough Melvin, Site 2

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr																
May	25.83	1.37	3.39	11.56	16.57	16.52		0.04	0.88	2.57	90.43	0.63	0.89	0.27	97.09	
Jun	27.95	0.95	2.46	8.28	18.24	23.91	0.17	0.33	1.68	0.77	5.28	0.06			148.34	136.35
Jul	21.74	1.15	3.10	10.21	6.87	24.02	0.54	0.51	0.63	3.58	47.70	0.21	1.30	0.24	154.98	6.24
Aug	23.69	1.21	3.34	10.16	18.39	23.56		0.36	1.16	0.97	41.29	0.58	1.30	0.03	158.67	0.82
Sep	23.40	1.16	3.19	9.21	22.38	24.17	0.18	0.38	0.93	7.91	99.34	1.93			166.98	8.15
Oct																
Nov																
Dec																

Table B.31: Mean monthly values. Lough Melvin, Site 3

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr																
May	26.39	1.40	3.56	11.47	15.28	17.55		0.03	0.03	1.26	103.22	0.79	0.85	0.18	97.90	
Jun	29.03	0.98	2.47	8.34	3.66	24.11		0.38	3.87	0.83	59.51	1.32			148.96	
Jul	22.09	1.16	3.19	10.22	8.05	24.05	0.83	0.47		4.04		0.53	0.86	0.04	153.44	6.80
Aug	24.42	1.18	3.26	10.18	13.32	23.24		0.17		0.43	68.61	0.99	1.51	0.18	159.76	1.43
Sep	22.61	1.13	3.17	9.07	13.99	23.74	0.19	0.20	1.40	1.29	110.40	1.54			162.43	2.21
Oct																
Nov																
Dec																

Table B.32: Mean monthly values. Lough Melvin, Site 4

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr																
May	26.21	1.38	3.43	11.39	15.35	17.68	0.06			0.56	112.13	0.85	0.03	0.05	97.36	0.34
Jun	31.11	1.08	2.65	8.79	1.74	24.29	0.17	0.42	1.15	0.87	37.48	0.45			150.10	0.91
Jul	21.49	1.18	3.15	10.33	8.58	24.16	0.11	0.47	0.95	4.46	22.83	0.38	1.46	0.21	153.37	4.45
Aug	24.91	1.18	3.29	10.17	13.04	24.39	0.05	0.40	2.45	1.20	75.57	1.27	1.03	0.12	162.05	0.32
Sep	22.38	1.15	3.08	9.01	19.57	23.63	0.19	0.24	2.78	3.06	73.69	1.13			164.69	3.50
Oct																
Nov																
Dec																

Table B.33: Mean monthly values. Lough Melvin, Site 5

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr																
May	25.50	1.35	3.36	11.39	16.79	17.34		0.05	0.60	0.68	111.32	0.77	0.43	0.05	95.54	
Jun	27.76	0.96	2.40	8.05	1.96	24.05		0.49	3.01	0.87	29.61	0.08		0.11	150.12	1.40
Jul	21.82	1.18	3.10	10.25	7.14	25.53	0.44	0.47	0.80	4.48	60.70	0.57	1.78	0.26	157.09	4.76
Aug	24.17	1.20	3.28	10.15	11.11	25.88		0.23	1.57	1.70	77.97	0.20	1.95	0.05	160.16	2.14
Sep	22.31	1.13	3.09	8.91	20.37	23.50		0.01	0.89	1.10	117.71	1.99			164.11	1.39
Oct																
Nov																
Dec																

Table B.34: Mean monthly values, Lough Melvin, Site 6

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr																
May	25.85	1.43	3.48	11.55	16.92	16.77	0.25	0.13	0.24	0.68	123.86	1.08	0.84	0.05	98.66	
Jun	28.77	1.00	2.42	8.07	5.00	25.46	0.01	0.34	1.56	1.42	20.77				150.43	0.76
Jul	21.45	1.19	3.11	10.02	7.97	24.68	1.22	0.71	2.17	9.00	21.48	0.52	1.75	0.35	157.20	15.37
Aug	25.44	1.29	3.39	10.50	12.62	25.53	0.36	0.23	0.84	1.31	37.16	1.35	1.34	0.01	158.31	1.70
Sep	21.85	1.11	3.14	8.97	20.10	25.30		0.32	3.83	1.10	110.83	2.17			164.14	1.54
Oct																
Nov																
Dec																

Table B.35: Mean monthly values, Lough Melvin, Site 7

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr																
May	26.95	1.48	3.50	11.79	18.67	17.88		0.05		0.72	155.16	0.52	0.24	0.09	98.05	
Jun	28.12	1.03	2.46	8.24	4.18	25.78	0.03	0.69	2.23	3.98	5.44	0.04		0.13	153.71	1.77
Jul	21.32	1.11	3.08	9.78	11.30	24.78	0.96	0.67	3.28	4.23	49.50	0.59	1.87	0.29	156.92	7.19
Aug	24.86	1.51	3.29	10.39	12.77	24.81	1.38	0.26		4.32	26.82	0.30	2.67	0.19	162.21	5.03
Sep	22.43	1.18	3.10	9.00	19.52	25.00		0.34	1.68	2.22	117.25	1.89			160.87	1.20
Oct																
Nov																
Dec																

Table B.36: Mean monthly values, Lough Melvin, Site 8

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan																
Feb																
Mar																
Apr																
May	26.12	1.46	3.55	11.99	15.83	16.71		0.07	0.46	0.65	101.70	0.77	0.35		98.48	
Jun	29.09	0.98	2.50	8.13	0.99	22.66	0.07	0.45	3.93	0.79	79.34			0.32	149.35	7.15
Jul	20.59	1.12	3.03	9.93	8.07	23.90	0.29	0.87	2.16	3.78		0.42	1.94	0.25	153.11	4.76
Aug	24.60	1.27	3.28	10.21	13.25	26.09	2.06	0.10		0.97	42.58	0.52	1.47		159.93	0.26
Sep	23.02	1.16	3.13	9.17	19.06	27.46	0.15	0.23	2.27	7.85	91.58	1.74			164.15	7.12
Oct																
Nov																
Dec																

Table B.37: Mean monthly values, Lough Sheelin

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	67.24	3.86	7.60	8.03	7.60	53.85	0.10	0.27	0.85	1.70	195.54	3.79	3.49	0.08	167.29	0.67
Feb	67.68	4.10	9.34	9.89	11.89	55.30	0.12	0.22	0.97	0.99	175.12	5.53	2.68	0.73	168.19	0.97
Mar	65.13	3.16	8.33	7.34	8.94	46.51	0.05	0.29	1.81	1.62	52.72	1.70	1.40	1.47	160.90	2.15
Apr	73.96	3.56	9.59	8.60	3.86	50.67	0.24	0.14	8.06	2.26	125.90	6.08	2.70	0.26	165.45	2.45
May	78.14	3.50	10.14	8.79	9.23	54.17	0.17	0.25	1.32	1.60	77.18	10.26	3.60		178.83	3.59
Jun	88.09	3.27	9.81	8.19	5.30	56.61	0.44	0.39	2.93	2.80	73.16	33.54	5.94	0.05	190.95	2.34
Jul	82.92	3.50	11.03	9.14	5.59	54.02	0.68	0.45	5.29	0.86	138.88	2.09	1.34	0.18	179.15	1.84
Aug	48.22	3.22	9.45	8.33	3.53	52.81	0.43	0.78	3.08	1.12	81.11	14.92	3.48	0.12	169.65	11.22
Sep	59.06	3.70	15.86	9.03	13.17	51.54	0.60	0.29	4.17	1.10	166.42	3.18	3.39	0.02	168.05	1.70
Oct	62.88	3.68	16.13	8.96	10.46	46.65	0.90	1.48	3.00	1.15	334.76	8.66	2.42	0.19	169.55	1.65
Nov	57.49	3.28	9.27	7.76	4.50	53.39	0.31	0.37	1.35	1.46	253.57	14.63	3.81	0.47	181.65	3.17
Dec	70.25	3.87	10.07	8.81	9.94	50.07	0.55	0.57	1.18	1.53	45.12	12.76	3.40	0.23	156.14	16.89

Table B.38: Mean monthly values, Lough Gowna, Dernaferst North

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	13.02	3.32	3.12	7.24	21.65	16.01	0.43	0.29	1.25	2.82	59.13	31.08	2.37	3.34	48.11	5.03
Feb	17.68	3.07	2.99	7.53	6.86	15.41	1.78	0.10	1.24	2.89	92.14	6.39	1.86	0.21	40.16	1.05
Mar	16.90	3.00	2.96	7.23	8.08	14.70	1.01	0.42	1.36	2.91	44.96	12.73	2.28	0.61	42.72	4.72
Apr	14.41	3.05	3.09	7.47	7.26	14.89	3.45	0.28	2.23	1.96	54.80	6.92	2.41	0.32	45.95	1.75
May	15.56	2.96	3.04	7.23	8.23	9.76	1.10	0.30	1.43	2.20	34.48	7.46	1.78	0.62	42.99	3.79
Jun	14.43	3.13	3.13	7.79	10.47	10.99	1.68	0.32	0.94	1.56	35.08	12.98	2.48	0.60	44.17	2.95
Jul	15.27	3.29	3.28	7.61	3.11	11.94	0.47	0.30	0.79	1.23	31.46	3.78	5.59	0.32	44.94	3.39
Aug	16.12	3.40	3.45	7.77	3.60	8.21	0.46	0.25	1.15	1.34	60.59	1.34	3.38	0.40	49.90	2.62
Sep	20.61	3.48	3.85	8.04	5.72	13.90	1.02	0.39	0.80	0.87	42.89	15.33	0.62	0.10	54.87	0.60
Oct	19.75	3.65	3.96	8.45	5.82	16.84	0.15	0.41	1.72	2.20	73.50	22.58	1.11	0.36	54.89	0.76
Nov	13.14	2.86	3.20	6.81	8.68	15.34	0.23	0.24	0.10	1.84	82.82	28.94	39.39	0.18	59.58	2.74
Dec	14.67	2.96	3.10	8.39	13.43	14.82	0.45	0.46	1.27	2.25	26.13	17.61	3.26	0.17	61.63	32.90

Table B.39: Mean monthly values, Lough Gowna, Dernaferst South

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	21.34	3.25	3.92	7.54	32.08	24.09	0.48	0.35	1.27	2.76	127.87	16.77	2.60	5.15	92.39	4.99
Feb	33.09	3.00	4.58	7.96	7.08	28.71	0.50	0.16	1.87	2.63	146.97	3.33	1.88	0.12	100.37	1.30
Mar	33.18	2.82	4.50	7.62	7.15	27.60	0.62	0.40	1.18	1.99	38.82	13.00	2.71	0.20	103.20	3.67
Apr	29.39	2.88	4.68	7.84	8.62	27.84	0.44	0.49	2.82	1.76	71.42	6.59	3.87	0.06	109.50	0.69
May	25.39	2.89	4.05	7.52	8.06	18.18	1.21	0.26	2.72	1.83	46.61	6.00	2.74	0.50	85.01	2.62
Jun	31.12	2.87	4.96	8.27	8.11	19.89	0.84	0.59	2.57	1.18	42.08	15.96	1.49	0.26	114.30	1.98
Jul	23.12	3.05	4.24	7.62	2.06	16.69	0.91	0.47	1.09	1.13	91.20	4.07	3.40	0.24	80.87	0.82
Aug	31.97	2.97	5.25	8.01	4.28	24.00	0.29	0.21	1.81	1.54	97.91	1.08	3.01	0.26	122.20	1.41
Sep	30.15	3.25	4.80	8.16	5.34	20.12	0.60	0.29	1.12	1.33	95.72	4.81	0.98	0.02	103.19	4.10
Oct	34.71	3.33	5.57	8.57	5.08	24.31	0.60	0.83	2.22	1.75	97.82	16.32	1.97	0.16	117.51	2.41
Nov	21.78	2.70	4.42	6.97	9.47	26.88	0.10	0.08	0.50	3.31	170.45	12.51	40.37	0.20	130.89	1.33
Dec	25.39	2.78	4.16	8.17	21.87	25.24	0.42	0.26	1.88	1.99	108.02	21.61	3.67	0.19	119.14	23.25

Table B.40: Mean monthly values, Lough Garadice

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	24.11	1.65	2.70	6.73	100.27	12.67	0.28	0.46	0.98	2.41	239.97	25.65	3.06	3.32	107.60	6.25
Feb	31.08	1.56	2.86	7.15	30.62	12.41	0.45	0.13	1.32	2.67	339.22	2.82	2.78	0.24	101.68	12.26
Mar	29.93	1.82	3.14	7.07	40.78	14.73	0.15	0.31	1.87	4.93	260.99	11.38	3.38	0.61	84.91	8.44
Apr	29.46	1.51	3.17	7.57	25.97	14.84	1.04	0.58	0.98	2.26	341.62	5.20	3.96	0.28	121.30	1.28
May	32.36	1.48	3.20	7.17	17.84	14.30	1.33	0.32	2.48	3.07	213.90	5.73	2.36	0.46	118.38	4.07
Jun	30.40	1.47	3.34	7.52	15.86	14.84	0.60	0.46	2.60	1.70	132.88	4.11	1.52	0.21	124.59	4.95
Jul	28.84	1.47	3.48	7.11	4.60	14.32	0.72	0.57	3.21	0.92	72.60	1.33	3.10	0.22	131.10	2.33
Aug	29.87	1.48	3.54	7.22	8.54	16.48	0.30	0.06	3.94	2.45	70.37	1.25	4.29	0.09	142.63	2.23
Sep	35.78	1.75	3.76	7.95	13.10	17.37	0.02	0.27	0.58	1.94	209.66	3.64	0.70	0.05	129.19	0.09
Oct	31.76	1.72	3.48	7.22	33.56	18.01	0.32	0.73	2.09	2.92	478.40	14.42	2.94	0.28	132.07	2.70
Nov	21.24	1.46	2.88	5.74	44.78	17.38	0.28	0.09	0.18	4.24	582.94	7.29	21.51	0.27	149.08	10.60
Dec	21.75	1.45	2.43	6.86	78.64	15.88	0.66	0.26	1.81	8.12	342.17	3.17	5.29	12.68	117.09	25.49

Table B.41: Mean monthly values, Lough Oughter, Eonish

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	25.72	3.89	4.01	8.10	46.23	30.81	0.22	0.52	0.76	3.90	138.51	35.86	2.19	6.06	101.53	1.77
Feb	33.01	3.40	4.29	8.84	15.95	30.99		0.16	2.35	3.42	217.28	6.83	2.43	0.15	98.91	4.30
Mar	34.12	3.27	4.13	8.36	17.19	31.70	0.47	0.44	1.99	2.02	107.61	11.88	3.47	0.11	101.83	3.57
Apr	32.64	3.51	4.60	9.34	12.89	33.17	0.58	0.52	1.25	1.97	80.05	7.93	2.30	0.07	116.24	2.18
May	35.97	3.37	4.48	9.23	11.97	28.66	1.59	0.32	2.31	2.12	52.13	16.25	2.86	0.41	110.22	1.80
Jun	32.89	3.32	4.81	10.85	16.63	31.11		0.94	2.43	0.94	63.51	16.55	6.48	0.03	124.00	0.76
Jul	34.35	3.63	5.28	11.22	3.88	29.54	0.71	0.66		1.51	119.53	2.95	2.61	0.23	135.66	2.66
Aug	34.56	3.65	5.32	11.98	2.90	33.28	0.16	0.27	2.82	1.21	80.33	1.99	4.38	0.14	154.66	0.77
Sep	43.37	4.60	5.82	13.48	8.93	36.82	0.33	0.26	1.41	1.65	93.29	5.75	0.95	0.09	156.86	0.10
Oct	39.03	4.83	5.66	12.58	10.68	36.61	0.47	1.33	2.56	2.85	149.06	7.77	3.25	0.27	146.84	2.20
Nov	28.09	4.10	4.65	10.32	16.16	37.82	0.10	0.21	0.15	2.16	263.69	22.94	10.88	0.20	167.84	2.96
Dec	26.21	3.70	3.64	8.65	50.16	34.66	0.76	0.29	2.70	3.24	221.50	7.56	2.79		106.32	21.72

Table B.42: Mean monthly values, Lough Oughter, Chalets

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	25.70	3.57	3.67	7.70	51.50	30.73	0.29	0.36	1.34	2.71	129.61	27.51	2.45	5.75	98.30	2.77
Feb	33.72	3.47	4.30	9.11	19.13	31.98	0.25	0.18	2.95	3.24	182.51	7.20	3.13	0.13	102.66	1.34
Mar	36.07	3.34	4.17	8.86	13.97	34.06	0.03	0.49	1.22	2.82	125.38	12.25	3.14	0.18	106.73	5.30
Apr	31.41	3.49	4.40	9.55	12.29	35.15	0.81	0.66	1.11	2.80	120.78	4.78	3.42	0.23	115.52	4.32
May	36.21	3.30	4.96	8.96	12.32	30.39	1.21	0.61	2.40	2.44	62.94	16.09	3.00	0.28	114.83	1.73
Jun	35.51	3.27	5.28	11.92	10.12	31.82	1.11	0.84	3.88	1.41	63.52	23.46	1.91	0.04	134.95	1.50
Jul	39.77	3.58	5.51	11.95	3.82	32.01	1.45	0.71	1.37	1.36	71.86	4.35	2.21	0.06	143.92	0.87
Aug	36.48	4.25	5.72	13.75	3.26	35.19	0.43	0.41	2.64	1.53	96.72	2.26	3.49	0.22	170.38	2.28
Sep	42.55	4.77	5.79	13.50	12.30	36.61	0.57	0.25	1.48	2.50	154.55	8.17	1.52	0.10	153.31	1.77
Oct	38.47	5.02	5.49	13.41	20.44	39.45	0.63	1.31	2.69	2.61	238.77	41.63	2.89	0.24	154.81	2.13
Nov	26.55	3.93	4.47	7.95	26.90	35.43	0.07	0.33	0.10	3.00	286.85	11.26	18.45	0.19	137.02	3.58
Dec	24.83	3.91	3.54	8.68	58.38	32.59	0.69	0.26	2.14	2.83	209.65	5.61	3.24	0.08	102.56	17.35

Table B.43: Mean monthly values, Lough Whitelake

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	25.89	5.24	3.77	9.04	46.53	20.32	0.18	0.58	1.14	3.14	194.98	66.14	4.42	7.71	82.11	2.95
Feb	33.49	4.75	4.10	10.49	10.33	21.87	0.15	0.28	1.61	2.67	164.65	20.76	5.16	0.13	78.32	25.47
Mar	37.14	4.86	4.15	9.80	10.29	22.43	0.30	0.61	1.86	2.81	100.31	15.39	5.19		83.58	1.97
Apr	31.62	4.71	4.57	10.11	13.90	18.72	0.57	0.67	1.96	2.95	100.30	3.99	5.91	0.08	87.07	9.54
May	34.85	4.57	4.45	9.48	18.47	17.45	1.40	0.86	3.95	3.46	117.24	12.74	5.70	0.44	89.80	1.62
Jun	33.17	4.87	4.93	10.94	10.05	18.88	0.80	1.26	2.85	1.48	54.15	16.49	4.13	2.51	94.89	0.72
Jul	39.01	5.20	4.69	10.25	2.39	17.61	0.72	0.78	4.83	1.13	132.37	5.95	2.90	0.28	72.23	0.90
Aug	29.48	5.22	4.90	11.25	2.35	23.27	0.46	0.34	3.84	2.16	153.61	2.71	4.88	0.14	98.62	2.68
Sep	35.51	7.46	5.08	11.09	10.30	25.34	0.49	0.51	2.34	3.09	108.36	2.85	3.37	0.20	98.13	1.36
Oct	34.83	7.31	5.01	10.22	12.14	25.78	0.88	1.42	2.11	3.40	285.80	20.09	5.21	0.44	94.58	1.03
Nov	24.38	5.61	4.14	8.00	21.31	24.50	0.10	0.14	0.79	3.37	265.99	7.85	19.29	0.37	103.29	5.94
Dec	22.59	4.98	3.31	8.34	50.29	24.39	0.72	0.04	1.28	4.57	123.90	2.22	5.56	0.25	82.13	31.47

Table B.44: Mean monthly values, Lough Sillan

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	17.81	3.79	3.61	7.55	21.80	22.41	0.30	0.45	1.05	2.28	76.96	12.28	2.00	4.68	65.47	2.80
Feb	20.10	3.53	3.47	7.99	7.00	23.30	0.45	0.19	1.42	2.86	87.63	3.66	1.96	2.59	58.16	2.49
Mar	20.43	3.65	3.64	8.18	4.57	23.35	0.52	0.70	1.40	1.93	41.29	10.81	2.61	0.17	60.38	2.75
Apr	20.70	3.72	3.80	8.35	6.80	22.26	0.32	0.80	1.89	2.65	41.93	5.52	2.21	0.67	61.32	4.51
May	21.73	3.53	3.82	8.08	9.25	20.13	1.81	0.86	2.69	2.68	37.36	84.63	2.20	0.43	60.41	2.26
Jun	19.39	3.53	3.72	8.44	10.56	20.43	1.17	1.03	2.76	1.32	31.22	54.17	2.11	0.96	61.24	3.67
Jul	31.07	6.37	4.25	8.77	3.13	23.38	0.50	1.06	1.69	1.25	83.85	1.68	2.93	0.36	89.81	1.87
Aug	24.92	4.64	4.29	9.37	7.58	22.32	0.07	0.28	2.47	2.23	23.71	4.47	3.98	0.18	78.27	4.49
Sep	23.49	4.08	3.93	8.60	4.80	26.13	1.42	0.28	1.84	1.63	56.30	4.55	0.41	0.18	64.91	2.75
Oct	22.94	4.37	4.15	8.84	5.34	23.70	0.52	1.44	2.60	2.25	108.18	5.35	1.83	0.26	63.97	2.14
Nov	16.34	3.91	3.53	7.15	16.99	25.90	0.35	0.30	0.47	1.73	113.60	7.15	10.26	2.92	75.05	4.85
Dec	17.09	3.41	3.38	8.19	16.86	24.90	0.77	0.29	1.22	2.45	47.83	3.22	2.42		74.75	15.67

Table B.45: Mean monthly values, Lough Annamakerrig

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	33.80	5.76	4.01	8.47	13.75	26.23	0.40	0.34	1.05	1.06	71.19	11.38	1.84	9.22	101.66	1.90
Feb	50.94	6.38	4.47	9.30	4.16	26.55	0.12	0.24	3.25	1.45	157.50	3.01	2.43	0.19	98.69	0.79
Mar	47.09	5.68	4.16	9.03	4.54	27.34	0.25	0.58	1.80	1.63	39.98	9.15	2.59		92.66	12.84
Apr	40.54	5.97	4.41	9.44	6.70	26.70	0.31	0.80	1.29	1.18	158.37	3.80	2.71	0.40	95.58	1.52
May	42.89	5.71	4.16	9.10	6.80	21.63	1.36	1.34	2.71	1.53	110.64	8.37	2.57	0.42	87.64	2.66
Jun	34.14	5.53	4.15	9.18	15.29	24.28	0.81	1.36	5.07	0.79	37.01	10.59	1.89	0.10	88.59	2.80
Jul	39.85	5.65	4.40	9.84	4.84	21.00	1.06	0.70	2.51	0.37	145.22	3.56	3.28	0.18	80.84	1.24
Aug	33.96	5.56	4.02	8.78	3.64	25.23	0.27	0.13	3.07	0.81	151.02	1.24	2.05	0.04	89.38	2.27
Sep	42.11	6.00	4.41	9.28	7.34	24.37	0.66	0.25	2.15	0.80	133.22	3.94	0.05	0.25	90.11	13.44
Oct	44.53	6.26	4.53	9.57	3.85	22.73	0.55	1.05	2.87	1.09	129.33	13.44	1.45	0.24	89.44	1.02
Nov	30.98	5.29	3.68	7.60	6.79	27.42	0.19	0.30	0.10	0.64	180.04	8.52	6.33	0.13	108.99	0.26
Dec	36.95	5.22	3.93	9.38	8.20	28.42	0.48	0.30	1.92	0.95	15.12	2.10	2.06	0.19	114.54	24.17

Table B.46: Mean monthly values, Lavey Lough

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	28.78	3.71	5.54	7.97	24.88	31.45	0.29	0.32	0.90	2.13	84.26	12.45	2.79	4.09	94.88	3.73
Feb	40.37	3.46	5.72	8.93	6.59	34.68	0.96	0.29	2.02	2.12	135.42	7.30	2.73	0.19	89.84	2.75
Mar	42.77	3.42	5.98	8.79	7.77	32.67	0.28	0.57	1.89	2.04	70.41	22.85	3.42	0.23	91.54	2.54
Apr	36.58	3.47	6.35	9.17	6.00	34.40	0.74	1.23	0.69	1.61	137.15	3.99	4.00	0.13	95.46	2.55
May	36.01	3.20	6.32	8.58	5.11	29.77	0.88	0.70	2.58	1.66	93.23	11.75	1.35	0.44	93.65	1.55
Jun	33.41	3.05	6.45	8.90	11.77	30.26	0.44	1.41	4.95	1.59	39.64	8.11	2.98	0.90	95.57	2.13
Jul	39.88	3.08	6.46	8.76	2.91	25.71	0.85	1.20	1.04	1.11	150.95	3.19	2.30	0.13	100.97	1.02
Aug	33.48	3.17	6.63	8.57	1.72	33.81	0.54	0.16	3.41	1.52	148.31	1.97	3.46	0.14	106.48	13.98
Sep	43.27	3.69	7.28	9.05	6.26	39.51	0.12	0.27	1.81	0.60	107.81	5.22	2.69	0.03	104.16	0.74
Oct	46.44	4.03	7.51	9.10	3.03	36.12	0.72	1.08	3.84	1.47	189.84	4.43	1.86	0.25	107.48	0.75
Nov	30.75	3.29	5.96	7.06	8.27	46.46	0.10	0.37	0.10	1.42	216.98	8.06	6.10	0.13	126.25	2.26
Dec	32.07	3.43	5.51	7.97	18.34	37.93	1.06	0.50	2.10	1.83	41.90	2.81	3.32	0.03	113.24	11.06

Table B.47: Mean monthly values, Lough Naback

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	13.26	2.46	3.57	6.12	44.73	14.39	0.37	0.40	0.99	2.83	99.63	8.76	1.71	7.99	36.32	3.90
Feb	15.92	2.21	3.64	6.66	24.71	16.46	0.60	0.20	1.38	3.16	133.20	4.04	1.62	2.35	32.22	1.75
Mar	22.94	2.11	3.67	7.06	25.76	15.29	0.36	0.43	1.16	3.51	167.89	7.75	2.95	0.07	57.63	3.55
Apr	13.93	2.25	3.87	6.66	19.16	16.63	0.43	1.10	2.28	2.55	80.03	3.47	1.74	0.11	33.18	4.00
May	16.16	2.16	3.85	6.38	15.25	13.40	1.45	0.77	2.34	2.39	54.43	3.66	2.44	0.34	32.93	2.19
Jun	16.88	2.14	3.83	6.61	12.95	11.59	0.74	1.65	5.06	1.38	34.57	9.90	2.04	0.18	32.00	2.53
Jul	16.56	2.22	3.79	6.45	5.97	18.01	0.94	0.71	2.47	2.03	64.27	2.24	1.46	0.47	58.45	4.07
Aug	12.79	2.31	3.87	6.46	6.57	11.24	0.54	0.41	3.30	2.48	40.61	1.45	2.14	0.07	34.95	5.23
Sep	17.28	2.87	4.75	7.75	13.57	11.10	0.09	0.42	3.42	1.81	33.66	13.99			34.05	3.14
Oct	20.18	2.73	4.53	7.38	9.14	14.17	0.82	1.08	3.14	2.68	98.97	13.55	1.63	0.15	36.03	1.79
Nov	12.62	1.97	3.60	5.56	15.66	19.17	0.10	0.42	0.16	2.63	93.52	10.91	5.87	0.20	74.57	2.39
Dec	14.58	2.26	3.48	6.90	44.28	16.61	0.29	0.31	3.24	2.81	98.56	3.29	1.57	0.57	42.16	37.72

CORRELATION FACTORS

Table B.48: Correlation factors from all the data used during lake analysis

	Ca	K	Mg	Na	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
Ca	1.00															
K	0.35	1.00														
Mg	0.82	0.54	1.00													
Na	0.50	0.20	0.26	1.00												
Al	-0.71	-0.44	-0.66	-0.40	1.00											
Ba	0.77	0.47	0.82	0.59	-0.71	1.00										
Cd	0.14	0.39	0.22	0.01	-0.33	0.16	1.00									
Co	0.06	0.50	0.31	-0.25	-0.09	0.08	0.13	1.00								
Cr	0.38	-0.06	0.28	-0.03	0.04	0.07	0.00	0.08	1.00							
Cu	-0.22	0.04	-0.16	0.24	-0.05	0.08	0.11	-0.20	-0.23	1.00						
Fe	0.73	0.34	0.57	0.49	-0.32	0.53	0.11	0.07	0.27	-0.07	1.00					
Mn	-0.52	-0.03	-0.39	-0.39	0.72	-0.54	-0.13	0.22	0.11	-0.26	-0.22	1.00				
Ni	0.57	0.48	0.65	0.02	-0.34	0.36	0.29	0.25	0.54	-0.21	0.55	0.00	1.00			
Pb	0.00	0.66	0.06	-0.01	-0.03	0.08	0.30	0.33	0.02	0.24	0.24	0.22	0.25	1.00		
Sr	0.82	0.11	0.74	0.49	-0.69	0.67	0.06	-0.07	0.31	-0.08	0.56	-0.57	0.49	-0.28	1.00	
Zn	-0.25	-0.25	-0.25	-0.18	0.44	-0.28	-0.13	-0.10	0.14	-0.02	-0.17	0.21	-0.18	-0.12	-0.30	1.00

CROSS-VALIDATION RESULTS

Test 1: Mean values of nine lakes with more than one sample point

Table B.49: Cross-validation using mean values of lakes with multiple sample points

Group	Allua	Carra	Conn	Corrib	Derrav	Gowna	Lene	Melvin	Oughter
Allua	9	0	0	0	0	0	0	0	0
Carra	0	2	0	0	0	0	0	0	0
Conn	0	0	4	0	0	0	0	0	0
Corrib	0	0	0	3	0	0	0	0	0
Derrav	0	0	0	0	2	0	0	0	0
Gowna	0	0	0	0	0	1	0	0	0
Lene	0	0	0	0	0	0	3	0	0
Melvin	0	0	0	0	0	0	0	8	0
Oughter	0	0	0	0	0	1	0	0	2
Total N	9	2	4	3	2	2	3	8	2
N Correct	9	2	4	3	2	1	3	8	2
Proportion	1.00	1.00	1.00	1.00	1.00	0.50	1.00	1.00	1.00

Total N: 35
N Correct: 34
Proportion Correct: 0.971

Test 2: Max, min and median values of all lakes

Summary of classification with cross-validation

Table B.50: Cross-validation using max, min and median values of all lakes

Group	AA	AK	AR	CA	CN	CB	DV	GA	GO	LV	LE	MK	ML	NB	OU	SH	SI	WH
Allua	25	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
Annama	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Arrow	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Carra	0	0	0	3	1	0	0	0	0	0	0	0	0	0	0	0	0	0
Conn	0	0	0	1	5	1	0	0	0	0	0	0	0	0	1	0	0	0
Corrib	0	0	2	1	0	3	0	0	0	0	0	3	0	0	0	0	0	0
Derrav	0	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0
Garadice	1	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0
Gowna	0	0	0	0	0	0	0	0	2	0	0	0	0	1	0	0	0	0
Lavey	0	0	1	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0
Lene	0	0	0	0	0	1	0	0	0	0	9	0	0	0	0	0	0	0
Mask	0	1	0	0	2	3	0	0	0	0	0	0	0	0	0	0	0	0
Melvin	0	0	0	1	4	0	0	0	0	0	0	0	24	0	0	0	0	0
Naback	0	0	0	0	0	0	0	3	2	0	0	0	0	0	0	0	0	0
Oughter	0	0	0	0	0	0	0	0	2	1	0	0	0	0	5	0	2	0
Sheelin	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	2	0	0
Sillan	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3
Whitelake	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0
Total N	27	3	3	6	12	9	6	3	6	3	9	3	24	3	6	3	3	3
N Correct	25	0	0	3	5	3	6	0	2	1	9	0	24	0	5	2	0	0
Proportion	0.93	0.00	0.00	0.50	0.42	0.33	1.00	0.00	0.33	0.33	1.00	0.00	1.00	0.00	0.83	0.67	0.00	0.00

Total N: 132
N Correct: 85
Proportion Correct: 0.644

Test 3: Small midland lakes

95 cases used in test – the remainder had missing values

Table B.51: Cross-validation of the eight small midland lakes

Group	Gowna	Garadice	Oughter	Whitelake	Sillan	Annamak	Lavey	Naback
Gowna	14	0	1	1	0	0	0	0
Garadice	0	13	0	0	0	0	0	0
Oughter	1	0	21	0	0	0	0	0
Whitelake	0	0	0	7	2	0	0	0
Sillan	0	0	1	0	8	0	2	0
Annamak	0	0	0	0	0	5	0	0
Lavey	0	0	0	0	0	0	8	0
Naback	0	0	0	0	0	0	0	11
Total N	15	13	23	8	10	5	10	11
N Correct	14	13	21	7	8	5	8	11
Proportion	0.93	1.00	0.91	0.88	0.80	1.00	0.80	1.00

Total N: 95
N Correct: 87
Proportion Correct: 0.916

Test 4: 16 lakes using only Group I and Group II elements

934 cases used in test – the remainder had missing values
Summary of classification with cross-validation

Table B.52: Cross-validation of 16 lakes using only Group I and II elements

Group	AK	AR	CA	CN	CB	DV	GA	GO	LV	LE	MK	NB	OU	SH	SI	WH
Annama	38	0	0	0	0	0	0	0	0	0	0	0	0	0	2	13
Arrow	0	31	3	0	6	0	0	0	0	0	0	0	0	0	0	0
Carra	0	0	56	5	1	0	0	0	0	0	1	0	0	0	0	0
Conn	0	0	2	141	2	0	0	0	0	0	0	0	2	0	0	0
Corrib	0	1	1	1	60	0	0	0	0	0	4	0	0	0	0	0
Derrav	0	0	0	0	0	34	0	0	0	0	0	0	0	0	0	0
Garadice	0	0	2	1	1	0	40	0	0	0	0	2	0	0	0	0
Gowna	0	1	0	0	0	0	0	68	0	0	0	2	2	0	10	4
Lavey	0	0	0	0	0	0	0	3	37	0	0	0	0	1	0	0
Lene	0	0	1	0	1	0	0	0	0	51	0	0	0	0	0	0
Mask	0	0	0	0	27	0	0	0	0	0	27	0	0	0	0	0
Naback	0	0	0	0	0	0	2	0	1	0	0	37	0	0	0	0
Oughter	0	0	0	0	0	0	0	8	2	0	0	1	75	0	2	0
Sheelin	0	0	0	0	0	0	0	0	1	0	0	0	0	46	0	0
Sillan	1	0	0	0	0	0	0	7	2	0	0	0	7	0	27	10
Whitelake	4	0	0	0	0	0	0	0	0	0	0	0	0	0	2	14
Total N	43	33	65	148	98	34	42	86	43	51	32	42	86	47	43	41
N Correct	38	31	56	141	60	34	40	68	37	51	27	37	75	46	27	14
Proportion	0.88	0.94	0.86	0.95	0.61	1.00	0.95	0.79	0.86	1.00	0.84	0.88	0.87	0.98	0.63	0.34

Total N: 934
N Correct: 782
Proportion Correct: 0.837

Test 5: Eight sites on Lough Melvin

33 cases used in test – the remainder had missing values

Table B.53: Cross-validation of the eight sites on Lough Melvin

Site	Mel 1	Mel 2	Mel 3	Mel 4	Mel 5	Mel 6	Mel 7	Mel 8
Mel 1	0	1	0	0	0	0	0	0
Mel 2	0	4	0	0	1	0	0	0
Mel 3	1	0	3	0	0	0	0	0
Mel 4	0	0	0	5	0	0	0	0
Mel 5	2	0	0	0	2	1	0	0
Mel 6	0	0	0	0	0	4	0	0
Mel 7	0	0	0	0	0	0	5	0
Mel 8	1	0	0	0	0	0	0	3
Total N	4	5	3	5	3	5	5	3
N Correct	0	4	3	5	2	4	5	3
Proportion	0.00	0.80	1.00	1.00	0.67	0.80	1.00	1.00

Total N: 33
N Correct: 26
Proportion Correct: 0.788

Appendix C.

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CORRIB RESULTS STATISTICS

Table C-1: Statistical summary of the data from 28 Lough Corrib rivers

	AVERAGE	MAX	MIN	Std Dev	N
Ca mg/L	58.44	481.84	0.57	65.01	2262
K mg/L	2.07	29.99	0.17	1.94	2244
Mg mg/L	3.89	14.1	0.45	2.50	2262
Na mg/L	12.63	42.48	3.86	3.51	2075
Al ug/L	34.69	432	0.03	48.88	2137
Ba ug/L	30.36	194.37	0.22	20.57	2262
Cd ug/L	0.41	2.67	0.01	0.39	1289
Co ug/L	0.51	29.3	0.01	1.50	1888
Cr ug/L	2.29	16.81	0.01	2.15	1648
Cu ug/L	1.45	202.5	0.01	4.79	2047
Fe ug/L	201.43	3898.2	0.02	273.22	1894
Mn ug/L	18.07	10957.44	0.01	276.66	2098
Ni ug/L	3.55	157.87	0.01	8.26	1504
Pb ug/L	0.21	5.36	0.01	0.27	1485
Sr ug/L	152.05	740.14	0.22	150.25	2262
Zn ug/L	7.79	318.98	0.01	14.30	1781

Table C-2: Statistics for individual river locations

Detailed statistical tables follow on the next two pages, with information on the maximum, minimum and standard deviation of each element in each river studied from the Lough Corrib catchment. This information is supplementary to the mean values for each lake reported in Table 4.3 (Chapter 4 of the main text).

Table C-2: Statistics for individual river locations

Sample	Stat	Ca mg/l	K mg/l	Mg mg/l	Na mg/l	Al ug/l	Ba ug/l	Cd ug/l	Co ug/l	Cr ug/l	Cu ug/l	Fe ug/l	Mn ug/l	Ni ug/l	Pb ug/l	Sr ug/l	Zn ug/l
RCR-1	Max	113.78	4.37	5.79	23.56	51.75	73.12	2.67	2.73	12.12	4.19	407.13	11.96	9.34	2.00	342.87	55.09
	Min	15.77	0.90	2.20	8.07	0.25	10.69	0.01	0.01	0.10	0.17	2.31	0.06	0.12	0.01	35.66	0.56
	Std Dev	21.55	0.52	0.64	2.11	7.75	10.18	0.47	0.43	2.36	0.82	81.63	1.62	1.71	0.30	50.96	8.63
RCR-2	Max	52.29	1.62	3.52	20.66	106.21	28.72	2.39	3.01	9.61	4.79	1107.09	70.89	12.47	0.68	129.49	31.39
	Min	4.84	0.50	0.90	6.66	1.03	4.79	0.02	0.01	0.02	0.09	3.50	0.31	0.05	0.02	15.98	0.07
	Std Dev	8.12	0.27	0.60	2.87	22.10	3.65	0.41	0.48	1.78	0.87	237.57	9.70	1.98	0.15	14.77	6.73
RCR-3	Max	50.72	2.49	3.80	23.09	78.57	38.24	0.92	2.81	11.36	5.60	473.04	65.43	11.50	0.89	72.37	55.82
	Min	12.93	0.86	1.87	8.86	0.53	7.31	0.01	0.01	0.14	0.03	2.48	0.42	0.08	0.01	30.97	0.06
	Std Dev	6.97	0.32	0.42	2.61	13.13	3.56	0.26	0.46	2.08	0.91	94.83	10.80	1.71	0.19	7.61	8.71
RCR-4	Max	88.98	3.10	4.41	25.84	48.20	36.81	0.92	3.67	16.81	2.60	227.36	43.17	12.85	5.36	97.57	75.57
	Min	14.27	1.12	2.03	9.11	0.31	6.07	0.01	0.01	0.01	0.08	0.36	0.10	0.01	0.01	31.06	0.04
	Std Dev	13.87	0.41	0.55	2.52	9.65	4.17	0.22	0.63	2.99	0.73	57.36	5.81	1.70	0.82	11.45	11.75
RCR-5	Max	96.51	3.97	4.69	26.74	50.13	68.54	1.03	3.76	15.87	4.43	216.99	289.92	13.72	0.40	109.87	38.06
	Min	20.24	1.00	2.09	9.31	1.10	8.75	0.01	0.01	0.08	0.30	0.13	0.02	0.29	0.01	39.40	0.10
	Std Dev	14.57	0.52	0.55	2.66	9.09	6.98	0.29	0.61	3.04	0.85	62.84	33.67	1.89	0.10	12.24	6.78
RCR-7	Max	59.73	1.77	4.60	17.45	114.01	114.10	1.53	4.56	15.18	5.35	523.15	94.12	15.54	1.45	123.04	65.46
	Min	4.46	0.24	1.11	6.95	2.02	10.63	0.01	0.01	0.02	0.08	26.20	0.34	0.08	0.01	19.32	0.04
	Std Dev	12.68	0.24	0.82	2.46	23.24	22.57	0.36	0.74	2.52	0.94	129.96	15.01	2.38	0.22	25.06	10.45
RCR-8	Max	18.71	0.95	2.67	18.10	89.53	117.44	1.91	5.37	13.17	3.46	826.36	96.75	18.32	1.93	103.00	117.83
	Min	1.35	0.17	0.84	6.30	2.86	15.81	0.01	0.02	0.01	0.01	17.68	0.57	0.02	0.01	19.75	0.11
	Std Dev	3.17	0.14	0.40	2.66	18.56	22.60	0.37	0.90	2.33	0.79	153.20	18.53	3.47	0.28	19.71	17.08
RCR-9	Max	10.15	1.73	2.66	18.33	268.25	132.45	1.80	5.49	16.44	60.05	1960.56	343.36	17.26	3.31	63.75	51.04
	Min	0.86	0.33	0.75	5.80	16.37	38.03	0.02	0.01	0.08	0.04	77.85	1.06	0.09	0.02	13.42	0.10
	Std Dev	1.52	0.29	0.41	2.65	56.84	17.69	0.42	0.94	2.32	6.85	445.99	81.26	3.27	0.43	10.79	9.31
RCR-10	Max	17.31	2.80	3.83	19.24	432.00	141.95	1.30	4.84	8.09	202.50	1484.47	261.07	10.90	1.81	103.16	105.62
	Min	3.16	0.55	1.24	8.11	23.48	38.83	0.02	0.04	0.01	0.12	99.71	0.47	0.02	0.01	17.43	0.42
	Std Dev	2.84	0.38	0.59	2.43	86.09	15.21	0.32	0.79	1.84	23.07	304.88	51.35	2.21	0.29	14.22	17.90
RCR-11	Max	20.89	1.98	3.10	17.83	164.22	92.61	1.89	4.35	6.00	7.64	1010.80	44.83	10.90	0.77	54.23	35.73
	Min	2.79	0.28	0.89	5.94	3.04	4.79	0.02	0.02	0.04	0.14	19.68	0.19	0.02	0.01	13.78	0.03
	Std Dev	4.42	0.30	0.57	2.70	25.76	9.54	0.41	0.76	1.60	1.19	211.92	6.99	1.99	0.17	10.66	8.05
RCR-12	Max	21.53	1.80	2.95	17.76	108.23	60.85	1.21	5.59	6.18	8.75	916.31	47.88	9.03	0.59	102.75	40.14
	Min	3.66	0.34	0.90	6.56	2.52	5.01	0.01	0.01	0.01	0.24	10.30	0.10	0.06	0.01	22.37	0.01
	Std Dev	4.87	0.23	0.49	2.44	20.91	7.08	0.32	0.95	1.65	1.25	154.84	7.93	1.55	0.12	22.05	9.78
RCR-13	Max	48.01	2.11	3.45	20.34	141.30	56.68	1.83	5.28	6.93	3.07	608.26	39.83	12.22	0.59	342.13	56.97
	Min	5.74	0.32	0.98	6.93	7.86	22.47	0.01	0.02	0.03	0.02	14.55	0.09	0.03	0.01	48.89	0.22
	Std Dev	9.71	0.34	0.52	2.41	30.06	7.16	0.36	0.95	1.69	0.68	128.75	5.80	2.07	0.12	70.88	8.62
RCR-14	Max	19.58	1.08	3.47	20.93	215.58	50.57	1.89	5.13	6.68	5.19	929.06	104.50	11.79	1.10	103.26	67.66
	Min	1.71	0.21	0.99	7.20	11.70	19.61	0.01	0.01	0.06	0.01	17.73	0.19	0.01	0.06	20.69	0.08
	Std Dev	3.90	0.18	0.58	2.94	43.23	6.13	0.42	1.02	1.52	0.86	239.03	15.26	2.62	0.19	22.80	9.90
RCR-15	Max	11.82	0.94	3.03	21.74	123.64	84.16	1.52	6.49	8.81	13.59	554.09	84.30	15.17	1.19	107.55	93.84
	Min	0.60	0.25	0.68	5.70	10.50	2.89	0.01	0.01	0.15	0.15	3.25	0.09	0.02	0.01	7.78	0.22
	Std Dev	2.43	0.16	0.57	3.53	23.85	13.24	0.31	1.11	1.83	1.82	96.05	13.25	4.17	0.22	18.55	16.12

Table C-2: Statistics for individual river locations

Sample	Stat	Ca mg/l	K mg/l	Mg mg/l	Na mg/l	Al ug/l	Ba ug/l	Cd ug/l	Co ug/l	Cr ug/l	Cu ug/l	Fe ug/l	Mn ug/l	Ni ug/l	Pb ug/l	Sr ug/l	Zn ug/l
RCR-16	Max	16.79	1.32	4.13	26.98	86.38	31.58	1.63	3.65	8.19	3.24	266.07	23.36	13.44	1.01	98.62	42.89
	Min	0.57	0.19	0.45	3.86	1.23	0.22	0.02	0.01	0.06	0.08	0.94	0.01	0.03	0.01	0.22	0.02
	Std Dev	4.03	0.18	0.63	3.72	17.09	3.51	0.41	0.57	1.43	0.66	49.63	4.36	2.09	0.18	22.26	6.99
RCR-17	Max	13.41	0.94	3.08	17.90	104.94	54.62	1.68	1.17	7.00	3.56	610.35	92.04	3.63	0.63	49.59	59.75
	Min	0.94	0.18	0.77	4.75	0.14	11.69	0.01	0.01	0.04	0.03	6.49	0.07	0.01	0.02	12.85	0.03
	Std Dev	2.86	0.15	0.50	2.59	23.19	7.35	0.36	0.26	1.39	0.59	107.73	15.38	0.90	0.10	8.77	9.17
RCR-18	Max	35.31	1.45	3.89	20.29	125.90	89.25	1.84	1.12	4.99	5.90	240.70	51.44	11.81	1.03	218.15	166.78
	Min	2.36	0.33	0.78	6.11	5.25	14.98	0.01	0.01	0.01	0.01	7.68	0.03	0.04	0.01	22.65	0.23
	Std Dev	7.73	0.22	0.76	2.97	24.29	18.29	0.43	0.23	1.14	0.79	59.19	7.95	1.83	0.15	51.54	23.01
RCR-19	Max	14.41	1.71	3.14	19.24	134.76	120.17	1.94	2.07	4.16	5.33	354.85	32.48	2.94	1.25	52.39	48.18
	Min	1.66	0.37	0.97	5.89	2.51	20.72	0.01	0.01	0.06	0.06	0.94	0.16	0.01	0.01	12.28	0.08
	Std Dev	2.70	0.22	0.49	2.71	23.19	13.26	0.45	0.36	0.96	0.97	58.48	5.95	0.78	0.20	7.33	7.77
RCR-20	Max	113.88	2.98	4.90	23.36	33.25	108.97	1.26	2.12	6.29	4.80	208.10	5.74	5.92	0.57	168.09	44.20
	Min	13.90	1.20	2.16	8.18	1.51	28.77	0.01	0.01	0.06	0.06	1.34	0.02	0.25	0.01	84.71	0.03
	Std Dev	15.46	0.31	0.58	2.20	5.54	12.71	0.35	0.35	1.28	0.75	45.13	0.93	1.10	0.11	16.69	7.46
RCR-21	Max	402.43	11.88	11.72	42.48	24.06	47.57	1.53	2.42	14.58	3.23	494.61	10.59	9.34	0.58	296.87	84.44
	Min	50.13	2.05	3.23	9.39	0.34	23.02	0.01	0.05	0.22	0.02	0.02	0.01	0.45	0.01	139.72	0.02
	Std Dev	54.61	1.13	1.71	3.76	4.68	5.90	0.38	0.41	2.53	0.65	115.43	1.53	1.76	0.14	30.60	14.87
RCR-22	Max	392.54	14.59	12.10	41.84	19.78	34.81	1.61	2.96	9.91	3.79	405.91	3.61	25.97	0.51	244.82	60.24
	Min	31.26	3.14	3.73	9.06	0.04	13.96	0.01	0.04	0.26	0.03	0.23	0.01	0.83	0.01	104.87	0.15
	Std Dev	52.24	1.35	1.54	3.80	3.92	3.67	0.35	0.40	2.38	0.66	89.97	0.86	3.10	0.09	21.08	9.86
RCR-23	Max	304.11	8.91	8.47	37.31	42.50	49.25	1.70	3.44	10.74	5.03	603.10	23.13	26.67	0.49	720.69	318.98
	Min	48.56	1.86	2.61	7.86	0.37	18.74	0.01	0.02	0.02	0.24	0.44	0.06	0.53	0.01	275.68	0.09
	Std Dev	50.44	0.91	1.25	3.36	9.09	5.92	0.36	0.48	2.32	0.95	101.87	3.79	3.28	0.10	82.98	43.40
RCR-24	Max	374.07	10.99	7.69	39.01	29.55	43.04	1.71	2.86	9.70	36.36	628.30	9.03	26.24	2.36	480.73	77.86
	Min	54.89	1.63	2.44	7.69	0.33	14.59	0.01	0.05	0.09	0.01	0.22	0.01	0.05	0.02	201.04	0.20
	Std Dev	54.59	1.08	1.07	3.52	6.00	4.81	0.40	0.48	2.11	4.04	114.54	1.73	3.39	0.40	46.19	11.96
RCR-25	Max	437.16	12.98	7.99	42.37	21.02	59.75	1.56	24.44	11.71	4.06	530.66	6.27	125.76	0.78	661.38	72.25
	Min	51.89	1.92	2.66	8.53	0.19	16.27	0.01	0.02	0.11	0.46	0.35	0.02	0.21	0.01	208.94	0.12
	Std Dev	58.96	1.28	1.03	3.90	4.80	6.30	0.39	2.80	2.14	0.75	112.40	1.23	14.15	0.16	62.46	11.56
RCR-26	Max	481.84	13.33	14.10	42.30	22.17	75.83	1.51	27.87	8.01	5.70	509.64	123.47	133.46	1.52	673.14	51.95
	Min	52.47	2.11	3.25	8.88	0.03	14.71	0.02	0.06	0.05	0.04	0.44	0.01	0.16	0.01	302.43	0.13
	Std Dev	61.77	1.59	1.86	3.76	3.93	8.70	0.40	3.21	2.11	0.92	129.64	14.50	15.24	0.26	87.63	9.10
RCR-28	Max	430.89	14.69	13.59	40.38	40.20	101.84	2.48	28.28	9.39	5.05	583.04	20.31	157.87	1.02	689.31	61.67
	Min	53.13	2.35	2.84	8.60	0.14	16.50	0.02	0.03	0.08	0.12	0.89	0.07	0.23	0.01	275.34	0.44
	Std Dev	59.35	1.73	1.49	3.61	7.07	10.82	0.49	3.27	2.28	0.96	110.92	3.28	18.07	0.16	73.89	13.87
RCR-29	Max	351.20	12.01	12.48	37.19	67.63	36.77	2.62	29.30	11.04	8.00	573.00	22.48	142.15	0.63	740.14	164.73
	Min	42.96	2.20	2.87	7.70	0.03	13.63	0.01	0.05	0.02	0.08	4.22	0.09	0.05	0.01	277.16	0.01
	Std Dev	54.04	1.40	1.40	3.53	11.27	4.37	0.47	3.37	2.47	1.07	95.38	3.22	16.21	0.13	76.83	23.17
RCR-30	Max	320.47	29.99	12.06	41.30	67.15	194.37	2.34	21.59	9.56	4.60	3898.20	10957.44	114.80	0.46	362.60	57.28
	Min	42.15	2.29	2.53	9.91	0.58	10.13	0.01	0.04	0.26	0.04	5.67	0.27	0.05	0.01	109.37	0.44
	Std Dev	47.34	4.09	1.36	4.09	15.68	21.79	0.49	2.48	1.95	0.94	622.73	1389.45	13.05	0.12	54.37	10.00

SPATIAL VARIATION

The following plots were generated from Table 4.3, and they represent visually the spatial variation of elements across the sites. Details of site locations can be found in Figure 4.1 and Table 4.2. Standard deviations are reported in Table B.3 above.

Calcium

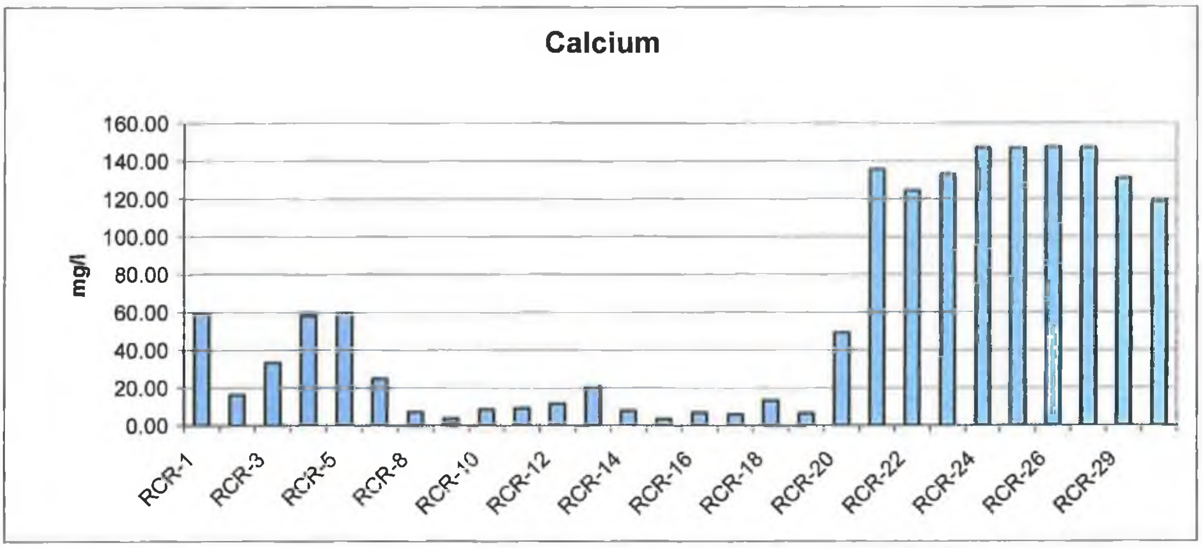


Figure C-1: Spatial variation in total mean calcium conc. in the Corrib rivers

It is clear how the sites to the eastern side of Lough Corrib (RCR-21 to RCR-30 inclusive) have a much higher mean concentration of calcium (all >100mg/l) than the sites on the eastern side of the lake (all <40mg/l). Sites on the boundaries of limestone and harder rock have intermediate values (e.g. RCR-1 and RCR-20).

Potassium

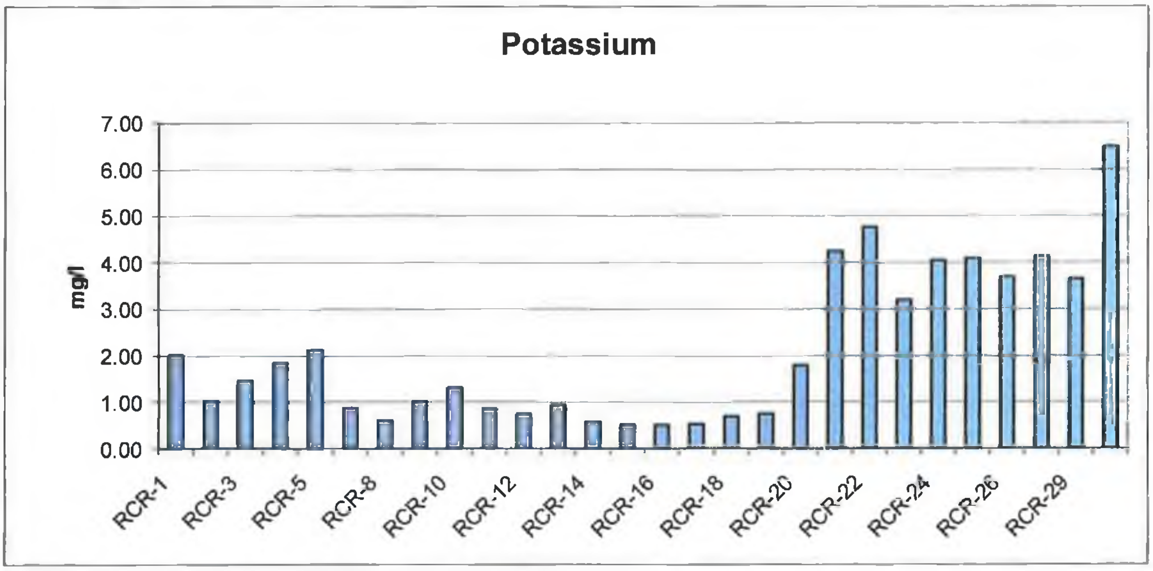


Figure C-2: Spatial variation in total mean potassium conc. in the Corrib rivers

Potassium shows a similar pattern to calcium, with all the streams on the east showing levels >3mg/l, and those on the west having levels <2mg/l.

Magnesium

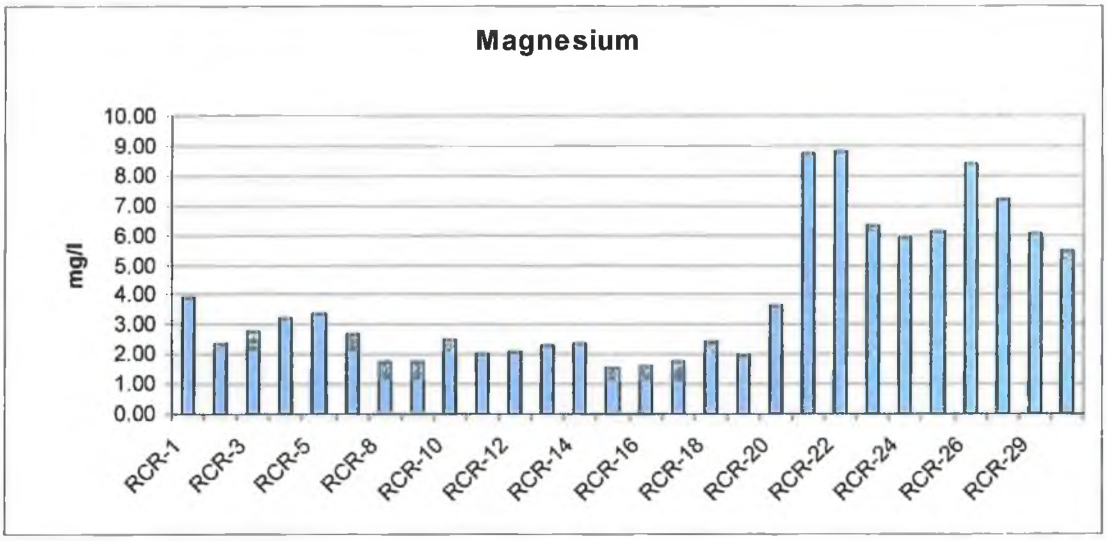


Figure C-3: Spatial variation in total mean magnesium conc. in the Corrib rivers

Again, a similar pattern to calcium is found with magnesium. All the sites on the east have concentrations >5mg/l, and those on the west have values <3mg/l. The boundary streams have intermediate values.

Sodium

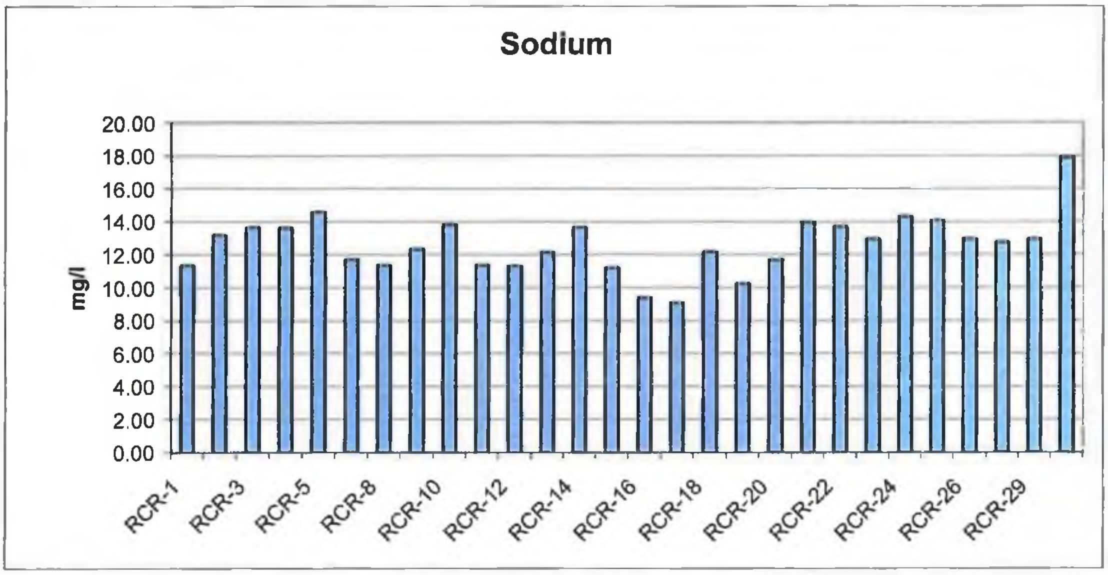


Figure C-4: Spatial variation in total mean sodium conc. in the Corrib rivers

There is little variation in the sodium concentration across the catchment, implying that the levels of this element have more to do with the influence of sea-spray rather than the geology. The highest levels (>17µg/l) were found in the Carrowbrowne Stream (RCR-

30) which is adjacent to the Galway city dump, possibly contributing to the elevated sodium concentration.

Aluminium

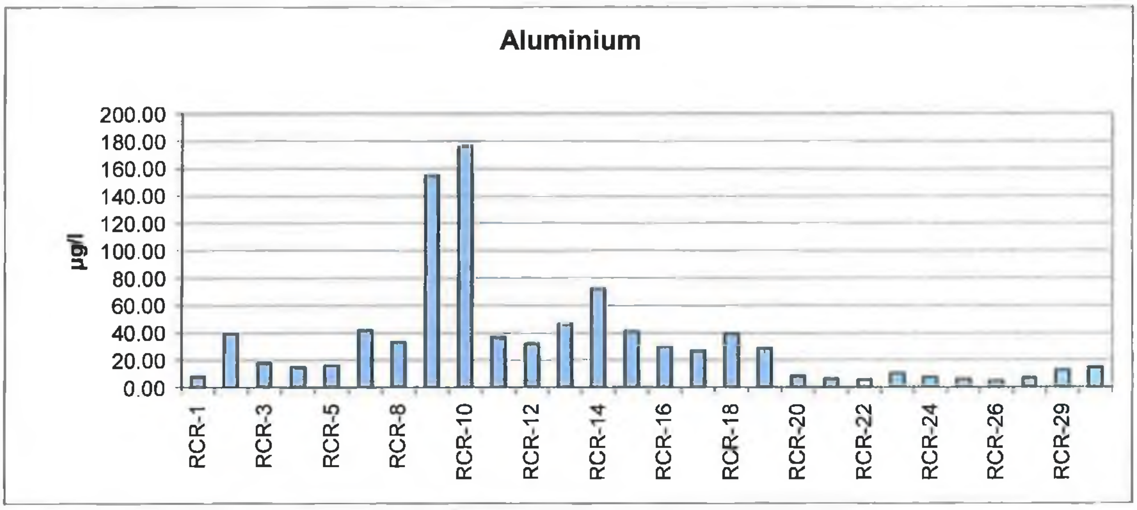


Figure C-5: Spatial variation in total mean aluminium conc. in the Corrib rivers

Aluminium concentrations are highest in RCR-9 and RCR-10, both of which originate from areas of granite bedrock and around which there are areas of forestry. Both of these streams have an aluminium level >140µg/l. The remaining streams to the west of the lake have levels ranging from 20-80µg/l. The eastern and boundary streams, however, all have aluminium levels <20µg/l.

Barium

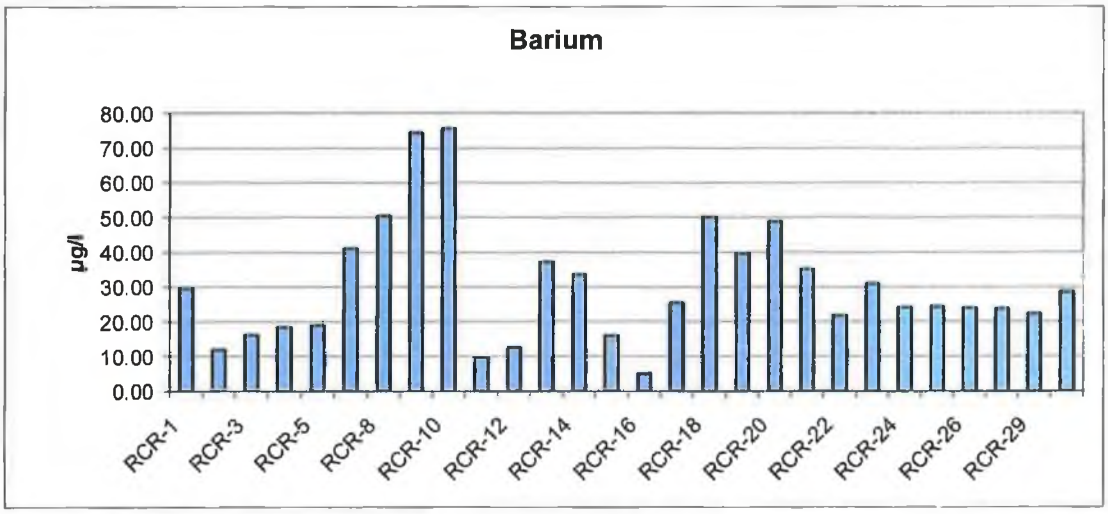


Figure C-6: Spatial variation in total mean barium conc. in the Corrib rivers

Barium exhibits an unusual spread of concentrations across the sample sites compared to other Periodic Table Group II elements. It would be expected that the streams to the east of the lake would have the highest values, with those to the west lower values. However, there is a more random distribution, with no clear pattern evident. The chart above shows that the two highest concentrations are in fact found in streams on the west of the lake – RCR-9 and RCR-10 – both of which have values >70µg/l. The lowest concentrations of this element are also found on the west in RCR-11 and RCR-16 both with mean values <20µg/l.

Cadmium

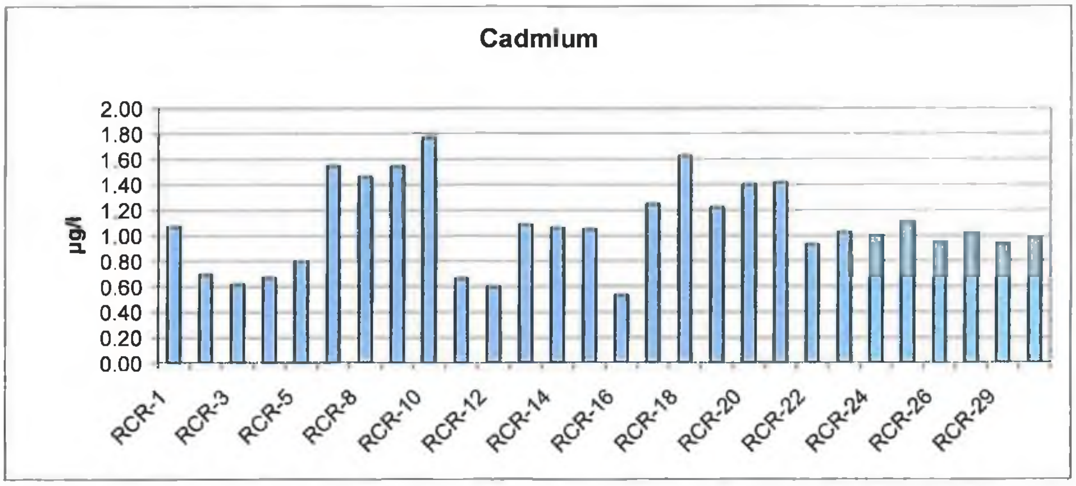


Figure C-7: Spatial variation in total mean cadmium conc. in the Corrib rivers

Cadmium concentrations are generally low, with no site exceeding a mean value of 1.8µg/l. There is no clear east/west distinction. The lowest concentrations are found on the western side on the lake in RCR-12 and RCR-16 (both <0.6µg/l). The highest values are also found on the west, with RCR-7, RCR-8, RCR-9, RCR-10 and RCR-18 all having a value >1.4µg/l.

Cobalt

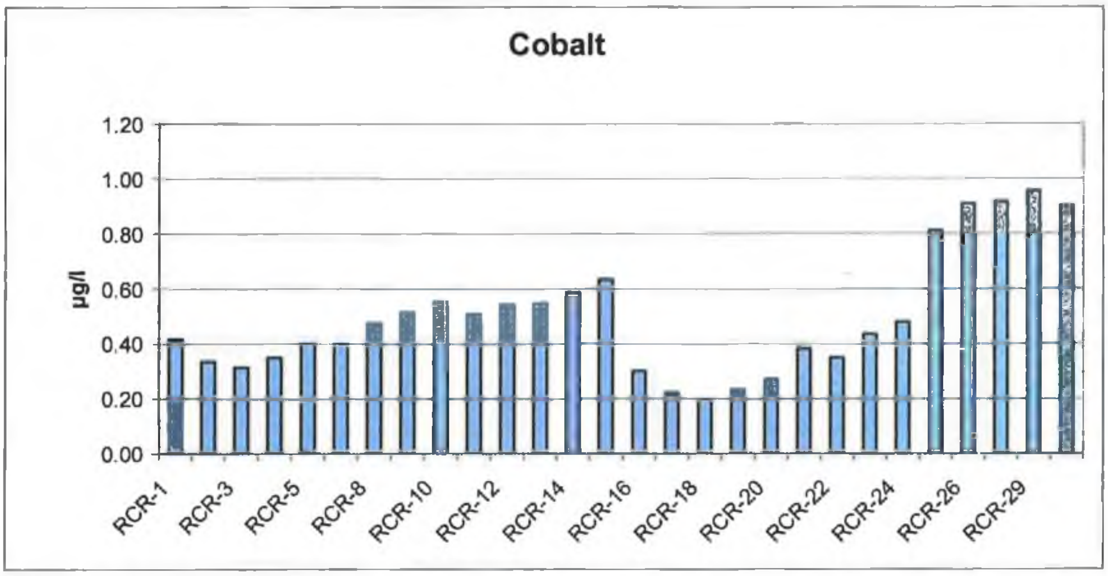


Figure C-8: Spatial variation in total mean cobalt conc. in the Corrib rivers

The mean concentration pattern for cobalt is interesting because it doesn't seem to follow the east/west trend like many other elements, but there seems to be more of a north/south influence. The chart above shows the lowest values (all <0.4µg/l) to the north, northwest and northeast of the lake (RCR-16 to RCR22 inclusive). There are also some low values to the southwest in the region of Ballyquirke lake. The highest values (all >0.8µg/l) are found in the sites to the southeast of the lake (RCR-25 to RCR-30 inclusive). Overall, there is a very narrow spread in the mean values for the sites, with only lead showing a smaller range.

Chromium

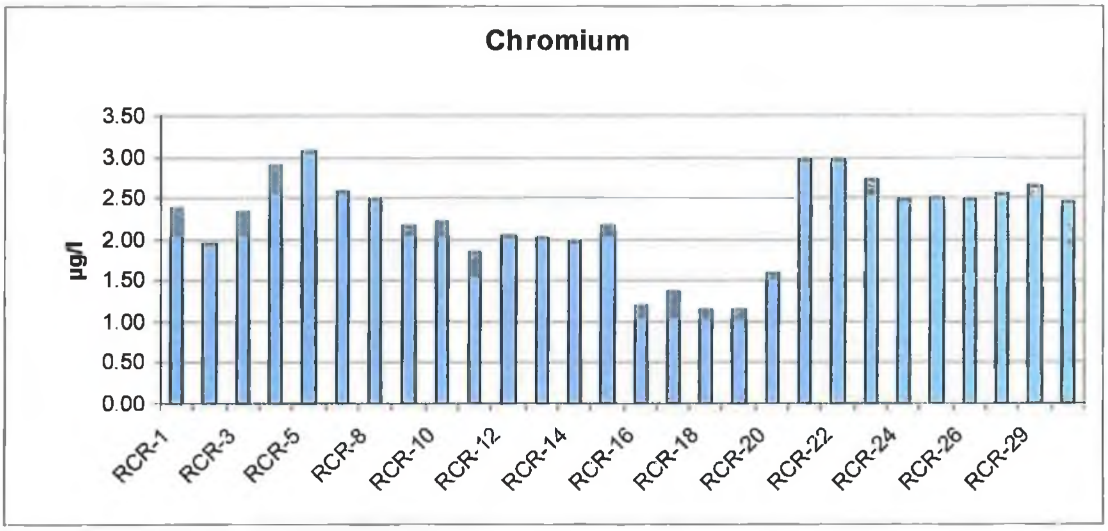


Figure C-9: Spatial variation in total mean chromium conc. in the Corrib rivers

All but one of the sites showed chromium values ranging between 1-3µg/l. The exception was the canal downstream of the sewage works near Ballyquirke (RCR-5). In general, the streams on the western side of the lake displayed the lowest concentrations in the range. Four of these, RCR-16 to RCR-19 inclusive, had extremely low values (all <1.5µg/l).

Copper

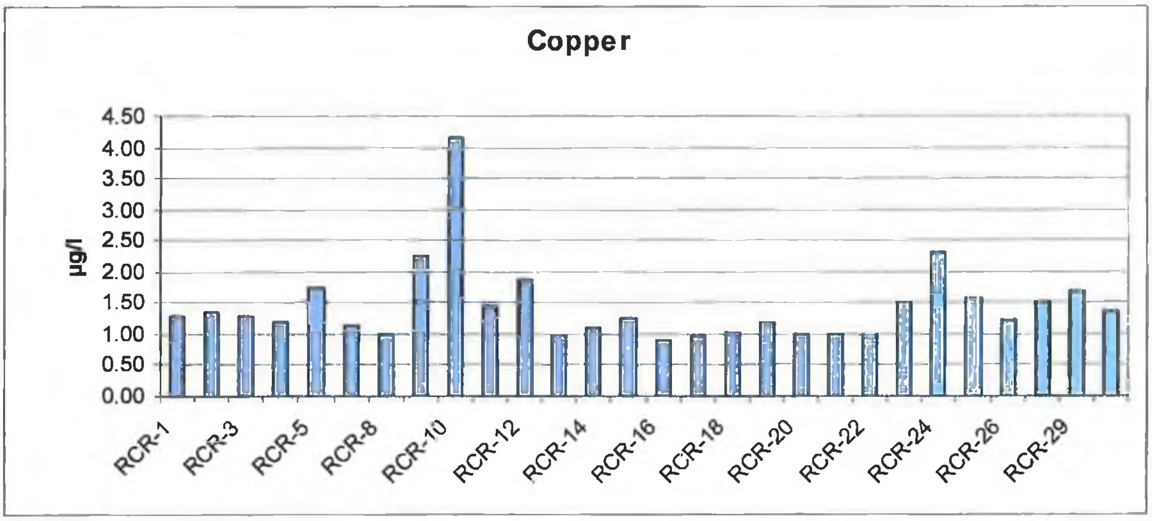


Figure C-10: Spatial variation in total mean copper conc. in the Corrib rivers

The Derrymoyle River (RCR-10) stands out as having a much higher level of copper than any of the other streams. At a level of >4µg/l it is almost double the next nearest sites of RCR-9 and RCR-24 (both >2µg/l). The remaining 25 sites have low levels of copper ranging between 0.5-2µg/l.

Iron

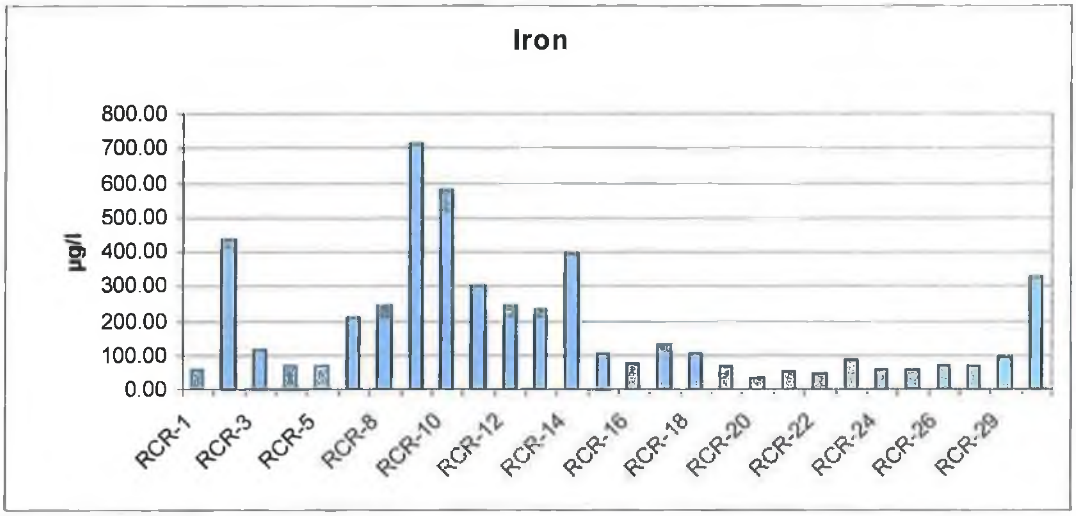
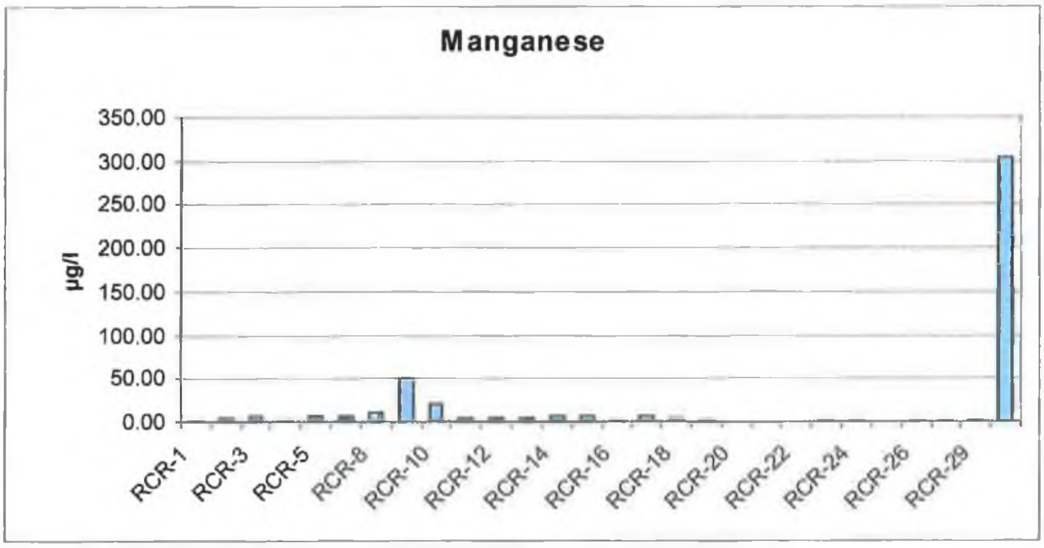


Figure C-11: Spatial variation in total mean iron conc. in the Corrib rivers

The concentration pattern for iron is very similar to that for aluminum, with the highest mean concentrations being found in the soft water streams to the west of the lake. RCR-9 and RCR-10 again have the highest values (both > 500µg/l) with RCR-2 and RCR-14 also having high values (~400µg/l). The Carrowbrowne Stream is unique from the streams on the east because it has a mean value >300µg/l, possibly due to its proximity to the Galway dump. (There are high concentrations of manganese and sodium also in this stream). The eastern and boundary streams all have mean iron concentrations <100µg/l.

Manganese

Two plots are given for manganese in order to illustrate the high mean values of this element in the Carrowbrowne stream discussed in Chapter 4. The first plot shows the contrast between manganese in this stream and all the other sites. The Carrowbrowne Stream has been removed from the second plot in order to best illustrate the other sites. It can be seen that RCR-9 (>50µg/l) and RCR-10 (>20µg/l) again display the highest mean values, and that in general the western streams have higher values than the eastern streams. Indeed, all the eastern streams have mean manganese concentrations below 3µg/l.



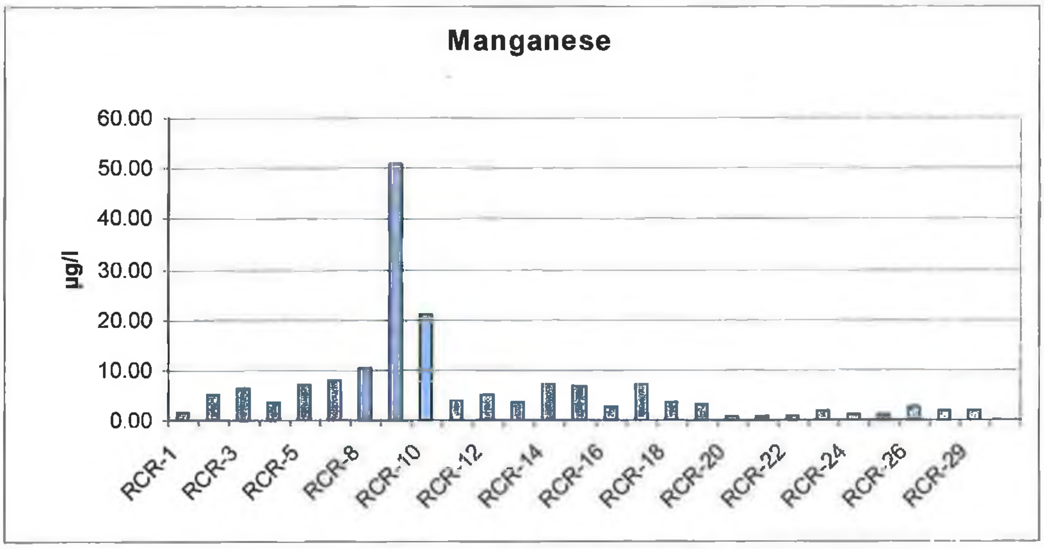


Figure C-12: Spatial variation in total mean manganese conc. in the Corrib rivers

Nickel

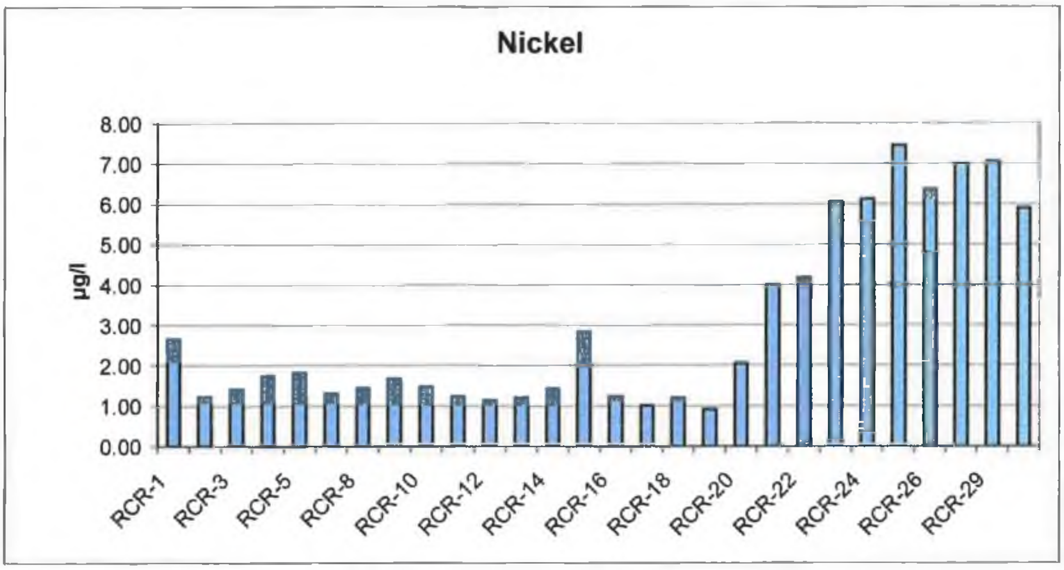


Figure C-13: Spatial variation in total mean nickel conc. in the Corrib rivers

The plot for mean nickel concentration hints at a strong correlation between this element and the Periodic Table Group II elements, such as calcium and magnesium. (This was later found to be true – see correlation discussion, Chapter 4). The eastern streams have the highest values, with all sites from RCR-21 to RCR-30 inclusive showing zinc >4µg/l. The border sites of RCR-1 and RCR-20, as well as RCR-15 have intermediate values >2µg/l. All the remaining sites have mean zinc concentrations ranging between 1-2µg/l.

Lead

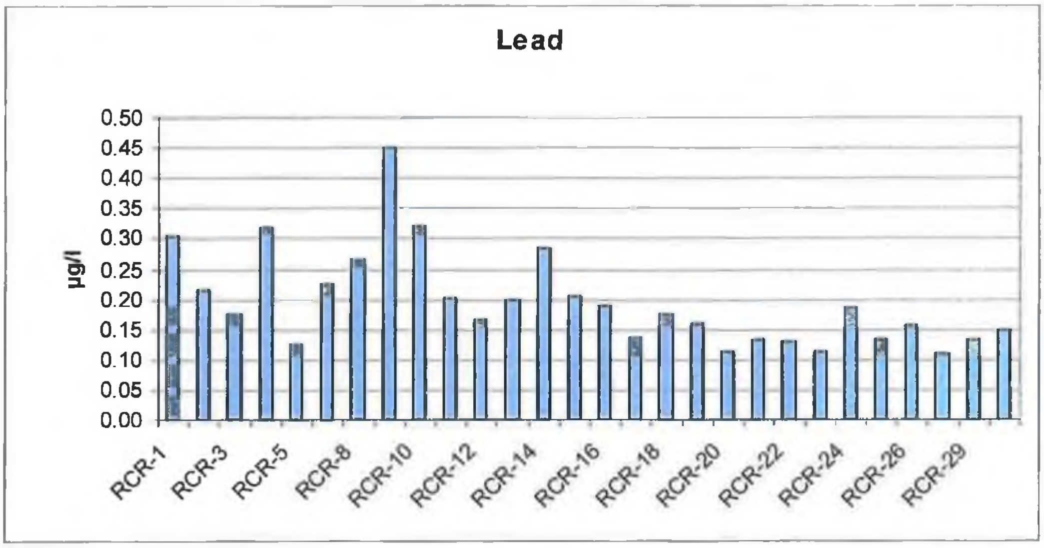


Figure C-14: Spatial variation in total mean lead conc. in the Corrib rivers

Lead shows a very narrow range in mean concentration, with all sites giving values between 0.11 and 0.45µg/l. The lowest values are generally found to the east of the lake, most of which are <0.15µg/l. The highest value is found in RCR-9, closely followed by RCR-4, RCR-10 and RCR-14.

Strontium

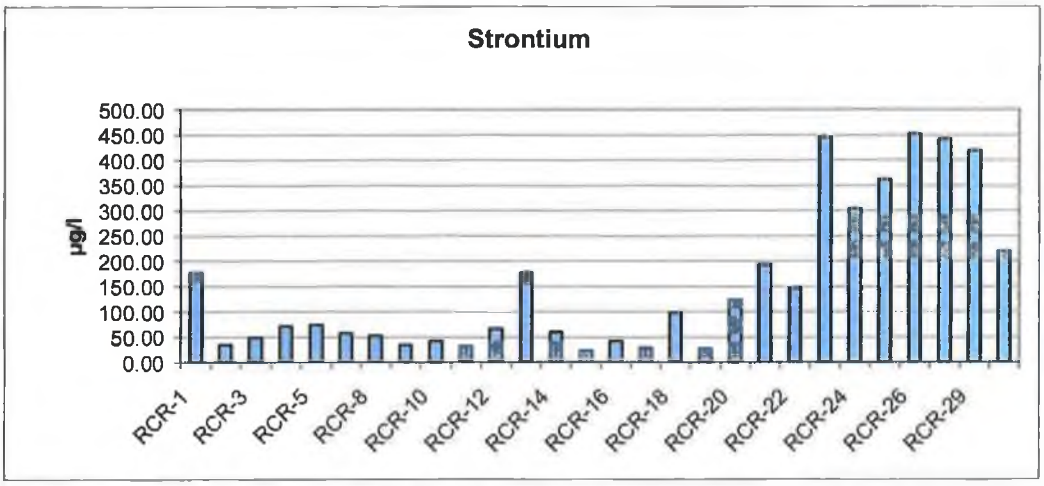


Figure C-15: Spatial variation in total mean strontium conc. in the Corrib rivers

As expected, strontium shows a pattern similar to calcium, with the highest concentrations visible in the streams to the east of the lake. RCR-23 to RCR-29 all have mean strontium values >300µg/l. The boundary streams have intermediate values, and the streams to the west of the lake all have concentrations <100µg/l, with one exception – RCR-13 has a value of 178µg/l. The reason for this is unclear, but may be due to a localized strontium-containing rock or mineral.

Zinc

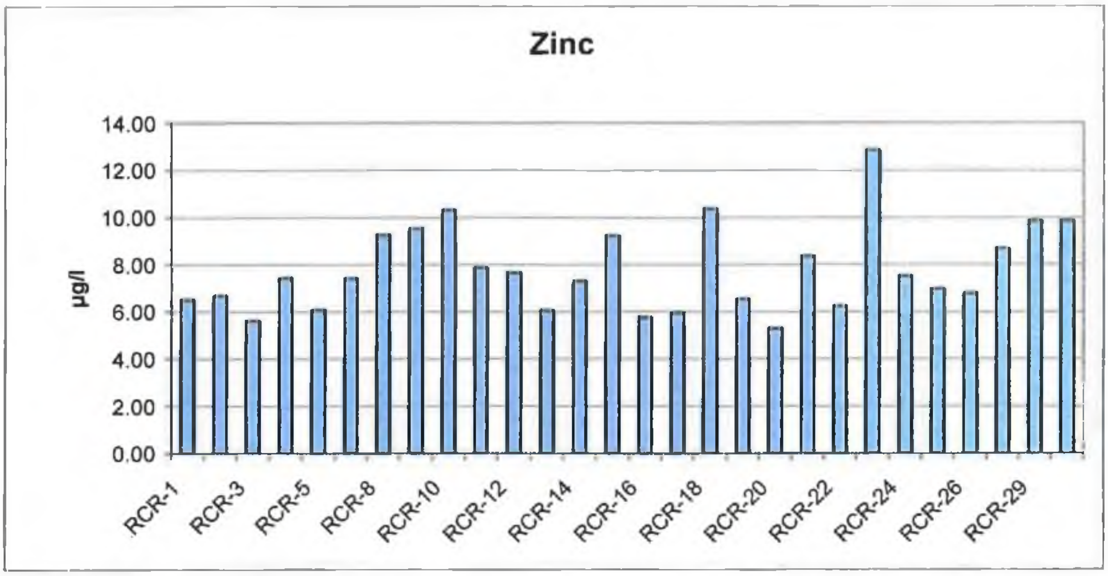


Figure C-16: Spatial variation in total mean zinc conc. in the Corrib rivers

There is no obvious pattern of zinc concentration across the 28 sample sites. All the sites have a mean value in the range 5-13µg/l. The highest concentration is found in RCR-23 (12.86µg/l) and the lowest concentration is found in RCR-20 (5.3µg/l).

TEMPORAL VARIATION

The tables on the following pages were generated by calculating a mean value from the element results at each lake site during each of the calendar months over the three years of this study. Blank values in the tables indicate that no data is available for that month.

Tables are also included with the overall monthly mean values for the eastern and western sides of Lough Corrib.

Table C-3: Mean monthly values, River Corrib

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	77.59	2.65	3.84	13.44	16.63	28.80	0.44	0.54	2.17	1.61	49.49	1.51	3.40	0.44	201.94	5.20
Feb	76.67	2.41	4.03	12.54	6.78	32.47	0.41	0.29	1.65	1.54	45.98	1.01	2.91	0.23	192.83	4.64
Mar	64.56	1.90	3.86	11.70	8.69	29.01	0.20	0.35	1.57	1.27	111.37	1.95	2.29	0.28	165.41	11.57
Apr	61.89	1.85	3.77	11.00	6.88	30.27	1.11	0.30	1.37	1.38	71.59	1.16	2.01	0.28	172.90	4.03
May	52.58	1.82	3.92	11.31	4.98	30.62	0.46	0.62	1.59	0.90	71.82	0.97	2.79	0.15	160.30	5.70
June	42.66	1.49	3.73	10.43	4.71	25.51	0.37	0.14	2.54	1.20	76.61	0.57	1.91	0.13	158.96	4.58
Jul	36.06	1.54	3.87	10.60	5.37	21.87	0.70	0.56	4.14	0.39	76.46	1.80	4.13	0.58	169.89	3.86
Aug	34.76	1.82	3.88	11.29	3.35	21.76	0.66	0.35	2.01	0.71	30.00	1.10	2.46	0.26	141.28	3.12
Sep	51.30	2.10	4.03	11.23	6.51	26.68	0.33	0.41	1.69	1.11	7.65	1.62	1.87	0.38	168.10	6.01
Oct	76.43	2.51	4.69	12.72	7.74	25.95	15.01	0.55	4.95	1.15	4.48	2.27	2.63	0.25	172.90	3.70
Nov	66.01	2.09	3.79	9.83	11.59	46.18	0.94	0.45	2.69	1.92	69.96	1.28	2.01	0.36	214.08	25.34
Dec	65.63	2.28	3.96	10.51	26.52	41.07	0.75	0.58	4.77	2.82	54.22	4.84	3.96	0.72	279.84	8.96

Table C-4: Mean monthly values, Loughkip

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	10.47	1.32	2.05	13.85	50.72	9.96	0.47	0.24	1.38	1.90	265.77	7.06	0.74	0.24	27.10	8.92
Feb	12.08	1.22	2.38	15.94	42.03	10.25	0.59	0.13	1.26	1.17	259.28	2.94	0.68	0.14	27.45	6.90
Mar	20.84	1.14	2.52	14.14	39.53	13.52	0.22	0.26	1.41	1.48	467.81	9.12	0.77	0.22	43.24	7.44
Apr	15.75	0.88	2.27	13.55	37.07	12.15	0.23	0.23	0.74	1.29	449.92	2.96	0.84	0.22	31.72	6.69
May	21.89	0.97	2.85	14.46	27.00	14.12	0.22	0.56	1.26	0.80	503.68	3.74	1.68	0.16	41.95	2.67
Jun	17.30	0.74	2.47	12.56	19.61	13.49	0.31	0.28	1.84	1.40	420.59	2.59	1.06	0.14	38.26	4.23
Jul	16.04	0.75	2.28	11.62	26.55	11.15	0.31	0.75	4.64	0.55	312.28	2.93	4.96	0.19	36.64	9.76
Aug	22.09	0.86	2.68	12.82	19.41	12.76	0.44	0.34	1.72	1.42	581.04	2.83	0.46	0.35	40.83	3.93
Sep	12.91	1.00	2.00	10.84	64.89	9.72	0.72	0.28	2.47	1.55	595.52	5.22	0.97	0.23	26.96	7.27
Oct	21.17	1.24	2.87	14.24	41.35	11.47	5.37	0.46	4.57	1.36	779.61	9.45	1.25	0.22	34.63	2.99
Nov	12.55	1.09	1.96	10.79	54.28	11.58	0.45	0.33	1.05	1.15	432.69	2.59	0.28	0.26	30.90	11.62
Dec	8.51	1.04	1.71	10.81	85.02	10.82	0.21	0.23	3.62	2.28	287.61	25.03	0.56	0.29	31.41	7.69

Table C-5: Mean monthly values, Outflow canal to Ballyquirke

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	34.95	1.70	2.60	14.86	28.85	17.00	0.16	0.20	1.08	1.47	107.22	5.92	1.29	0.12	51.22	9.83
Feb	37.02	1.83	2.97	15.67	21.00	14.73	0.14	0.12	1.47	1.07	115.86	3.04	0.94	0.07	49.30	3.37
Mar	36.91	1.47	2.83	14.91	18.18	15.13	0.23	0.22	1.81	0.88	100.56	7.13	0.81	0.17	49.16	10.10
Apr	35.39	1.39	2.82	14.33	11.61	16.06	0.39	0.19	1.25	1.17	81.27	2.68	0.81	0.27	51.30	4.53
May	32.22	1.37	2.80	14.19	14.52	15.55	0.11	0.58	1.79	0.83	114.33	9.27	2.00	0.11	45.51	1.66
Jun	30.35	1.20	2.69	12.99	8.87	15.91	0.34	0.22	1.78	1.02	46.41	8.81	1.32	0.09	48.11	3.43
Jul	29.15	1.21	2.58	12.63	7.47	15.97	0.45	0.71	4.89	1.61	53.63	2.42	5.24	0.30	46.94	2.24
Aug	29.44	1.22	2.74	13.10	5.38	18.35	0.60	0.30	2.47	1.61	51.08	1.95	1.61	0.12	47.04	3.09
Sep	27.22	1.30	2.55	11.97	19.31	15.42	0.53	0.33	2.73	0.89	139.24	6.60	0.84	0.39	42.67	4.34
Oct	38.27	1.70	3.07	13.62	22.66	15.39	4.00	0.67	3.35	1.57	328.25	18.52	1.86	0.18	44.19	2.77
Nov	32.45	1.47	2.54	11.05	27.99	17.78	0.20	0.32	3.73	1.73	170.21	4.52	0.18	0.18	54.72	22.43
Dec	29.58	1.54	2.58	12.47	55.75	18.43	0.20	0.31	5.96	3.21	127.09	15.56	1.11	0.21	63.29	8.52

Table C-6: Mean monthly values, Inflow canal to Ballyquirke

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	48.91	1.95	2.74	14.74	24.78	19.12	0.13	0.19	1.67	1.52	69.45	4.16	1.27	0.10	67.38	7.42
Feb	56.57	2.01	3.30	15.23	17.83	16.82	0.26	0.13	1.57	1.27	57.14	1.60	1.79	0.13	66.84	4.88
Mar	62.37	1.83	3.34	14.65	17.16	17.79	0.24	0.23	1.63	0.90	55.88	2.83	1.32	0.88	71.80	6.99
Apr	60.50	1.62	3.20	13.94	10.96	18.96	0.53	0.23	1.31	0.90	56.35	2.69	1.43	0.11	73.12	5.73
May	57.55	1.71	3.28	13.80	8.37	16.47	0.25	0.91	1.92	0.98	43.67	3.77	1.93	0.09	66.50	2.03
Jun	56.15	1.69	3.24	12.90	10.43	19.60	0.17	0.15	2.70	1.07	83.80	0.54	1.79	0.42	69.38	19.24
Jul	57.42	1.75	3.05	12.76	9.80	17.56	0.33	0.99	8.77	0.59	104.21	3.26	3.28	0.20	73.64	2.12
Aug	63.90	1.83	3.45	13.18	6.52	20.21	0.40	0.29	3.71	1.37	40.57	0.91	2.20	0.10	73.92	3.98
Sep	59.87	2.12	3.36	13.19	15.12	17.87	0.24	0.29	3.59	1.27	56.82	2.36	1.24	0.12	73.77	19.96
Oct	74.93	2.31	3.98	14.59	14.56	17.38	6.35	0.71	7.09	1.69	116.44	13.75	2.10		75.37	3.10
Nov	53.97	1.80	2.97	11.20	19.82	19.32	0.25	0.27	2.34	1.32	87.03	3.27	0.72	0.42	77.33	15.57
Dec	40.73	1.64	2.78	11.82	44.02	19.83	0.18	0.35	7.30	2.13	108.17	8.20	2.16	0.97	81.36	9.90

Table C-7: Mean monthly values, Inflow canal d/s sewage works

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	53.87	2.14	2.92	15.57	23.91	22.99	0.15	0.22	1.75	1.75	75.31	4.22	1.11	0.09	68.53	8.14
Feb	57.21	2.15	3.41	15.45	18.80	16.86	0.32	0.13	1.58	1.51	58.78	1.94	1.40	0.11	66.49	3.66
Mar	57.36	1.90	3.30	15.09	15.84	17.85	0.25	0.28	1.49	2.06	68.91	1.85	1.51	0.13	71.41	9.68
Apr	67.21	2.28	3.53	15.66	12.45	20.82	0.68	0.31	1.70	1.51	46.10	49.83	1.64	0.09	81.42	6.29
May	61.50	2.01	3.43	14.74	9.41	17.40	0.30	0.67	2.03	1.28	37.46	3.27	1.99	0.09	71.33	2.81
Jun	59.82	1.89	3.26	14.12	11.90	18.35	0.16	0.31	3.10	1.85	84.55	1.69	1.61	0.15	73.27	2.51
Jul	59.10	2.38	3.14	14.53	13.80	18.73	0.33	0.89	7.49	1.93	116.58	5.67	6.38	0.26	77.12	3.56
Aug	64.86	2.36	3.52	14.77	7.51	18.67	0.43	0.58	4.05	1.70	50.61	0.83	4.16	0.18	81.28	4.76
Sep	59.92	2.16	3.39	13.38	13.35	18.34	0.59	0.31	3.73	1.74	52.75	2.92	0.90	0.25	73.53	6.94
Oct	79.22	2.59	4.17	15.38	14.72	17.73	5.75	0.67	4.30	2.02	123.03	12.73	1.20	0.04	78.45	3.55
Nov	56.71	2.04	3.04	11.82	20.78	21.86	0.66	0.58	3.03	2.05	65.62	1.95		0.16	82.94	18.81
Dec	43.29	1.71	2.88	12.24	43.83	16.90	0.16	0.24	7.95	2.17	89.49	9.12	2.22	0.16	80.42	4.66

Table C-8: Mean monthly values, Drimneen River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	17.08	0.97	2.24	12.13	48.32	29.27	0.12	0.20	1.72	1.94	120.72	11.77	0.59	0.18	45.59	14.22
Feb	17.27	0.86	2.51	14.16	39.47	23.37	0.31	0.17	1.76	1.07	93.04	1.77	0.63	0.11	40.67	6.07
Mar	26.40	0.94	2.78	13.77	40.98	36.58	0.22	0.22	1.70	0.79	202.90	12.06	0.76	0.17	53.83	10.18
Apr	23.15	0.76	2.46	12.37	41.12	35.00	0.67	0.19	0.98	0.73	215.14	4.12	1.38	0.28	51.02	3.35
May	33.57	0.97	3.27	12.52	24.69	54.97	0.63	0.93	1.86	0.94	212.57	3.26	1.24	0.18	71.38	3.12
Jun	30.69	0.80	3.10	11.52	24.29	59.58	0.22	0.25	2.39	1.49	163.73	3.48	1.73	0.24	72.89	2.31
Jul	27.47	0.76	2.73	10.27	28.83	56.44	0.65	1.04	5.60	0.49	200.22	5.38	7.96	0.17	68.58	2.28
Aug	27.88	0.78	2.88	10.58	24.93	53.99	0.43	0.38	3.16	0.99	168.94	2.14	3.20	0.49	67.33	2.93
Sep	18.85	0.72	2.06	9.01	77.76	29.03	0.64	0.30	4.30	1.15	414.64	8.38	0.56	0.19	43.65	18.11
Oct	36.60	1.07	3.38	12.00	49.72	45.89	14.13	0.54	3.81	1.61	459.82	19.75	1.47	0.18	62.44	2.86
Nov	21.74	0.87	2.24	9.31	58.05	39.82	0.34	0.56	2.22	0.58	269.01	7.81		0.25	58.81	13.43
Dec	14.98	0.92	1.95	9.91	95.13	30.56	0.20	0.25	5.30	2.37	266.42	33.37	0.34	0.39	53.61	7.88

Table C-9: Mean monthly values, Owenriff River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.76	0.64	1.60	11.79	46.04	35.48	0.28	0.29	1.35	1.92	149.55	16.87	2.06	0.29	38.76	11.59
Feb	6.07	0.72	2.04	14.55	33.95	40.09	0.23	0.16	1.24	0.67	167.19	6.60	0.84	0.37	42.18	5.48
Mar	8.02	0.65	1.95	13.37	36.63	47.61	0.25	0.27	1.52	0.72	306.35	22.97	0.31	0.30	48.50	8.62
Apr	7.45	0.57	1.73	11.90	29.66	53.80	0.57	0.23	2.22	0.65	245.34	5.51	1.56	0.15	53.39	19.61
May	9.94	0.65	1.99	12.29	23.17	73.03	0.54	0.99	1.89	1.15	317.27	8.34	1.13	0.37	70.52	11.45
Jun	8.24	0.55	1.85	11.19	14.38	64.81	0.16	0.48	2.24	0.71	197.14	5.80	0.49	0.15	67.84	13.73
Jul	7.58	0.45	1.62	9.90	18.27	61.86	0.75	2.78	4.76	0.06	176.12	3.83	9.42	0.17	63.57	1.91
Aug	7.30	0.54	1.73	10.80	12.27	53.95	0.37	0.44	3.26	1.05	162.18	1.80	1.13	0.21	56.02	2.23
Sep	4.75	0.49	1.30	8.21	50.76	31.60	0.38	0.37	4.49	0.98	250.59	4.53	0.13	0.05	34.24	7.81
Oct	8.92	0.65	1.81	10.82	39.32	44.51	24.81	0.50	7.09	0.95	535.96	22.79	0.67	0.24	48.09	3.26
Nov	5.57	0.67	1.40	8.80	46.98	47.50	0.26	0.30	1.34	1.15	273.34	5.66		0.38	45.97	14.94
Dec	4.07	0.54	1.23	8.79	84.87	28.49	0.19	0.22	4.27	2.01	243.00	27.81	0.13	0.26	40.34	6.28

Table C-10: Mean monthly values, Derrylaura Stream

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	2.82	1.03	1.68	12.44	161.15	86.94	0.29	0.33	1.11	2.17	285.57	131.24	1.48	0.29	30.26	13.28
Feb	3.28	1.18	2.09	14.90	138.37	86.46	0.17	0.14	1.75	1.26	325.33	48.72	0.63	0.25	30.51	7.33
Mar	4.35	1.17	1.89	14.24	158.63	80.59	0.38	0.28	1.96	1.42	558.60	50.32	0.82	0.58	33.95	16.50
Apr	3.28	0.94	1.59	12.38	137.13	68.14	0.79	0.12	0.92	1.18	591.22	21.38	0.36	0.45	30.40	5.43
May	4.38	1.14	2.00	13.63	136.50	80.61	0.89	1.19	1.61	1.20	885.04	95.64	2.10	0.62	46.57	5.03
Jun	4.36	0.74	1.72	11.95	145.33	67.68	0.34	0.37	1.69	1.14	919.56	8.53	1.22	0.36	40.86	4.26
Jul	3.14	0.68	1.58	10.60	129.46	61.86	1.07	1.46	4.77	15.15	845.98	10.43	9.24	0.85	39.42	14.91
Aug	3.19	1.01	1.82	12.29	162.84	66.89	0.50	0.42	2.63	1.90	1450.31	9.26		0.35	42.23	4.46
Sep	2.50	0.96	1.28	9.58	191.19	54.96	0.49	0.52	2.83	1.22	825.92	14.48	0.71	0.23	25.40	10.79
Oct	4.02	1.23	1.72	12.61	148.15	60.73	18.51	0.94	4.01	1.84	1110.20	45.30	1.23	0.43	30.37	9.74
Nov	2.81	1.14	1.47	10.30	185.48	82.09	0.44	0.52	1.51	1.62	665.63	23.50		0.52	33.81	16.94
Dec	2.61	1.01	1.31	9.95	243.59	67.17	0.14	0.36	2.94	2.76	534.37	130.76	0.55	0.46	29.70	10.53

Table C-11: Mean monthly values, Derrymoyle River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	6.44	1.38	2.14	13.90	208.35	78.56	0.23	0.66	1.35	24.09	429.46	80.88	2.02	0.38	33.68	22.16
Feb	7.93	1.67	2.57	16.27	150.35	70.64	0.22	0.17	1.22	1.05	329.97	5.46	0.56	0.27	34.29	5.88
Mar	9.81	1.29	2.56	15.09	175.68	72.13	0.24	0.30	2.00	1.50	575.67	22.92	0.82	0.33	37.88	28.54
Apr	8.22	1.07	2.29	13.56	168.58	68.11	0.66	0.30	1.01	1.34	502.67	10.09	0.70	0.31	36.36	4.82
May	10.70	1.43	3.00	14.34	136.70	80.63	0.15	1.18	2.02	0.99	685.44	6.48	1.29	0.28	51.60	3.01
Jun	9.03	1.09	2.89	13.49	111.04	85.42	0.40	0.46	1.92	1.52	614.55	6.58	1.52	0.25	54.81	3.06
Jul	9.19	1.27	2.65	12.35	121.27	91.03	0.37	0.68	3.94	1.09	411.16	3.36	4.75	0.28	55.81	4.19
Aug	9.34	1.23	2.79	14.04	117.14	76.72	0.39	0.43	2.49	1.75	515.75	4.64	1.79	0.37	50.43	4.38
Sep	7.07	1.16	2.04	12.18	286.10	61.72	0.42	0.54	3.43	1.76	879.75	7.61	1.03	0.15	30.28	12.57
Oct	9.87	1.47	2.78	15.34	248.74	74.29	18.50	0.97	4.54	2.17	1237.08	39.58	1.54	0.67	37.85	3.63
Nov	7.00	1.37	2.09	12.10	216.53	75.54	0.38	0.42	2.39	1.67	556.35	3.50		0.31	38.32	14.50
Dec	5.68	1.20	1.78	11.46	368.71	67.80	0.36	0.53	4.63	3.10	750.82	97.21	1.50	0.45	37.74	8.31

Table C-12: Mean monthly values, Owenkilla River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	6.09	0.74	1.79	12.46	38.05	9.35	0.05	0.27	1.16	2.20	131.30	9.70	0.18	0.11	25.76	12.25
Feb	6.94	0.94	2.07	14.60	37.90	9.00	0.38	0.18	1.51	1.05	108.28	1.55	0.38	0.12	26.49	6.10
Mar	9.09	0.84	2.00	12.72	34.89	8.56	0.35	0.30	1.35	1.14	221.98	2.72	0.69	0.16	28.69	12.67
Apr	8.64	0.70	1.83	11.26	32.14	8.61	0.51	0.25	1.14	0.98	224.63	2.85	1.02	0.25	29.13	4.15
May	11.37	0.96	2.32	12.14	23.63	8.78	0.43	1.20	1.25	1.24	293.50	2.82	1.78	0.15	35.94	3.30
Jun	11.35	0.76	2.30	10.84	19.63	8.66	0.59	0.51	1.48	1.54	279.92	1.71	1.52	0.18	39.84	7.67
Jul	12.14	0.98	2.22	9.94	27.53	8.22	0.64	1.08	2.29	2.08	329.38	2.40	6.18	0.28	39.53	4.12
Aug	12.92	1.07	2.53	11.10	19.39	9.03	0.83	0.73	2.31	1.21	524.24	2.12	1.32	0.40	43.36	2.99
Sep	6.56	0.73	1.51	8.10	69.10	6.41	0.45	0.41	3.37	1.34	570.41	3.20	0.93	0.22	23.75	9.43
Oct	10.72	1.05	2.34	11.65	39.04	8.23	2.82	0.85	5.61	1.78	788.71	8.05	1.56	0.12	30.51	3.32
Nov	7.26	0.88	1.69	9.58	60.74	27.86	0.27	0.53	1.96	1.60	300.80	2.52		0.43	28.32	23.10
Dec	4.98	0.67	1.42	9.50	88.76	10.52	0.36	0.27	3.43	2.62	293.67	15.08		0.24	29.01	6.81

Table C-13: Mean monthly values, Owenaraha River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	7.38	0.87	1.83	12.44	35.56	14.87	0.32	0.25	1.40	1.66	107.97	7.98	0.31	0.11	48.45	8.01
Feb	9.51	1.01	2.14	14.26	32.97	10.65	0.29	0.14	1.26	1.68	143.56	1.63	0.64	0.07	52.23	4.54
Mar	9.76	0.74	1.99	11.81	37.39	11.50	0.48	0.28	1.80	2.41	312.67	11.43	0.73	0.17	58.05	18.77
Apr	12.19	0.58	1.97	11.23	31.82	11.03	0.37	0.27	0.91	1.46	300.29	3.43	0.95	0.16	61.09	3.79
May	15.00	0.59	2.26	11.74	22.62	11.25	0.61	1.21	2.31	1.17	273.50	4.12	1.57	0.18	73.56	2.09
Jun	12.24	0.54	2.18	10.41	15.70	12.94	0.31	0.65	2.50	2.11	147.90	2.08	0.95	0.19	87.29	3.49
Jul	11.97	0.58	2.19	10.41	22.52	11.45	0.54	1.04	3.12	1.13	165.98	2.89	4.25	0.15	84.11	1.45
Aug	16.23	0.70	2.50	11.30	14.50	12.31	0.35	0.68	1.63	2.25	238.84	1.76		0.23	87.33	8.46
Sep	10.82	0.77	1.80	9.50	61.18	9.71	0.26	0.56	2.75	2.89	454.57	5.06	1.07	0.15	57.82	14.52
Oct	14.47	0.98	2.42	12.22	28.55	11.37	5.20	1.55	3.43	1.77	536.45	4.31	0.29	0.29	68.61	2.84
Nov	11.11	0.92	1.81	10.19	40.41	16.45	0.78	0.34	1.98	1.36	236.41	4.00		0.20	59.08	17.10
Dec	6.53	0.86	1.65	9.11	70.25	27.00	0.08	0.27	3.57	3.34	224.22	18.54	0.80	0.26	62.42	6.84

Table C-14: Mean monthly values, Curraghaduff Stream

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	12.46	1.35	1.98	13.15	54.27	36.22	0.11	0.31	1.29	1.22	109.53	8.31	0.42	0.22	120.19	7.07
Feb	14.78	1.27	2.32	14.46	48.23	35.98	0.32	0.12	1.46	1.07	162.26	2.77	0.59	0.14	126.15	4.46
Mar	15.83	1.00	2.22	12.72	55.85	33.74	0.11	0.24	1.97	1.05	231.25	4.11	0.63	0.24	140.97	9.32
Apr	21.80	0.81	2.20	12.18	48.28	36.70	0.35	0.30	1.01	1.14	275.77	2.87	1.00	0.19	165.13	4.61
May	28.53	0.71	2.53	12.54	31.42	40.91	0.29	1.48	1.81	0.67	255.55	2.81	1.59	0.22	211.13	2.63
Jun	23.61	0.66	2.46	11.37	21.70	39.94	0.33	0.51	2.99	0.94	145.13	1.36	1.00	0.15	238.37	2.36
Jul	23.79	0.64	2.41	11.53	29.19	39.67	0.44	1.09	4.46	0.37	181.01	1.81	6.73	0.24	240.36	2.05
Aug	30.17	0.87	2.84	12.42	18.80	39.42	0.83	0.52	1.31	0.77	190.53	1.18	0.12	0.18	267.27	2.46
Sep	19.26	0.85	2.01	10.62	82.05	32.17	0.28	0.62	3.01	1.16	455.69	3.48	1.19	0.11	154.98	9.56
Oct	25.25	0.97	2.70	12.90	42.40	37.76	12.12	1.79	2.90	0.97	463.02	3.02	1.87	0.17	184.14	2.11
Nov	19.23	0.92	1.94	10.49	60.77	36.45	0.19	0.38	1.21	1.14	293.61	2.34		0.25	159.85	23.91
Dec	10.99	1.14	1.97	9.63	96.08	35.33	0.26	0.24	2.43	1.95	264.23	12.43	1.25	0.23	166.36	5.90

Table C-15: Mean monthly values, Owenree River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.38	0.74	2.08	14.88	81.50	34.74	0.37	0.42	1.51	1.00	102.52	20.62	2.50	0.24	43.43	8.48
Feb	5.80	0.76	2.45	16.90	68.91	32.76	0.77	0.09	1.56	0.69	162.89	3.75	0.56	0.13	46.36	6.69
Mar	6.69	0.67	2.30	14.66	76.90	31.03	0.25	0.31	2.26	0.91	336.96	7.15	0.59	0.25	56.10	11.18
Apr	8.55	0.52	2.11	13.35	69.55	32.42	0.53	0.35	1.01	1.11	370.68	3.68	0.53	0.24	55.44	3.08
May	11.43	0.52	2.55	14.00	51.39	35.56	0.07	1.54	1.38	0.77	490.57	4.84	1.33	0.34	74.27	2.55
Jun	8.33	0.38	2.52	12.81	37.79	35.56	0.43	0.58	1.35	1.36	366.63	3.34	0.97	0.23	76.53	3.50
Jul	8.64	0.39	2.36	12.53	54.68	34.32	0.56	1.41	3.16	0.39	484.22	3.11	5.73	0.48	72.84	6.46
Aug	12.19	0.51	2.88	13.87	37.74	36.31	0.40	0.52	3.22	1.48	724.01	2.72	0.52	0.43	85.96	7.44
Sep	6.86	0.52	2.00	12.65	139.51	30.96	0.26	0.59	3.76	1.08	663.78	5.43	1.26	0.40	43.81	11.20
Oct	9.12	0.60	2.48	13.80	73.37	29.78	11.70	1.03	4.25	0.95	759.15	3.47	0.33	0.32	60.55	2.03
Nov	7.14	0.61	1.88	11.67	91.42	32.02	0.18	0.31	1.14	1.70	333.02	2.56		0.29	46.83	26.69
Dec	3.35	0.61	1.74	10.70	163.81	31.22	0.14	0.14	3.26	2.86	315.99	32.56	0.39	0.41	45.32	6.81

Table C-16: Mean monthly values, Folore River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	3.25	0.63	1.94	14.41	45.25	24.21	0.19	0.39	1.30	0.97	61.27	17.89	3.19	0.17	31.23	7.31
Feb	4.53	0.70	2.26	17.05	46.47	24.15	0.29	0.18	1.18	1.48	89.67	4.59	0.28	0.13	33.04	7.43
Mar	3.64	0.55	1.71	12.57	50.77	18.38	0.24	0.43	2.41	1.02	163.40	9.03	2.36	0.19	34.44	19.41
Apr	5.58	0.53	1.82	12.14	44.52	22.37	0.41	0.33	1.20	1.00	223.41	5.06	1.27	0.17	36.78	3.90
May	2.66	0.58	1.52	12.13	32.20	10.80	0.19	1.36	2.28	0.60	72.62	2.64	1.74	0.33	15.23	4.46
Jun	3.21	0.38	1.22	9.51	22.55	6.64	0.29	0.56	2.19	1.08	36.10	1.35		0.09	16.38	2.47
Jul	2.81	0.38	1.13	9.33	26.20	7.66	0.50	1.77	3.70	0.82	38.96	3.22	3.78	0.21	13.52	3.31
Aug	2.20	0.42	1.22	9.62	21.85	6.71	0.59	0.84	2.14	1.20	51.56	1.11		0.25	13.63	3.87
Sep	1.42	0.33	0.96	7.45	51.94	6.59	0.47	0.66	2.73	3.23	111.72	3.78	15.17	0.59	10.39	23.25
Oct	2.65	0.47	1.12	8.27	46.66	9.52	16.55	1.87	5.10	1.29	137.20	3.12		0.13	12.28	6.48
Nov	1.94	0.47	1.22	8.89	57.61	31.62	0.51	0.43	1.95	1.02	140.15	4.78		0.21	16.33	35.88
Dec	1.79	0.44	1.19	8.52	81.49	15.65	0.45	0.20	3.53	1.82	160.91	23.64		0.23	21.80	5.48

Table C-17: Mean monthly values, Failmore River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.34	0.60	1.74	12.27	29.65	8.70	0.35	0.38	0.44	1.37	18.34	6.12	3.08	0.22	35.38	8.39
Feb	5.21	0.71	2.02	16.40	23.10	6.13	0.65	0.15	0.92	0.69	29.29	2.38	0.38	0.08	32.65	4.74
Mar	6.33	0.51	1.57	9.52	25.82	4.55	0.57	0.19	0.81	0.61	75.52	3.70	0.46	0.21	41.41	7.98
Apr	7.40	0.48	1.56	9.56	28.58	4.76	0.87	0.22	2.54	0.86	81.10	1.63	1.74	0.14	41.82	3.61
May	10.60	0.57	1.86	9.88	25.98	5.28	0.33	0.90	1.32	0.74	76.23	2.35	0.65	0.27	57.50	2.49
Jun	6.61	0.39	1.53	8.38	21.40	4.45	0.17	0.09	0.88	0.58	66.37	1.24	1.02	0.14	52.41	0.47
Jul	8.72	0.37	1.54	7.81	27.53	4.14	0.36	0.31	1.30	0.75	107.45	1.26	1.08	0.34	57.41	6.49
Aug	6.58	0.36	1.16	6.52	40.42	3.65	0.23	0.19	1.96	0.95	90.16	0.69	0.84	0.24	38.86	4.61
Sep	5.85	0.34	1.01	5.75	54.67	3.78	0.70	0.16	0.52	1.62	142.50	1.20	1.76	0.26	33.75	7.60
Oct	8.80	0.57	1.59	8.57	22.35	5.28	4.22	0.40	0.50	0.71	96.08	1.34	0.78	0.17	40.38	2.91
Nov	4.56	0.53	1.36	9.09	27.55	4.34	0.44	0.20	0.82	0.52	59.38	0.69	1.50	0.22	22.26	15.15
Dec	3.17	0.44	1.22	7.61	48.69	5.12	0.22	0.16	1.06	1.86	52.05	10.53	0.29	0.11	37.09	5.56

Table C-18: Mean monthly values, Bealanabrack River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	3.34	0.62	1.62	10.19	47.18	28.61	0.48	0.17	1.11	1.01	63.40	17.22	0.81	0.08	25.37	4.13
Feb	4.48	0.64	1.97	13.14	19.64	25.90	0.45	0.24	0.84	0.73	65.50	5.61	0.34	0.04	26.64	3.90
Mar	4.92	0.52	1.75	9.73	31.39	25.96	0.31	0.19	1.40	0.81	202.04	13.61	0.75	0.17	28.56	7.16
Apr	6.06	0.45	1.68	9.16	26.42	25.43	0.65	0.19	2.22	0.98	125.74	2.40	1.30	0.15	27.72	2.98
May	7.39	0.55	1.98	9.49	23.27	27.27	0.26	0.37	0.72	0.94	162.00	5.39	1.10	0.19	32.71	3.20
Jun	5.40	0.42	1.64	7.68	12.83	25.36	0.25	0.07	2.03	0.81	137.18	4.26	0.51	0.06	33.31	8.87
Jul	5.84	0.41	1.79	8.09	15.43	23.88	0.35	0.12	1.67	0.78	162.46	3.58	2.19	0.25	31.78	4.38
Aug	6.75	0.47	1.77	7.94	11.35	23.01	0.27	0.26	2.10	1.07	109.69	1.16	1.79	0.10	31.91	7.98
Sep	6.83	0.44	1.56	7.28	26.78	21.94	0.26	0.14	0.88	1.21	199.46	4.48	1.16	0.12	27.16	6.93
Oct	8.19	0.62	1.93	9.15	23.34	23.18	11.24	0.60		0.95	273.14	1.86	0.75	0.15	27.98	7.63
Nov	6.25	0.55	1.58	8.22	33.55	22.60	1.68	0.13	0.37	0.73	131.03	6.66	1.23	0.17	26.09	22.88
Dec	2.77	0.51	1.36	7.66	64.14	22.20	0.20	0.13	0.93	2.16	86.48	23.50	1.39	0.14	28.03	5.62

Table C-19: Mean monthly values, Letterfore River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	6.00	0.62	1.95	13.34	47.46	39.41	0.37	0.29	0.59	0.97	60.10	9.14	0.46	0.12	61.07	6.01
Feb	8.23	0.72	2.32	15.87	41.39	39.11	0.91	0.05	0.85	0.92	65.53	1.55	2.11	0.15	63.06	8.18
Mar	11.43	0.73	2.33	12.72	42.05	48.17	0.38	0.08	0.65	1.53	97.37	5.28	0.78	0.30	88.19	14.63
Apr	13.12	0.60	2.21	12.09	40.68	47.60	0.81	0.10	1.79	0.88	139.60	1.36	1.24	0.09	88.02	4.56
May	20.29	0.78	2.90	13.10	28.55	61.66	0.22	0.37	1.50	0.78	96.29	1.95	1.59	0.15	131.12	3.10
Jun	15.35	0.59	2.73	11.12	20.04	67.88	0.36	0.04	1.74	0.74	84.96	1.90	0.78	0.16	154.32	56.42
Jul	17.73	0.79	2.82	12.02	22.79	61.39	0.30	0.25	1.73	0.68	89.70	1.52	1.84	0.24	136.02	6.71
Aug	20.62	0.92	3.15	12.27	17.02	68.00	0.28	0.31	1.32	0.80	75.67	0.68	0.57	0.14	152.98	1.87
Sep	9.91	0.49	1.81	9.36	68.18	36.80	0.11	0.19	0.55	1.30	221.07	2.19	1.50	0.19	65.00	8.67
Oct	16.30	0.78	2.69	12.36	38.41	41.14	28.42	0.28	0.92	0.91	178.73	1.89	0.31	0.22	92.06	2.72
Nov	9.14	0.61	1.81	10.36	57.89	35.65	0.33	0.16	0.44	0.91	155.80	1.39	2.60	0.12	58.47	25.16
Dec	5.50	0.51	1.70	9.16	88.63	36.56	0.23	0.16	1.13	3.02	72.74	21.55	0.33	0.26	67.75	10.43

Table C-20: Mean monthly values, Cornamona River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	4.81	0.95	1.87	12.42	39.39	47.87	0.27	0.23	0.93	1.56	40.99	6.28	0.59	0.11	25.46	6.97
Feb	5.46	0.81	2.10	13.74	23.15	38.29	0.69	0.17	1.40	0.80	41.71	1.63	0.44	0.04	24.27	4.20
Mar	6.39	0.79	1.99	10.74	28.27	38.33	0.50	0.13	1.02	1.15	71.53	6.99	0.77	0.18	25.76	14.01
Apr	6.69	0.66	1.92	10.15	23.17	39.79	0.62	0.18	1.04	0.76	42.58	1.45	0.53	0.09	26.77	3.82
May	8.46	0.76	2.22	10.70	19.00	41.24	0.15	0.60	0.87	0.92	58.89	2.51	1.43	0.23	30.43	3.15
Jun	6.93	0.57	1.93	9.04	12.32	41.55	0.22	0.06	0.97	0.85	48.59	1.24	1.48	0.09	32.85	3.08
Jul	7.04	0.66	2.09	9.78	16.82	38.89	0.39	0.28	1.12	0.86	79.26	2.28	1.27	0.19	30.48	3.33
Aug	7.26	0.72	1.97	9.13	15.47	35.13	0.32	0.26	2.08	0.94	60.73	0.71	0.82	0.05	28.26	3.81
Sep	5.82	0.66	1.57	8.22	41.11	29.32	0.54	0.05	1.36	1.45	117.21	1.86	1.30	0.20	21.11	8.58
Oct	5.29	0.80	1.83	9.73	38.61	20.95	32.78			1.18	103.70	0.76		0.03	20.22	3.01
Nov	5.57	0.77	1.63	9.35	47.76	42.58	0.52	0.10	0.82	1.19	81.72	0.91	0.60	0.10	22.67	20.78
Dec	3.52	0.75	1.43	7.96	92.29	38.24	0.37	0.43	0.73	4.15	250.09	14.72	1.80	0.55	26.69	7.55

Table C-21: Mean monthly values, Cong River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	52.39	1.93	3.38	13.82	10.89	55.61	0.31	0.24	0.59	1.14	21.03	1.39	1.99	0.07	126.85	3.82
Feb	47.34	1.84	3.63	12.95	9.12	52.33	0.36	0.15	0.85	0.81	24.15	0.81	1.70	0.01	114.44	3.88
Mar	47.83	1.78	3.75	12.15	8.84	53.39	0.60	0.10	1.28	0.91	20.74	1.11	2.41	0.19	121.26	11.05
Apr	57.45	1.77	3.69	11.59	7.67	53.35	0.63	0.26	1.29	0.78	44.22	0.78	2.22	0.20	130.08	2.29
May	56.03	1.92	3.73	11.63	5.33	42.54	0.62	0.76	1.37	0.66	37.93	0.77	1.59	0.14	126.17	2.36
Jun	36.54	1.57	3.25	10.23	7.55	39.91	0.30	0.10	2.67	0.98	64.34	0.99	2.24	0.05	123.66	0.67
Jul	43.35	1.79	3.59	11.21	5.34	40.50	0.31	0.19	1.46	0.75	131.51	0.56	1.50	0.18	120.76	3.85
Aug	41.97	1.72	3.51	10.93	5.72	36.52	0.37	0.39	3.49	0.76	52.77	0.64	2.10	0.04	118.12	2.18
Sep	46.35	1.73	3.55	10.91	5.32	39.14	0.49	0.15	1.54	0.94	7.58	0.78	2.44	0.14	117.87	7.68
Oct	54.35	2.11	4.35	12.79	8.42	42.16	14.93	0.48	0.60	1.09	8.80	1.22	2.09	0.08	121.56	3.11
Nov	55.76	1.57	3.61	10.77	9.73	58.19	0.87	0.23	2.39	1.45	22.69	0.25	1.40	0.09	118.60	27.07
Dec	44.74	1.52	3.81	10.79	26.25	81.51	0.16	0.29	2.11	3.54	38.19	2.15	3.55	0.14	154.37	12.44

Table C-22: Mean monthly values, Cross River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	154.90	4.86	6.84	18.40	8.86	31.18	0.63	0.37	1.61	1.24	21.74	1.89	4.14	0.18	188.08	6.23
Feb	137.40	4.47	7.73	15.18	4.43	27.82	0.41	0.20	1.84	0.89	23.26	0.62	3.70	0.11	166.89	3.15
Mar	120.46	3.84	8.43	13.95	4.90	31.94	0.56	0.25	2.49	0.86	13.30	1.05	4.85	0.27	174.45	33.29
Apr	147.86	3.91	8.49	13.49	5.55	34.83	0.53	0.36	2.11	0.92	106.22	0.34	4.82	0.08	183.48	3.98
May	150.88	3.97	9.83	14.26	4.33	36.90	0.36	0.69	1.59	0.69	85.42	1.22	3.73	0.11	198.50	1.93
Jun	118.78	3.58	9.10	13.01	3.42	39.15	0.45	0.08	3.09	0.57	60.04	0.32	3.11	0.03	207.52	2.25
Jul	129.24	4.44	9.66	13.32	4.92	39.61	0.36	0.51	4.58	0.54	147.31	0.40	3.01	0.19	196.40	2.61
Aug	115.29	4.77	10.52	13.15	3.58	41.80	0.13	0.54	3.84	0.94	24.63	0.54	3.75		203.59	1.45
Sep	139.08	5.03	9.15	13.40	6.38	39.20	0.58	0.46	5.19	1.15	27.16	0.73	4.89	0.04	193.22	12.24
Oct	162.64	4.64	9.96	14.48	6.58	33.67	13.61	0.52	2.52	1.98	3.00	0.61	3.04	0.22	193.56	3.74
Nov	130.00	4.06	8.06	12.66	7.39	36.37	0.61	0.36	4.85	1.12	47.04	0.67	3.93	0.22	209.93	19.25
Dec	105.07	3.78	6.98	11.40	21.62	32.06	0.29	0.20	4.79	2.39	26.33	3.79	4.39	0.09	244.19	4.88

Table C-23: Mean monthly values, Ballynalty River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	146.53	6.04	7.05	18.44	6.61	20.94	0.46	0.32	1.53	1.17	23.17	0.80	4.38	0.06	146.22	5.01
Feb	143.54	5.71	8.33	15.47	4.35	20.99	0.49	0.15	2.39	0.94	34.82	0.75	4.73	0.07	137.59	5.53
Mar	115.02	4.60	8.43	13.56	8.93	20.93	0.35	0.20	1.98	0.97	12.62	0.88	4.79	0.14	147.12	14.75
Apr	141.13	4.25	9.00	13.39	5.28	21.91	0.24	0.36	1.34	0.82	74.84	0.41	4.65	0.09	148.63	2.15
May	131.47	4.40	9.84	14.03	3.54	22.61	0.19	0.66	1.78	0.86	70.44	1.06	3.03	0.11	152.21	1.30
Jun	98.50	3.90	9.42	12.51	3.06	22.22	0.21	0.13	3.11	0.62	83.05	0.25	2.60	0.09	147.41	3.26
Jul	104.40	4.17	9.03	12.27	6.14	20.68	0.37	0.43	5.69	0.95	99.23	0.87	7.15	0.22	138.02	1.81
Aug	101.35	4.82	9.92	12.14	3.47	23.29	0.42	0.38	3.55	0.71	15.29	0.73	4.21	0.14	141.00	1.43
Sep	119.65	4.98	8.81	12.89	4.82	21.55	0.50	0.48	5.79	1.11	14.01	0.63	3.72	0.12	139.06	8.03
Oct	143.65	5.41	10.12	14.63	6.60	20.80	27.09	0.77	2.72	1.72	3.00	0.83	2.94	0.13	148.41	2.86
Nov	121.72	4.84	8.19	13.04	6.75	22.75	0.55	0.38	4.62	1.21	40.98	1.23	2.97	0.18	158.17	24.69
Dec	101.67	4.38	7.12	11.32	11.66	20.14	0.23	0.26	2.73	1.61	27.03	1.39	4.56	0.14	177.56	4.61

Table C-24: Mean monthly values. Black River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	143.18	3.97	5.01	16.31	21.13	30.56	0.31	0.46	1.09	1.93	68.24	3.05	6.07	0.10	378.13	8.37
Feb	145.88	3.82	5.78	13.76	10.77	26.61	0.32	0.19	1.40	1.89	89.99	1.24	6.00	0.23	370.29	5.19
Mar	122.55	3.17	6.14	13.10	10.57	28.95	0.49	0.24	1.46	1.79	74.92	3.58	7.02	0.08	419.55	15.84
Apr	148.50	2.93	6.08	12.72	9.64	28.80	0.39	0.47	2.88	1.44	120.17	0.66	6.62	0.08	427.95	4.16
May	152.30	2.86	7.25	13.46	4.88	32.08	0.24	0.82	1.91	0.73	96.33	1.51	4.90	0.09	467.64	1.53
Jun	117.04	2.43	7.09	12.24	3.52	35.18	0.23	0.26	2.33	0.90	61.04	0.69	6.28	0.07	515.14	318.98
Jul	121.00	2.51	7.01	12.32	6.06	34.51	0.44	0.48	4.97	1.08	134.01	1.00	7.65	0.25	530.00	1.19
Aug	111.09	3.21	7.29	12.76	3.65	35.08	0.20	0.49	4.65	1.11	47.82	0.64	5.12	0.05	500.47	2.05
Sep	131.32	3.71	6.50	12.62	11.14	31.55	0.49	0.43	4.70	1.80	52.99	1.49	6.96	0.14	439.83	5.20
Oct	167.95	3.84	7.47	13.83	10.69	33.19	35.59	0.66	3.40	1.98	74.21	1.19	5.73	0.22	468.38	5.16
Nov	119.63	3.36	5.62	11.46	14.54	30.48	0.49	0.44	3.58	1.40	104.95	4.00	4.02	0.09	430.43	20.16
Dec	91.06	3.07	4.75	9.55	30.88	26.51	0.10	0.34	3.81	2.78	121.24	9.13	5.81	0.12	446.98	9.53

Table C-25: Mean monthly values. Cloneen River. Galway Rd

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	171.20	4.80	4.97	18.22	10.23	24.14	0.62	0.35	1.43	2.10	33.60	1.41	6.08	0.10	284.77	7.14
Feb	165.05	4.61	5.55	15.24	7.94	20.12	0.34	0.24	1.69	2.04	42.62	1.18	6.23	0.14	261.68	3.61
Mar	125.72	3.76	5.77	13.93	7.51	22.63	0.54	0.27	1.43	1.91	22.82	1.60	6.20	0.11	290.39	14.43
Apr	163.49	3.79	5.87	13.92	6.52	24.66	0.60	0.56	2.41	1.53	97.06	0.69	7.44	0.63	300.42	3.52
May	158.31	3.70	6.40	14.59	4.45	22.95	0.31	0.74	1.54	1.58	78.06	1.47	5.17	0.10	303.94	3.81
Jun	115.57	3.18	5.91	12.91	3.05	24.74	0.37	0.38	2.02	1.14	109.01	0.66	4.28	0.04	335.42	2.05
Jul	145.65	3.73	6.19	14.51	7.73	26.08	0.42	0.46	4.40	1.18	89.04	2.09	8.14	0.21	328.40	3.73
Aug	134.59	4.17	6.61	14.89	4.23	26.71	0.65	0.55	4.38	7.50	31.94	0.93	5.88	0.52	340.57	6.35
Sep	146.51	4.91	6.26	14.16	5.96	24.98	0.40	0.55	4.20	2.30	21.01	0.85	7.20	0.09	299.76	10.64
Oct	172.24	4.62	6.91	15.29	7.58	21.91	13.36	1.35	3.15	2.57	18.92	1.23	6.28	0.06	317.09	5.77
Nov	132.96	4.12	5.52	12.50	13.03	28.72	0.57	0.49	2.06	1.99	47.23	1.66	4.56	0.12	307.77	24.67
Dec	107.18	3.59	4.69	11.04	20.65	20.68	0.36	0.26	3.91	3.39	40.48	3.48	5.95	0.09	324.71	7.36

Table C-26: Mean monthly values. Cloneen River. Lisheenageeba Bridge

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	175.41	5.20	5.15	18.33	7.87	23.31	0.42	3.34	1.38	1.77	34.29	1.00	20.67	0.12	362.34	5.31
Feb	160.76	4.61	5.78	14.71	4.69	19.80	0.32	0.29	1.75	1.63	36.71	0.55	5.07	0.02	357.61	3.62
Mar	130.18	3.75	6.05	13.44	4.62	21.59	0.53	0.29	1.64	1.36	22.47	1.31	6.45	0.18	394.10	19.13
Apr	163.20	3.81	6.21	13.71	5.72	22.86	0.48	0.58	2.86	1.33	100.71	0.74	7.43	0.14	361.96	3.52
May	158.28	3.73	6.64	14.50	3.67	24.11	0.38	0.87	1.49	1.11	79.50	1.29	5.34	0.07	337.78	2.05
Jun	114.50	3.11	6.00	12.91	2.90	27.09	0.54	0.30	1.99	1.31	155.95	0.56	4.37	0.04	333.47	0.69
Jul	132.72	3.59	6.29	14.02	8.63	26.63	0.63	0.59	5.43	1.33	118.10	1.16	7.87	0.17	321.90	2.47
Aug	136.47	4.12	6.78	14.85	3.66	34.18	0.46	0.60	4.46	1.10	25.75	1.06	4.98	0.16	339.92	3.82
Sep	143.00	4.99	6.43	13.94	8.53	26.57	0.54	0.67	3.55	2.01	20.04	0.71	6.88	0.40	355.04	8.93
Oct	173.61	4.64	7.31	14.58	6.91	21.52	15.01	0.58	2.72	2.54	26.22	0.99	5.49	0.07	382.63	5.10
Nov	132.98	4.20	5.74	12.15	8.24	24.10	0.75	0.47	2.47	1.72	52.00	1.58	3.87	0.12	407.55	22.79
Dec	111.03	3.59	4.92	10.78	16.42	21.36	0.06	0.31	2.96	3.20	28.59	2.31	7.00	0.11	450.88	7.94

Table C-27: Mean monthly values, Kilroe River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	180.86	5.07	6.34	17.62	4.35	21.82	0.52	3.76	1.02	1.51	30.93	0.62	20.92	0.09	369.44	8.08
Feb	172.54	5.26	7.74	13.64	3.68	19.30	0.31	0.21	1.90	0.95	47.34	0.47	4.05	0.03	363.50	2.98
Mar	133.23	3.43	7.74	12.96	4.65	21.04	0.29	0.28	1.50	0.98	12.69	0.82	5.12	0.13	393.08	11.03
Apr	163.83	3.24	8.65	12.69	6.48	23.54	1.03	0.53	1.49	0.96	201.36	15.81	5.03	0.38	458.27	3.25
May	155.87	3.28	9.36	13.27	4.06	22.89	0.35	1.26	1.42	0.87	79.38	1.36	4.46	0.11	462.25	2.69
Jun	112.60	2.82	9.13	11.63	3.01	25.41	0.16	0.23	2.64	0.53	112.53	0.57	3.07	0.07	502.15	5.23
Jul	128.92	2.98	9.78	12.22	7.01	22.77	0.58	0.58	5.13	0.77	99.88	1.21	6.27	0.17	555.25	2.60
Aug	128.33	3.02	10.20	12.14	4.27	23.72	0.45	0.67	3.83	0.98	35.26	0.83	4.06	0.03	590.28	3.98
Sep	129.87	4.18	8.39	12.01	3.09	22.42	0.47	0.58	3.64	1.33	13.75	0.74	3.75	0.30	449.47	6.05
Oct	173.92	3.82	9.22	13.45	7.98	22.59	12.76	1.27	3.17	3.19	3.07	2.08	4.80	0.14	436.67	4.75
Nov	137.18	3.55	7.41	11.76	6.89	41.29	0.78	0.55	3.92	2.07	56.47	2.54	5.60	0.22	449.25	29.30
Dec	125.16	3.76	6.80	11.64	9.93	23.52	0.28	0.46	2.35	1.78	17.65	1.23	4.83	0.03	503.50	6.17

Table C-28: Mean monthly values, Cregg River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	186.09	5.68	6.23	17.21	11.31	37.80	0.54	3.82	0.79	2.26	51.15	2.15	24.28	0.07	380.90	10.93
Feb	181.13	5.94	7.44	13.46	7.70	20.81	0.44	0.28	2.26	1.20	78.54	1.93	4.82	0.12	369.00	3.62
Mar	132.80	4.02	7.31	12.73	7.50	21.17	0.32	0.28	1.37	1.62	42.08	2.82	6.07	0.31	412.45	23.67
Apr	149.46	3.62	7.25	12.55	8.58	20.95	0.51	0.55	1.31	1.03	135.46	1.08	5.64	0.06	445.03	2.83
May	154.04	3.60	7.91	13.20	3.23	22.06	0.65	1.13	1.03	0.93	76.85	1.64	4.72	0.12	456.59	2.11
Jun	119.00	3.15	7.24	11.46	3.51	21.86	0.30	0.28	2.60	1.26	90.83	0.49	3.16	0.04	496.14	3.15
Jul	133.69	3.29	7.34	12.45	6.38	21.64	0.85	0.54	6.01	1.26	108.43	1.24	6.69	0.11	494.25	2.16
Aug	121.34	3.28	7.54	12.38	3.68	21.74	0.20	0.56	3.78	1.26	28.44	1.09	3.58	0.02	502.48	3.39
Sep	128.20	4.48	6.74	11.96	4.97	21.76	0.71	0.57	4.64	1.92	40.20	1.19	4.79	0.07	423.14	7.48
Oct	173.52	4.48	8.37	13.33	6.87	23.66	8.90	1.53	2.91	2.67	27.36	1.99	4.23	0.08	459.13	2.45
Nov	136.25	4.13	6.69	11.14	8.51	26.64	0.48	0.61	2.80	1.23	60.35	5.06	2.20	0.20	459.01	17.97
Dec	120.47	4.29	6.18	10.65	22.94	24.14	0.22	0.39	5.22	3.33	62.04	5.91	8.44	0.13	473.79	22.40

Table C-29: Mean monthly values, Clare River

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	156.01	4.63	5.24	16.18	21.98	21.71	0.60	3.99	0.81	2.23	91.64	2.17	22.84	0.19	394.23	14.86
Feb	162.96	4.99	6.13	13.37	12.60	18.56	0.29	0.29	1.93	2.20	126.70	1.63	4.80	0.05	364.64	5.69
Mar	120.65	3.46	6.14	12.49	14.29	21.09	0.53	0.30	1.33	1.58	58.69	2.13	6.12	0.15	416.74	33.46
Apr	141.45	2.99	5.69	12.31	11.76	21.83	0.38	0.58	1.10	1.27	124.61	1.03	5.79	0.06	412.42	3.12
May	143.63	3.12	6.75	13.76	5.27	22.63	0.38	1.17	1.58	1.07	90.49	2.26	4.78	0.12	437.69	1.97
Jun	99.96	2.93	6.19	12.35	4.71	22.48	0.58	0.39	2.16	1.23	71.56	0.92	2.93	0.16	432.17	16.50
Jul	113.51	3.09	6.19	13.09	8.06	22.94	0.71	0.62	4.94	1.16	111.12	1.55	6.78	0.13	421.09	1.36
Aug	104.47	3.68	6.74	14.29	4.34	24.70	0.31	0.68	4.35	1.21	43.32	1.18	3.95	0.10	435.22	2.23
Sep	117.70	3.96	5.75	12.14	12.20	21.28	0.41	0.82	4.70	2.16	69.76	1.44	5.58	0.15	395.81	11.55
Oct	161.79	4.11	7.12	13.33	10.28	21.64	11.53	1.16	3.28	2.17	79.28	2.42	5.75	0.11	434.95	3.75
Nov	117.40	3.73	5.47	10.85	20.74	25.37	0.57	0.58	4.80	1.69	121.93	3.84	5.26	0.15	451.39	16.58
Dec	96.60	3.49	4.98	9.61	37.30	26.18	0.27	0.31	2.68	2.92	132.32	8.38	4.56	0.29	503.02	6.28

Table C-30: Mean monthly values, Carrowbrowne stream

Month	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al ug/L	Ba ug/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Ni ug/L	Pb ug/L	Sr ug/L	Zn ug/L
Jan	108.06	6.17	4.59	20.54	34.76	24.79	0.63	3.22	1.01	2.88	561.73	607.86	18.17	0.25	179.83	18.32
Feb	125.72	8.34	5.65	18.49	13.50	18.34	0.39	0.25	1.71	1.63	278.77	4.61	4.55	0.08	179.95	7.66
Mar	107.87	6.39	5.22	18.31	10.20	27.78	0.47	0.37	1.45	1.04	282.42	321.29	5.97	0.16	205.50	12.72
Apr	137.93	8.33	5.19	17.03	9.50	44.48	0.47	0.73	1.55	0.69	479.60	1453.46	5.15	0.06	220.61	6.47
May	146.37	6.09	6.16	19.41	5.26	29.27	0.49	1.23	1.34	0.89	241.92	153.52	5.21	0.11	250.72	6.87
Jun	111.96	4.32	5.36	16.64	5.16	29.32	0.71	0.53	3.06	0.65	95.27	6.32	2.99	0.25	239.65	10.11
Jul	124.30	6.26	5.72	17.89	6.56	29.09	0.63	0.54	3.77	0.73	187.27	6.02	5.89	0.18	256.15	4.82
Aug	120.72	7.61	6.55	19.18	5.41	30.55	0.26	0.63	3.67	0.90	82.32	2.19	3.34	0.14	276.93	3.99
Sep	103.94	5.36	5.23	16.23	16.12	22.67	0.84	0.72	4.42	1.71	245.78	6.46	4.45	0.13	208.33	14.50
Oct	140.11	6.31	5.82	17.55	5.68	23.09	12.42	1.07	3.11	1.46	131.92	37.65	3.18	0.11	207.81	4.97
Nov	96.45	6.51	4.91	16.79	25.16	33.44	0.57	0.65	2.31	1.77	1018.36	272.68	2.76	0.09	215.24	13.17
Dec	57.52	3.86	4.30	13.17	56.00	16.79	0.18	0.33	3.39	3.03	280.44	17.91	3.14	0.27	193.36	14.55

Table C-31: Mean monthly values for streams on the Western side of Lough Corrib

Month	Ca mg/l	K mg/l	Mg mg/l	Na mg/l	Al ug/l	Ba ug/l	Cd ug/l	Co ug/l	Cr ug/l	Cu ug/l	Fe ug/l	Mn ug/l	Ni ug/l	Pb ug/l	Sr ug/l	Zn ug/l
Jan	6.69	0.89	1.89	12.80	67.73	34.58	0.28	0.32	1.23	3.23	143.32	25.14	1.27	0.20	42.27	9.93
Feb	7.65	0.92	2.22	15.10	54.15	34.04	0.42	0.15	1.32	1.01	139.02	6.81	0.68	0.16	44.50	5.75
Mar	9.44	0.80	2.08	12.59	61.17	35.17	0.34	0.25	1.72	1.16	263.55	13.31	0.78	0.26	52.03	13.94
Apr	10.17	0.67	1.95	11.63	55.09	34.87	0.58	0.23	1.33	1.00	257.74	5.10	1.12	0.21	53.93	5.09
May	13.49	0.79	2.34	12.19	44.81	41.16	0.30	1.06	1.62	0.94	302.62	11.21	1.41	0.28	69.80	3.88
Jun	11.18	0.61	2.16	10.72	37.29	40.04	0.32	0.40	1.90	1.14	274.04	3.49	1.13	0.20	74.44	7.15
Jul	11.24	0.64	2.09	10.35	42.60	38.52	0.50	0.94	3.26	1.92	277.80	3.51	4.70	0.31	71.80	4.63
Aug	12.51	0.74	2.25	10.91	39.52	37.32	0.46	0.43	2.27	1.27	346.62	2.30	1.13	0.27	74.27	4.42
Sep	8.19	0.65	1.61	9.07	92.33	27.31	0.40	0.41	2.93	1.57	408.25	5.12	1.48	0.21	43.95	11.46
Oct	12.92	0.90	2.27	11.73	73.00	35.94	0.40	0.77	4.16	1.36	569.73	14.88	0.89	0.28	55.31	3.70
Nov	8.45	0.81	1.71	9.89	79.07	39.49	0.42	0.36	1.51	1.14	281.58	5.49	1.48	0.28	46.88	20.80
Dec	5.38	0.74	1.53	9.23	122.03	31.99	0.23	0.25	3.19	2.62	270.92	35.51	0.88	0.31	49.68	7.23

Table C-32: Mean monthly values for streams on the Eastern side of Lough Corrib

Month	Ca mg/l	K mg/l	Mg mg/l	Na mg/l	Al ug/l	Ba ug/l	Cd ug/l	Co ug/l	Cr ug/l	Cu ug/l	Fe ug/l	Mn ug/l	Ni ug/l	Pb ug/l	Sr ug/l	Zn ug/l
Jan	164.27	5.03	5.85	17.59	11.54	26.43	0.50	2.10	1.22	1.78	49.03	1.67	13.67	0.11	313.01	8.35
Feb	158.66	4.93	6.81	14.35	7.07	21.75	0.36	0.23	1.90	1.47	66.25	1.04	4.91	0.08	298.90	4.13
Mar	125.08	3.75	7.00	13.27	7.87	23.67	0.44	0.27	1.66	1.38	36.37	1.86	5.83	0.16	330.99	20.25
Apr	152.37	3.57	7.15	13.10	7.44	24.92	0.49	0.50	1.94	1.17	117.84	2.51	5.95	0.20	342.27	3.34
May	150.60	3.58	8.00	13.88	4.19	25.78	0.35	0.92	1.53	0.99	82.74	1.48	4.49	0.10	352.07	2.17
Jun	111.95	3.14	7.54	12.37	3.40	27.27	0.36	0.26	2.50	0.95	88.82	0.58	3.74	0.07	371.87	24.21
Jul	126.14	3.48	7.68	13.02	6.86	26.86	0.55	0.53	5.15	1.03	110.71	1.17	6.76	0.18	373.16	2.31
Aug	119.12	3.88	8.20	13.32	3.86	28.90	0.36	0.56	4.08	1.87	32.52	0.88	4.44	0.16	381.69	3.13
Sep	131.91	4.53	7.25	12.89	7.14	26.17	0.50	0.57	4.55	1.72	36.97	1.00	5.47	0.17	336.92	8.86
Oct	166.16	4.45	8.31	14.11	8.20	26.26	0.41	0.99	2.99	2.35	39.55	1.45	4.78	0.13	355.10	4.22
Nov	128.52	4.00	6.59	11.94	11.09	29.47	0.59	0.49	3.73	1.55	71.14	2.62	4.09	0.16	359.19	21.67
Dec	107.28	3.75	5.80	10.75	21.42	24.32	0.24	0.32	3.51	2.68	56.96	4.45	5.69	0.12	390.58	8.65

CORRELATION FACTORS

Table C-33: Correlation factors from all the data used during Corrib river analysis

	Ca	*K*	*Mg*	*Na*	*Al*	*Ba*	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*	*Sr*	*Zn*
Ca	1.00															
K	0.79	1.00														
Mg	0.83	0.76	1.00													
Na	0.44	0.55	0.38	1.00												
Al	-0.40	-0.29	-0.41	-0.09	1.00											
Ba	-0.13	-0.03	-0.05	0.09	0.44	1.00										
Cd	0.01	0.00	0.04	0.01	-0.07	0.06	1.00									
Co	0.11	0.07	0.09	0.04	-0.05	0.05	0.01	1.00								
Cr	0.12	0.11	0.17	-0.01	-0.02	0.04	0.00	0.26	1.00							
Cu	0.00	0.01	-0.02	-0.02	0.10	0.04	0.01	0.01	-0.01	1.00						
Fe	-0.26	-0.02	-0.23	0.04	0.57	0.36	0.12	0.02	0.06	0.04	1.00					
Mn	0.05	0.39	0.04	0.08	0.03	0.21	-0.01	0.03	0.01	0.01	0.36	1.00				
Ni	0.31	0.21	0.24	0.08	-0.12	0.01	0.01	0.88	0.42	0.02	-0.06	0.02	1.00			
Pb	-0.12	-0.11	-0.13	-0.04	0.24	0.17	0.00	0.01	0.04	0.23	0.23	-0.01	0.01	1.00		
Sr	0.74	0.57	0.75	0.17	-0.37	-0.05	0.00	0.10	0.14	0.00	-0.24	0.02	0.27	-0.11	1.00	
Zn	0.00	-0.01	-0.03	-0.06	0.09	0.02	-0.05	0.00	-0.01	0.20	0.01	-0.01	0.04	0.14	0.03	1.00

CROSS-VALIDATION RESULTS

Table C-34: Cross-validation using max, min and median values from the 28 rivers

Group	R1	R2	R3	R4	R5	R7	R8	R9	R10	R11	R12	R13	R14	R15
RCR1	2	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR2	0	3	0	0	0	0	0	1	0	2	1	0	0	0
RCR3	0	0	2	3	3	0	0	0	0	0	1	0	0	0
RCR4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR5	0	0	1	0	0	0	0	0	0	0	0	0	0	0
RCR7	0	0	0	0	1	0	1	0	0	0	0	1	0	0
RCR8	0	0	0	0	0	1	2	1	0	0	0	0	0	0
RCR9	0	0	0	0	0	0	0	1	3	1	0	0	0	0
RCR10	0	0	0	0	0	0	0	1	0	0	0	0	0	0
RCR11	0	0	0	0	0	0	0	0	0	0	1	0	1	0
RCR12	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR13	0	0	0	0	0	0	0	0	0	0	0	2	0	0
RCR14	0	0	0	0	0	0	0	0	0	0	0	0	1	0
RCR15	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR16	0	0	0	1	0	0	0	0	0	0	0	0	1	2
RCR17	1	1	1	0	0	3	1	0	0	1	1	0	1	1
RCR18	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR19	0	0	0	0	0	0	0	0	1	0	0	0	0	1
RCR20	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR21	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR22	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR23	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR24	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR25	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR26	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR28	1	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR29	0	0	0	0	0	0	0	0	0	0	0	1	0	0
RCR30	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Total N	4	4	4	4	4	4	4	4	4	4	4	4	4	4
N Correct	2	3	2	0	0	0	2	1	0	0	0	2	1	0
Proportion	0.50	0.75	0.50	0.00	0.00	0.00	0.50	0.25	0.00	0.00	0.00	0.50	0.25	0.00

Group	R16	R17	R18	R19	R20	R21	R22	R23	R24	R25	R26	R28	R29	R30
RCR1	0	0	0	0	1	1	0	0	0	1	0	0	0	1
RCR2	0	1	0	0	0	0	0	0	0	0	0	0	0	0
RCR3	1	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR5	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR7	0	1	0	0	0	0	0	0	0	0	0	0	0	0
RCR8	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR9	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR11	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR12	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR13	0	0	0	0	0	0	0	0	1	0	0	0	0	0
RCR14	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR15	1	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR16	1	0	0	0	0	0	0	0	0	0	0	0	0	0
RCR17	1	2	1	1	0	0	0	0	0	0	0	0	0	0
RCR18	0	0	0	1	1	0	0	0	0	0	0	0	0	0
RCR19	0	0	3	2	0	0	0	0	0	0	0	0	0	0
RCR20	0	0	0	0	2	0	0	0	0	0	0	0	0	0
RCR21	0	0	0	0	0	2	0	0	0	0	0	0	0	0
RCR22	0	0	0	0	0	1	3	0	0	0	0	0	0	1
RCR23	0	0	0	0	0	0	0	0	0	1	0	0	1	0
RCR24	0	0	0	0	0	0	0	1	1	2	0	0	0	0
RCR25	0	0	0	0	0	0	0	2	2	0	1	1	0	0
RCR26	0	0	0	0	0	0	0	0	0	0	1	2	0	0
RCR28	0	0	0	0	0	0	0	1	0	0	1	0	3	0
RCR29	0	0	0	0	0	0	0	0	0	0	1	1	0	0
RCR30	0	0	0	0	0	0	1	0	0	0	0	0	0	2
Total N	4	4	4	4	4	4	4	4	4	4	4	4	4	4
N Correct	1	2	0	2	2	2	3	0	1	0	1	0	0	2
Proportion	0.25	0.50	0.00	0.50	0.50	0.50	0.75	0.00	0.25	0.00	0.25	0.00	0.00	0.50

Total N: 112
N Correct: 29
Proportion Correct: 0.259

Table C-35: Cross-validation using hard water rivers only

Group	RCR21	RCR22	RCR23	RCR24	RCR25	RCR26	RCR28	RCR29
RCR21	23	14	0	0	0	10	7	2
RCR22	18	46	0	1	2	2	3	0
RCR23	2	0	42	14	16	3	4	27
RCR24	1	0	2	23	13	0	0	9
RCR25	2	0	5	16	19	4	5	11
RCR26	16	6	4	0	0	36	16	0
RCR28	10	9	3	6	10	17	37	9
RCR29	3	0	19	15	14	3	3	17
Total N	75	75	75	75	74	75	75	75
N Correct	23	46	42	23	19	36	37	17
Proportion	0.307	0.613	0.560	0.307	0.257	0.480	0.493	0.227

Total N: 599
N Correct: 243
Proportion Correct: 0.406

Table C-36: Cross-validation using soft water rivers only

Group	RCR7	RCR8	RCR9	RCR10	RCR11	RCR12	RCR13	RCR14	RCR15	RCR16	RCR17	RCR18	RCR19
RCR7	39	0	0	0	0	0	23	0	0	0	0	5	0
RCR8	6	32	1	0	9	7	0	3	6	4	0	5	0
RCR9	1	0	50	12	4	6	7	1	0	0	0	0	3
RCR10	0	0	10	48	14	3	3	0	0	0	0	0	3
RCR11	3	2	1	7	13	7	8	0	0	1	1	1	7
RCR12	7	3	0	0	9	4	1	0	0	3	0	2	2
RCR13	13	1	0	0	0	7	25	1	0	2	0	2	0
RCR14	0	1	0	0	0	1	0	53	11	6	7	8	3
RCR15	0	9	3	1	5	0	0	7	38	4	2	4	0
RCR16	4	24	3	0	9	11	1	6	10	33	16	12	7
RCR17	0	1	3	0	0	4	0	1	5	14	37	5	15
RCR18	2	2	0	0	2	21	5	1	0	6	4	28	3
RCR19	0	0	4	7	10	2	0	0	0	0	7	1	29
Total N	75	75	75	75	75	73	73	73	70	73	74	73	72
N Correct	39	32	50	48	13	4	25	53	38	33	37	28	29
Proportion	0.520	0.427	0.667	0.640	0.173	0.055	0.342	0.726	0.543	0.452	0.500	0.384	0.403

Total N: 956
N Correct: 429
Proportion Correct: 0.449

Table C-37: Cross-validation using only rivers of intermediate hardness

Group	RCR1	RCR2	RCR3	RCR4	RCR5	RCR20	RCR30
RCR1	51	0	0	3	2	19	6
RCR2	1	53	6	1	2	0	0
RCR3	0	21	66	5	4	0	0
RCR4	0	0	2	42	33	3	6
RCR5	1	0	1	22	31	1	4
RCR20	21	1	0	2	2	50	1
RCR30	1	0	0	0	0	0	56
Total N	75	75	75	75	74	73	73
N Correct	51	53	66	42	31	50	56
Proportion	0.680	0.707	0.880	0.560	0.419	0.685	0.767

Total N: 520
N Correct: 349
Proportion Correct: 0.671

Table C-38: Division of sites into three geological groupings

Water Hardness	Approximate hardness (mg/l)	Sample Sites
Hard	>300mg/l	RCR-21, RCR-22, RCR-23, RCR-24, RCR-25, RCR-26, RCR-28, RCR-29
Intermediate	75-300mg/l	RCR-1, RCR-3, RCR-4, RCR-5, RCR-20, RCR-30
Soft	< 75 mg/l	RCR-2, RCR-7, RCR-8, RCR-9, RCR-10, RCR-11, RCR-12, RCR-13, RCR-14, RCR-15, RCR-16, RCR-17, RCR-18, RCR-19

Table C-39: Cross-validation using three general geological groupings

Group	Hard	Intermediate	Soft
Hard	8	0	0
Intermediate	0	6	0
Soft	0	0	14
Total N	8	6	14
N Correct	8	6	14
Proportion	1.000	1.000	1.000

Total N: 28
N Correct: 28
Proportion Correct: 1.000

Table C-40: Division of sites into nine geological groupings

Number of observations for each site in parenthesis

Geology type	Sample Sites
Border sites between different geologies (BOR)	RCR-1 (11), RCR-20 (4), RCR-30 (17)
Granite (GRA)	RCR-2 (10), RCR-9 (6), RCR-10 (14), RCR-18 (7)
Schist, Gneiss and Silurian (SGS)	RCR-11 (4)
Schist and Gneiss (SG)	RCR-12 (8), RCR-13 (10), RCR-14 (6), RCR-16 (6), RCR-17 (6), RCR-19 (3)
Granite, Schist and Gneiss (GSG)	RCR-15 (4)
Sandstone and Limestone (SL)	RCR-21 (5)
Limestone (LIM)	RCR-22 (5), RCR-23 (14), RCR-24 (11), RCR-25 (9), RCR-26 (9), RCR-28 (10), RCR-29 (12)
Schist, Gneiss and Limestone (SGL)	RCR-7 (7), RCR-8 (8)
Unclassified sites (UNC)*	RCR-3 (6), RCR-4 (10), RCR-5 (6)

** Note: These sites were assigned as "unclassified" because unlike all the other sites they are not from rivers flowing over bedrock. These three sites are canals flowing into and out of Ballyquirke.*

Table C-41: Cross-validation using nine geological groupings

Site	UNC	BOR	GSG	GRA	LIM	SL	SG	SGL	SGS
UNC	20	4	0	0	0	0	1	1	0
BOR	0	25	0	0	3	0	0	0	0
GSG	0	0	2	1	0	0	4	0	0
GRA	0	0	0	18	0	0	4	2	0
LIM	0	1	0	0	62	0	0	0	0
SL	0	0	0	0	5	5	0	0	0
SG	1	0	1	7	0	0	15	5	2
SGL	1	1	0	5	0	0	10	5	0
SGS	0	1	1	6	0	0	5	2	2
Total N	22	32	4	37	70	5	39	15	4
N Correct	20	25	2	18	62	5	15	5	2
Proportion	0.909	0.781	0.500	0.486	0.886	1.000	0.385	0.333	0.500

Total N: 228
N Correct: 154
Proportion Correct: 0.675

Sites were then reassigned to different geological groupings as follows:

RCR-2 was reclassified from GRA to SG
RCR-8 was reclassified from SGL to SG
RCR-14 was reclassified from SG to GSG
RCR-18 was reclassified from GRA to SG
RCR-19 was reclassified from SG to SGL
RCR-22 was reclassified from LIM to SL

Table C-42: Cross-validation after reassignment of six sites to different geological groupings

Site	UNC	BOR	GSG	GRA	LIM	SL	SG	SGL	SGS
UNC	18	1	0	0	0	0	4	0	0
BOR	0	26	0	0	3	0	0	0	0
GSG	0	0	7	0	0	0	5	1	0
GRA	0	0	0	20	0	0	0	0	0
LIM	0	0	0	0	62	0	0	0	0
SL	0	0	0	0	0	10	0	0	0
SG	1	0	1	0	0	0	26	1	2
SGL	2	4	1	0	0	0	9	8	0
SGS	1	1	1	0	0	0	11	0	2
Total N	22	32	10	20	65	10	55	10	4
N Correct	18	26	7	20	62	10	26	8	2
Proportion	0.818	0.812	0.700	1.000	0.954	1.000	0.473	0.800	0.500

Total N: 228
N Correct: 179
Proportion Correct: 0.785

Table C-43: Local variation in element concentrations around Lough Corrib

Location	Calcium		Aluminium	
	mg/l	std dev	µg/l	std dev
Maam Bay	9.55	3.18	17.19	13.09
Cornamona Bay	29.77	2.84	9.16	4.76
Inner Ballindiff Bay	51.57	15.48	4.64	1.84
Cregg River Bay	92.67	27.44	6.12	2.37
Mouth of River Clare	106.48	33.50	6.52	4.78
Out from River Clare	96.10	38.09	6.51	3.91

Appendix D.

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SAMPLING SITES ON THE CANALS

Table D.1: Sampling sites on the Royal Canal

Site Code	No. of Samples	Sample Location
R01	3	Lock 1, Amiens St., North Strand
R02	3	Cross Guns Bridge
R03	3	Lock 8 to 11
R04	3	Lock 11 to Kennan Br.
R05	3	Kennan Br. To Pakenham Br.
R06	3	Pakenham Br. To Cope Br.
R07	2	Cope Br. To Deey Br.
R08	1	Cope Br. To Deey Br.
R09	1	Cope Br. To Deey Br.
R10	2	Deey Br. To Mullen Br.
R11	2	Mullen Br. To Jackson Br.
R12	3	Jackson Br. To Shaws Br.
R13	2	Jackson Br. To Shaws Br.
R14	1	Jackson Br. To Shaws Br.
R15	3	Shaws Br. To Lock 17
R16	3	Shaws Br. To Lock 17
R17	3	Lock 17 to 2.5 km west.
R18	3	Cloncurry Bridge to Enfield Br.
R19	3	Cloncurry Bridge to Enfield Br.
R20	3	Enfield Br. To Blackwater Aqueduct.
R21	3	Moyvalley Br. To Blackshade Br.
R22	3	Blackshade Br. to Ballasport Bridge
R23	2	
R24	3	D'Arcys Br. to Lock 21
R25	3	Lock 21 to McNeads Br.
R26	3	McNeads Br. to Downs Bridge
R27	2	Baltrasna Bridge to Morans Br., Mullingar
R28	2	Baltrasna Bridge to Morans Br., Mullingar
R29	3	Baltrasna Bridge to Morans Br., Mullingar
R30	3	Morans Bridge to L. Owel feeder, Mullingar
R31	3	Morans Bridge to L. Owel feeder, Mullingar
R32	3	Scanlans Bridge
R33	2	Footbridge, 1km outside Mullingar
R34	3	Belmont Bridge
R35	3	Shanonagh Bridge
R36	1	Shanonagh Bridge
R37	3	Kildallan Bridge
R38	3	Ballynacargy Bridge
R39	3	Ballynacargy Bridge
R40	2	Ballynacargy Bridge
R41	1	Kellys Bridge
R42	1	Kellys Bridge
R43	2	Quinns Bridge, Abbeyshrule
R44	1	Ballybrannigan Harbour

Table D.2: Sampling sites on the Grand Canal

Site Code	No. of Samples	Sample Location
G01	2	Grand Canal Basin
G02	2	Grand Canal Basin
G03	2	Grand Canal Basin
G04	2	Grand Canal Basin
G05	2	Grand Canal Basin
G06	2	Grand Canal Basin
G07	2	Grand Canal Basin
G08	2	Baggot St. Bridge
G09	2	Parnell Bridge, Dolphins Barn
G10	2	Lock 3, Inchicore
G11	2	Lock 8, Ballyfermot
G12	2	Lock 9, Clondalkin
G13	1	Hazelhatch Bridge
G14	1	Henry Bridge
G15	1	Ponsonby Bridge
G16	1	Lock 15
G17	1	Lock 15
G18	1	Sallins
G19	1	Digby Bridge
G20	1	Burgh Bridge
G21	1	Burgh Bridge
G22	1	Robertstown
G23	3	Lowtown
G24	1	Bond Bridge, Allenwood
G25	1	Bord Na Mona Railway Bridge
G26	1	Kilpatrick Briquette Factory
G27	1	Lock 20
G28	1	Blundell Aqueduct, Edenderry
G29	1	Georges Bridge, Edenderry
G30	2	Toberdaly Bridge
G31	3	1km u/s Daingean
G32	3	2km d/s Daingean
G33	3	2km d/s Daingean
G34	3	2km d/s Daingean
G35	3	Ballycommon
G36	3	Lock 23
G37	3	Tullamore
G38	3	Shra Bridge
G39	3	Corcorans Bridge, Rahan
G40	2	Corcorans Bridge, Rahan
G41	3	Lock 31, Cornaclour Bridge
G42	1	Lock 31, Cornaclour Bridge
G43	3	Plunkett Bridge, Pollagh
G44	3	1km D/S Derry Bridge
G45	3	Lock 33, Belmont
G46	3	Lock 34, Clononey Bridge
G47	3	Shannon Harbour

Table D.3: Sampling sites on the Barrow Canal

Site Code	No. of Samples	Sample Location
B01	3	Lock 20, Ballyteague Castle
B02	2	Lock 20, Ballyteague Castle
B03	3	2km u/s Glenaree Bridge
B04	2	1 km u/s Rathangan
B05	3	1 km u/s Rathangan
B06	3	1 km u/s Rathangan
B07	3	1 km d/s Rathangan, Offaly Castle
B08	2	1 km d/s Rathangan, Offaly Castle
B09	3	0.5km d/s Umeras Bridge
B10	3	Shepards Brook Bridge, Monasterevin
B11	1	Shepards Brook Bridge, Monasterevin
B12	2	Clogheen Bridge
B13	3	Fisherstown Bridge
B14	3	1km u/s Vicarstown Bridge
B15	3	1km u/s Vicarstown Bridge
B16	3	Camac Aqueduct
B17	2	Lock 26, Lennons Bridge
B18	2	Lock 28, Athy

Table D.4: Sampling sites on the Shannon/Erne canal

Site Code	No. of Samples	Sample Location
S01	3	Navigation markers on entrance from L.Erne
S02	3	L.Amoneen
S03	1	L.Amoneen
S04	4	L.Teemore
S05	4	Aghalane Bridge
S06	2	Kennedy's mooring
S07	2	Lock 1 - Corraquil
S08	3	Cloncoohy Bridge
S09	3	Lock 2
S10	3	Ballyconnell moorings
S11	1	d/s Bellaheady Bridge
S12	3	Bellaheady Bridge
S14	2	Lock 3, Skelan
S15	3	L.Coologe
S16	3	L.Derrycassan
S17	3	L.Ballymaguran
S18	3	Ballinacur Bridge
S19	3	L.Garadice
S20	3	L.Garadice
S21	3	Carrickmakeegan Bridge
S22	2	Lisnatullagh Bridge
S23	3	Aghoo Bridge
S24	3	Ballinamore Bridge
S25	3	Ballinamore golf course
S26	3	Ballyduff Bridge

Table D.4: Sampling sites on the Shannon/Erne canal continued...

Site Code	No. of Samples	Sample Location
S27	3	L.Kiltybarden
S28	3	L.Kiltybarden
S29	3	St.Johns Lough
S30	3	L.Muckross
S31	3	Lock 8, Castlefore
S32	3	L.Marrave
S33	3	Bridge 12, Rossy
S34	3	L.Scur
S35	3	L.Scur
S37	2	L.Carrickaport
S38	2	Lough Scur Bridge
S39	3	Kilclare Bridge
S40	2	Lisconor Bridge
S41	2	Crossycarwell Bridge
S42	2	Leitrim village
S43	2	L.Keshcarrigan
S44	1	Rag River
S45	1	R.Duvogue
S46	1	R.Blackwater @ Derrycassan
S47	1	Old Yellow River
S48	2	Yellow River
S49	2	Aghacashlan River
S50	2	Lough Castlefore
S51	1	Lough Drumlaheen
S56	1	Woodford Lough

SPATIAL VARIATION IN MINERAL ELEMENTS ON THE CANALS

Note: Red markers illustrate feeders and tributaries of the main canal channel. The arrows at the top of each diagram indicate the direction of water flow.

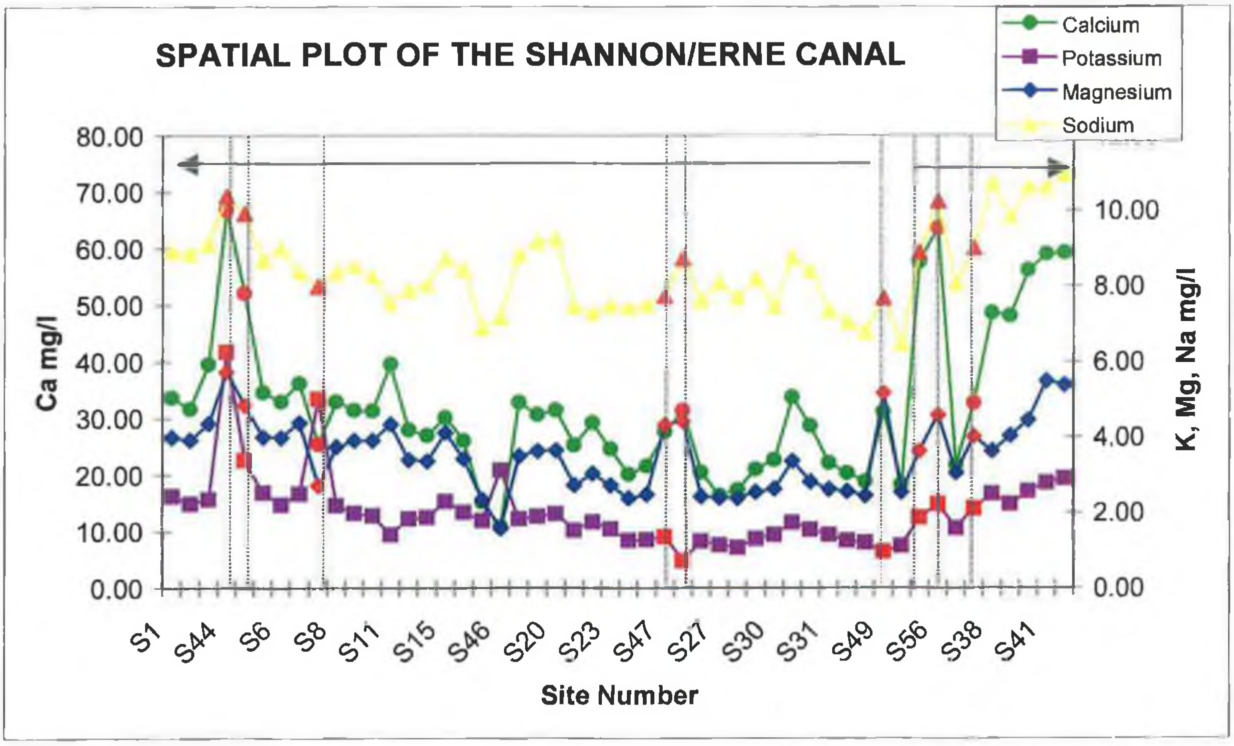

Figure D.1: Spatial plot of the Shannon/Erne Canal

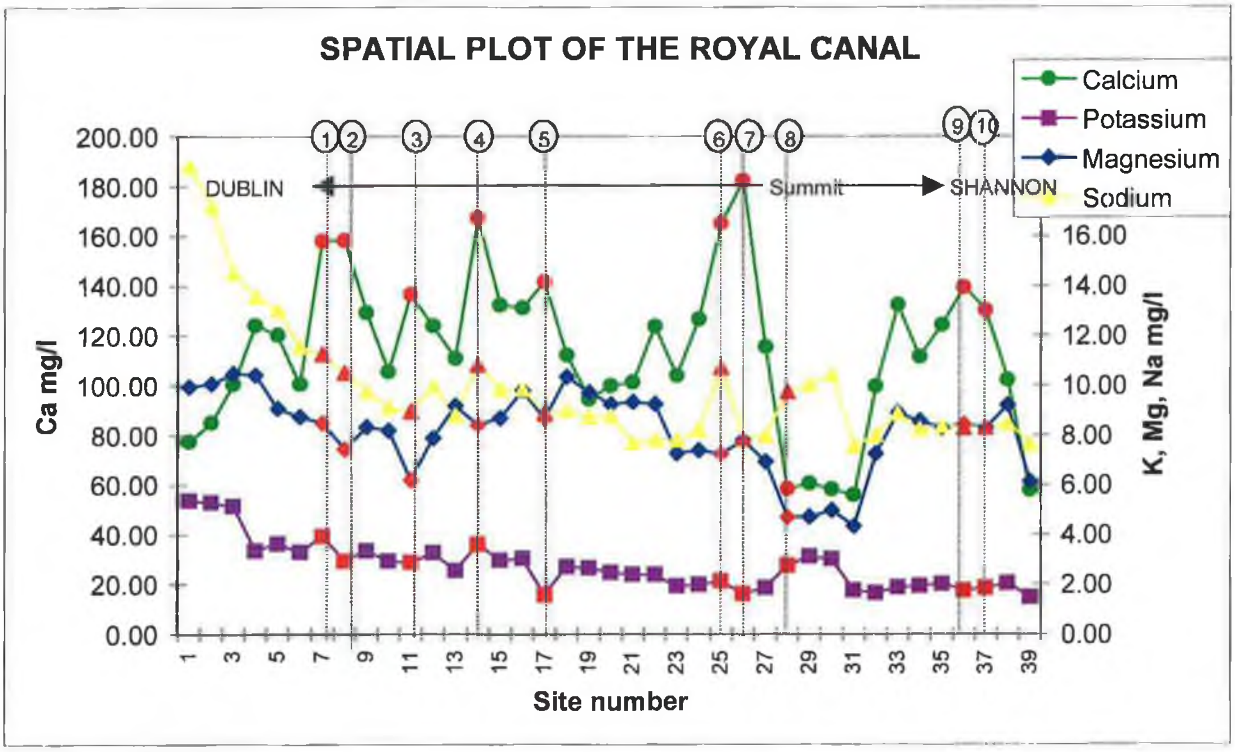

Figure D.2: Spatial plot of the Royal Canal

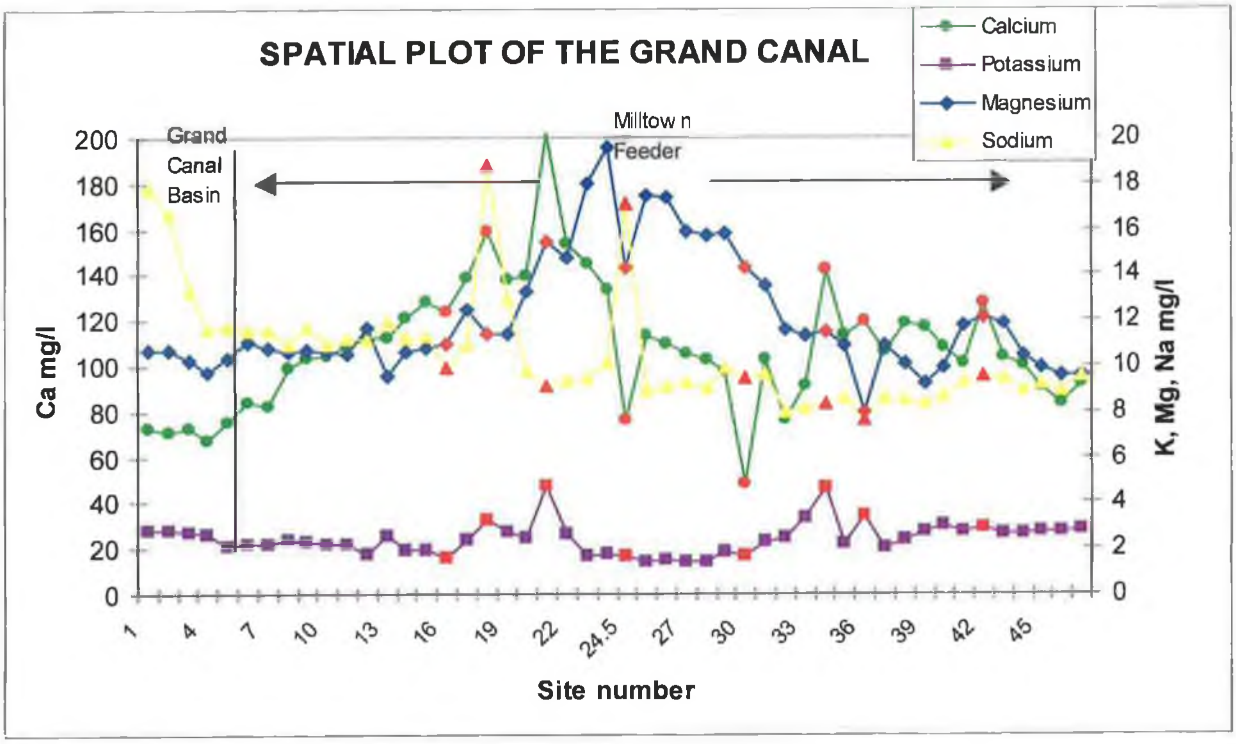

Figure D.3: Spatial plot of the Grand Canal

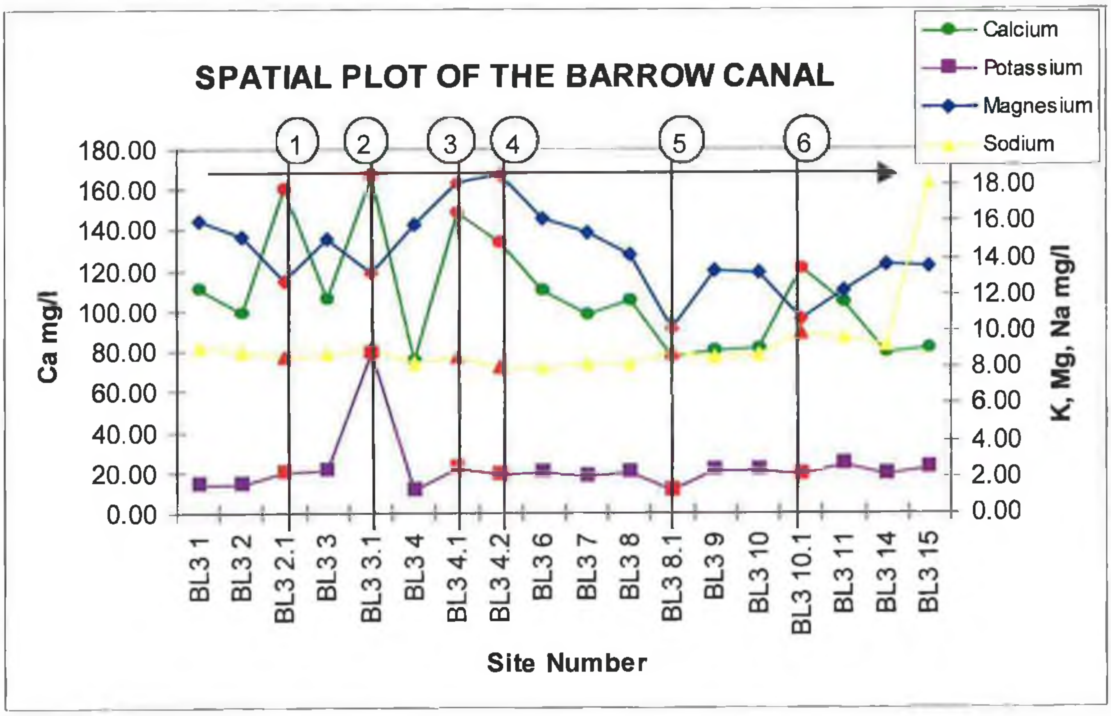

Figure D.4: Spatial plot of the Barrow Canal

CORRELATION VALUES FOR THE CANALS

Table D.5: Correlation based on mean values of each element in the four canals

	Barrow	Grand	Royal	Shannon/Erne
Barrow	1.0000			
Grand	0.9930	1.0000		
Royal	0.9682	0.9755	1.0000	
Shannon/Erne	0.3239	0.4086	0.3340	1.0000

(Correlation based on Table 5.1)

Table D.6: Correlation calculated after removing Group II elements and iron

	Barrow	Grand	Royal	Shannon/Erne
Barrow	1.0000			
Grand	0.6486	1.0000		
Royal	0.8095	0.9339	1.0000	
Shannon/Erne	0.7181	0.8429	0.9053	1.0000

Table D.7: Correlation for all the canals data

	Ca	K	Mg	Na	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
Ca	1.00															
K	0.32	1.00														
Mg	0.58	0.00	1.00													
Na	0.23	0.40	0.28	1.00												
Al	-0.36	-0.03	-0.35	-0.21	1.00											
Ba	0.51	0.16	0.66	0.27	-0.22	1.00										
Cd	0.01	-0.04	0.06	-0.10	-0.08	-0.05	1.00									
Co	0.50	0.26	0.28	-0.10	-0.02	0.22	0.24	1.00								
Cr	0.22	0.29	0.14	0.20	0.02	0.12	0.04	0.32	1.00							
Cu	-0.39	0.11	-0.25	0.07	0.35	-0.12	0.09	-0.14	-0.11	1.00						
Fe	-0.49	-0.19	-0.47	-0.28	0.67	-0.24	-0.02	-0.11	-0.18	0.37	1.00					
Mn	0.04	0.11	-0.12	-0.04	0.18	0.04	-0.12	0.04	-0.12	0.10	0.21	1.00				
Ni	0.21	0.22	-0.22	-0.08	0.18	-0.13	0.00	0.10	0.27	0.14	0.13	0.14	1.00			
Pb	-0.25	-0.04	-0.22	-0.12	0.36	-0.10	0.00	0.02	-0.05	0.28	0.74	0.06	0.12	1.00		
Sr	0.69	0.32	0.20	0.29	-0.29	0.12	-0.01	0.30	0.18	-0.23	-0.35	-0.06	0.35	-0.16	1.00	
Zn	-0.26	-0.03	0.04	0.20	0.23	-0.04	0.24	-0.12	0.02	0.64	0.23	0.00	0.08	0.24	-0.20	1.00

Table D.8: Correlations for Grand Canal data

	Ca	K	Mg	Na	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
Ca	1.00															
K	0.43	1.00														
Mg	-0.10	-0.70	1.00													
Na	-0.01	-0.01	-0.10	1.00												
Al	0.04	0.57	-0.43	-0.26	1.00											
Ba	0.48	-0.04	0.09	0.02	-0.12	1.00										
Cd	-0.44	0.07	-0.07	0.17	-0.04	-0.16	1.00									
Co	0.37	0.32	-0.11	-0.33	0.16	0.25	-0.12	1.00								
Cr	-0.16	0.04	-0.14	0.62	0.10	0.13	0.23	-0.26	1.00							
Cu	-0.26	0.02	-0.01	0.03	0.19	0.15	0.34	0.20	0.14	1.00						
Fe	0.35	0.35	-0.09	-0.07	0.37	0.59	-0.04	0.29	0.09	0.33	1.00					
Mn	0.53	0.27	0.16	-0.06	-0.04	0.35	-0.15	0.25	-0.14	-0.09	0.43	1.00				
Ni	0.60	0.50	-0.29	0.30	0.00	0.37	0.01	-0.09	-0.02	-0.12	0.34	0.42	1.00			
Pb	0.18	-0.05	0.13	-0.13	0.16	0.24	-0.22	0.20	-0.26	0.03	0.14	0.00	0.18	1.00		
Sr	0.65	0.21	-0.15	0.32	-0.21	0.72	-0.14	0.17	0.23	-0.13	0.27	0.23	0.53	0.11	1.00	
Zn	-0.20	-0.02	0.01	0.48	-0.10	-0.05	0.51	-0.23	0.37	0.11	0.01	-0.02	0.20	-0.02	0.05	1.00

Table D.9:Correlations for Royal Canal data

	Ca	K	Mg	Na	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
Ca	1.00															
K	-0.15	1.00														
Mg	0.33	0.13	1.00													
Na	-0.11	0.90	0.21	1.00												
Al	-0.03	0.00	0.06	-0.04	1.00											
Ba	-0.08	0.28	0.12	0.22	0.03	1.00										
Cd	-0.07	-0.29	0.03	-0.25	-0.17	-0.10	1.00									
Co	0.28	-0.20	0.57	-0.24	0.20	-0.16	0.16	1.00								
Cr	0.03	0.23	0.47	0.19	0.27	0.13	-0.28	0.42	1.00							
Cu	-0.11	0.30	-0.15	0.22	-0.05	0.38	-0.10	-0.12	-0.13	1.00						
Fe	0.35	-0.01	-0.27	-0.02	-0.08	0.01	-0.04	-0.03	-0.16	0.43	1.00					
Mn	0.26	0.40	-0.10	0.38	0.02	-0.02	-0.19	-0.08	-0.09	0.34	0.57	1.00				
Ni	0.39	-0.28	0.01	-0.37	-0.23	-0.08	0.00	0.08	-0.10	0.14	0.44	0.13	1.00			
Pb	-0.27	0.25	0.00	0.23	0.15	-0.14	-0.34	0.05	0.28	-0.03	-0.13	-0.02	-0.15	1.00		
Sr	0.41	0.07	0.08	0.14	-0.08	-0.47	-0.02	-0.13	-0.12	-0.20	0.06	0.16	0.38	-0.09	1.00	
Zn	-0.36	-0.14	0.14	-0.01	-0.01	-0.05	0.16	0.11	0.02	0.47	-0.06	-0.12	-0.16	0.10	-0.32	1.00

Table D.10: Correlation for the Shannon/Erne Canal data

	Ca	K	Mg	Na	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
Ca	1.00															
K	0.43	1.00														
Mg	0.27	0.17	1.00													
Na	0.43	0.37	0.83	1.00												
Al	-0.39	0.09	-0.24	-0.27	1.00											
Ba	-0.07	-0.16	0.61	0.35	0.02	1.00										
Cd	-0.08	-0.25	0.30	0.18	-0.13	0.15	1.00									
Co	-0.03	0.12	-0.05	-0.10	0.40	0.21	-0.06	1.00								
Cr	0.24	0.35	-0.05	0.12	0.16	-0.25	-0.11	-0.03	1.00							
Cu	-0.19	0.28	0.72	0.54	0.27	0.61	0.31	0.17	-0.01	1.00						
Fe	-0.45	-0.23	-0.22	-0.39	0.62	0.43	-0.03	0.44	-0.18	0.18	1.00					
Mn	-0.22	-0.15	-0.31	-0.33	0.55	-0.02	-0.05	0.53	-0.16	0.02	0.39	1.00				
Ni	0.28	0.57	-0.01	0.10	0.40	0.03	-0.36	0.14	0.40	0.15	0.19	-0.06	1.00			
Pb	-0.10	0.01	0.00	-0.10	0.30	0.45	0.03	0.42	-0.07	0.21	0.73	0.08	0.17	1.00		
Sr	0.67	0.12	0.28	0.30	-0.28	0.29	-0.06	0.08	0.13	-0.04	-0.16	-0.21	0.28	0.00	1.00	
Zn	-0.11	0.17	0.80	0.62	0.24	0.66	0.27	0.10	0.03	0.93	0.19	-0.07	0.19	0.27	0.02	1.00