AN ASSESSMENT OF THE ACIDIFYING EFFECTS OF AFFORESTATION IN ACID-SENSITIVE CATCHMENTS IN COUNTY WICKLOW

by

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* This project is submitted in part-fulfillment of the HETAC requirements for the award of M.Sc. in Environmental Protection.

September, 2004.

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ABSTRACT

This investigation aimed to determine the extent of forestry-induced acidification of salmonid rivers and streams in acid sensitive catchments of County Wicklow.

The study involved a detailed chemical examination of four selected acid sensitive catchments from January to May 2004, *viz.* Vartry Reservoir Inflows, Cloghoge River, Glendalough Lake Upper and the King's River. Sampling sites varied as to the characteristics of their catchment, *e.g.* afforested, partially afforested, moorland and areas harvested of trees, allowing for comparisons of chemical data.

It was demonstrated that streams draining afforested catchments were artificially acidified compared to non-forested streams. Statistical analysis rejected the null hypothesis (ANOVA: F > F Critical, T-Test: t stat > t Critical) that there was no significant difference in surface water chemical quality between afforested and moorland sampling sites and afforested and clearfelled sites. There were highly significant differences between afforested and moorland sites for pH, alkalinity, total aluminium, colour, TON, chloride and calcium at all catchments. Streams draining heavily afforested catchments were shown to experience greater acid episodes compared to partially or non-forested streams.

The data presented in this report furthers our understanding of acidification due to afforestation in Ireland and coupled with past and present research, should assist in a review of the Forestry and Water Quality Guidelines, especially with regard to designation of acid-sensitivity and remediation measures.

ACKNOWLEDGEMENTS

I would like to express my profound gratitude to Ms. Frances Lucy (IT Sligo) for her interest, guidance, encouragement and all her help throughout this project, from start to finish. Go raibh maith agat.

I would also like to thank the following for their help and support;

Dr. Jim Bowman, EPA
Mr Hugh Horan, EPA (ICP-MS analysis)
Hydrometric Section, EPA (Hydrometric data)
Staff and colleagues at the EPA, Dublin

Thanks also to the following organisations for providing information;

Dublin City Council
Eastern Regional Fisheries Board
Geological Survey of Ireland (GSI)
Ordnance Survey of Ireland (OSI)
Wicklow County Council

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1. INTRODUCTION

Scientific surveys have highlighted the potential acidification of surface waters due to afforestation in areas of low buffering capacity. Evidence indicates that closed-canopy coniferous forests exacerbate acidification in surface waters in certain geologically sensitive catchments with low buffering capacity such as granite and quartzite. Streams in afforested catchments have been shown to be more acidic and contain higher concentrations of aluminium than streams in non-forested but otherwise similar catchments. The phenomenon has been observed only in ‘acid-sensitive’ catchments where the bedrock is resistant to weathering and where both bedrock and soils are low in base cations.

Research on this topic has been conducted in Ireland since the early 1980s yet afforestation is still carried out in acid-sensitive areas despite the results of a number of research projects highlighting the acidification of surface waters in some of these areas and the subsequent effect on biota.

This study is concerned with the potential acidification of surface waters due to afforestation in areas of low buffering capacity. Streams flowing through afforested and moorland (non-forested) areas in these catchments were sampled and analysed fortnightly. The project focuses on four poorly buffered catchments in County Wicklow, namely the Vartry River catchment, Cloghoge River catchment, Glendalough Upper Lake catchment and King’s River catchment.

Afforested, partially afforested, moorland and harvested sites within the four catchments were sampled and analysed every fortnight from January to May 2004 inclusive. Statistical analysis of the chemical data allowed for comparisons between the afforested and moorland sites to determine the extent of acidification and record any acid episodes over the wettest period of the year, which is January to May.

In County Wicklow the main tree species planted in afforestation is Sitka Spruce (*Picea sitchensis*) at 81 percent of the total tree cover in the Coillte estate. The uplands of County Wicklow were deemed suitable only for afforestation in the middle of the last century due to physical characteristics such as high elevation, exposure and soils composed mainly of podzols at 48 percent and peat at 18 percent. Coniferous afforestation greatly increased from the 1950s onwards, with Wicklow now having the greatest level of afforestation in Ireland.

2. LITERATURE REVIEW

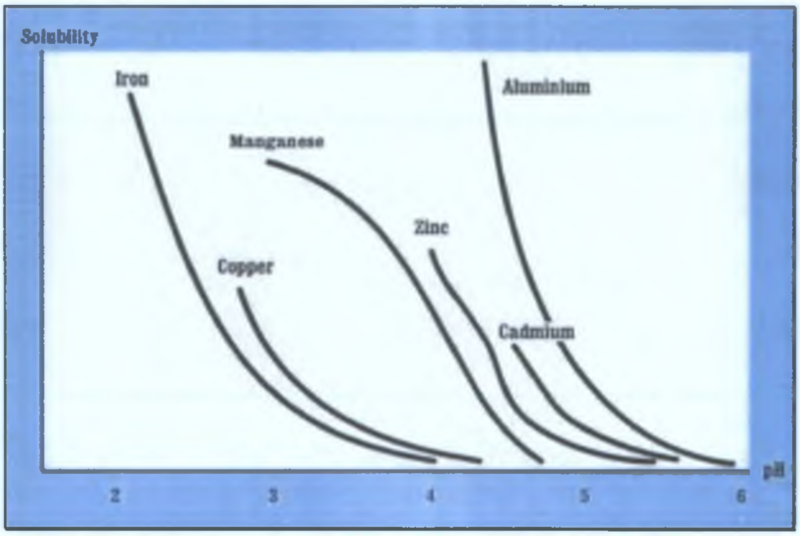
2.1 ACIDIFICATION

2.1.1 Introduction

Rain is naturally slightly acidic due to the presence of dissolved carbon dioxide from the atmosphere (Likens & Bormann, 1974). In addition stronger acids occur naturally in the atmosphere e.g. sulphur dioxide from volcanic activity. Oxides of nitrogen formed during electrical storms generate sulphuric and nitric acid. Changes in acidic deposition that now appear to be taking place worldwide cannot be accounted for solely by natural phenomena. In addition, we need to consider not only rain, but also other forms of both wet and dry deposition, as causes of surface water acidification. Acid rain has elevated levels of H^+, NH_4^+, NO_3^- and SO_4^{2-}, and reduced HCO_3^-. When deposited on a catchment with a low buffering capacity, it may lead to raised levels of Al^{3+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, and K^+ in solution as sulphates and nitrates.

Acid deposition results from increased concentrations of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3) in the atmosphere. Both SO_2 and NO_x originate from the combustion of fuel while NH_3 originates mainly from agriculture. These pollutants reach the land surface in dry, wet and occult (cloud and mist) deposition and can have adverse impacts on forest and freshwater systems. Although acidification of surface waters occurs through direct input, most occurs *via* runoff from the catchment. Acid deposition may be neutralised as it travels through the base-rich soils of certain catchments. However, in areas with base-poor soils the input of these pollutants can exceed the soil buffering capacity (UK Forestry Commission, 2000).

The mobility of many heavy metals increases when soils become acidified (Fig. 2.1) and their chemical speciation can also be altered. One of the more serious consequences of higher aqueous metal concentrations is their negative effect on many of the decomposers that live in the soil (Henriksen & Brodin, 1995a).



Ref: Elvingson & Ågren, 2004

Fig. 2.1: Solubility of metals from mineral soil as a function of pH

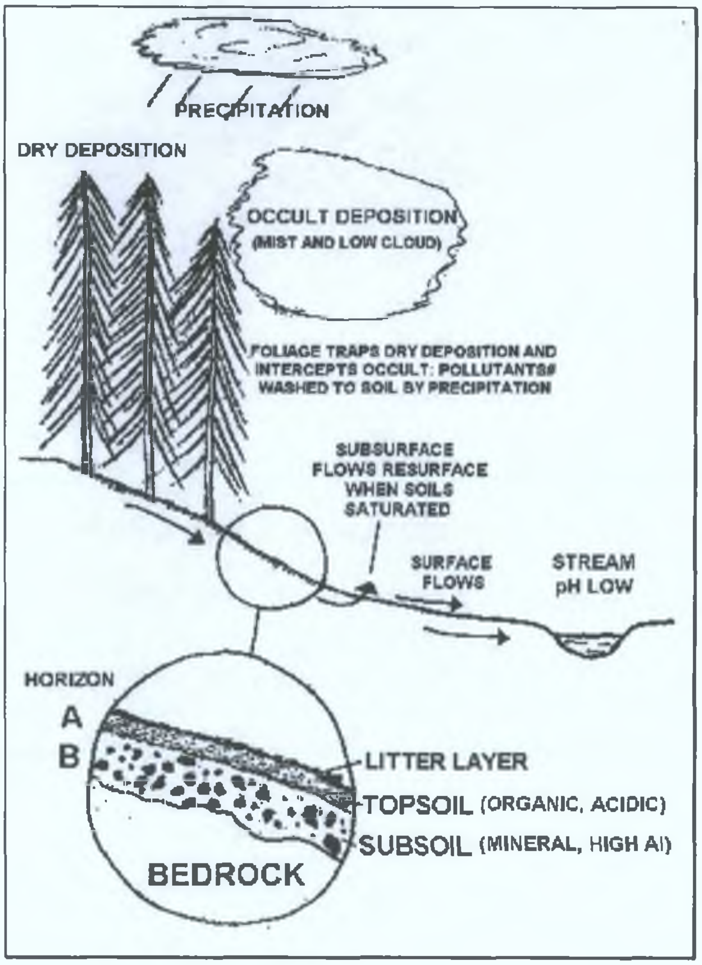
Another effect of surface water acidification is hydrochemical changes. Phosphates can be complexed to the mobilised aluminium (in the form of aluminium phosphate) and will reduce the primary production of the aquatic plants. As phosphate is a limiting nutrient for plants, the decrease in plant food will thereby limit the populations higher in the food chain. The shortage of phosphate is aggravated by the fact that decomposition in the soil slows down under acid conditions (Elvingson & Ågren, 2004).

All soils are not equally susceptible to acidification. The buffering capacity of soil depends on mineral content, texture, structure, pH, base saturation, salt content and soil permeability. Areas with naturally acidic soils and base-poor bedrock are therefore particularly vulnerable to the effects of acid deposition.

2.1.2 Influence of coniferous afforestation on acid deposition

Evergreen or plantation forestry has been shown to exacerbate the acidification processes in soft-water streams draining areas that receive heavy loads of atmospheric pollutants (Harriman & Morrison, 1982; Ormerod *et al.*, 1991; Allot *et al.*, 1993). It has been found that soft-water lakes and streams in forested catchments are more acidic than those in non-forested areas (Harriman & Morrison, 1982; Allot *et al.*, 1990).

The uptake of ammonium by trees during growth leads to the dissociation of this ion with the subsequent release of H^+ ions into the soil solution. The trees themselves scavenge and concentrate air-borne pollutants from the atmosphere on their leaves and branches, in the form of dry deposition (particulate) which is subsequently washed off by rainfall (Harriman & Morrison, 1982). This leads to a highly acidic solution reaching the soil after a long dry period (Fig 2.2). It is most pronounced in the case of mature trees with closed canopies. The presence of trees may also alter the drainage pattern of the soil, allowing more rapid run-off. In forest planting, drainage is deliberately improved before the trees are planted. The acid solution will then be in contact with the mineral subsoil for a shorter period and will be less neutralised.



Ref: Kinross, 2003.

Fig. 2.2: Influence of coniferous trees on soil acidification in base-poor soils

Drains and sediment traps should be installed during ground preparation (Irish Forest Service (2000c). The Forestry and Water Quality Guidelines state that drainage channels should taper out before entering the buffer zone. This ensures that the discharged water gently fans out over the buffer zone before entering the aquatic zone, with sediment filtered out from the flow by ground vegetation within the zone.

Conifers may also exacerbate the situation by removing base cations, such as calcium and magnesium, which might otherwise be available for neutralisation (Stoner & Gee, 1985). The leaves of coniferous trees are lower in bases (i.e. more acidic) than those of deciduous trees. This causes the creation of a layer of acidic litter on the soil surface, which greatly encourages soil acidification.

2.1.3 Impacts of acidification on biodiversity

Catchment characteristics influence the ecological and physico-chemical characterisitics of freshwater systems (Hynes, 1975). Geology, soil type, vegetation cover as well as precipitation and land-use activities play an important role. Acid water, and the high aluminium concentration associated with it, presents a hostile environment to a range of aquatic life, from microscopic algae, to plankton, larger aquatic plants, aquatic insects, fish and water birds (Dudley & Stolton, 1996). Acidification leads to the loss of many ‘acid sensitive species’ and an overall decline in biodiversity (Brodin, 1993).

In considering the effects of acidification on freshwater organisms, two factors need to be taken into account: firstly the differences between lentic and lotic habitats and their biota, and secondly whether the acidification stress is chronic or acute (‘acid shock’). Organisms that are exposed to a slow acidification have a chance to adapt, within limits. More acid-tolerant ones may gradually replace more sensitive species, while the ecosystem functions such as biomass and productivity may be little affected. On the other hand, acid shock, which can occur after snowmelt or with the first rain after a dry spell in which the dry deposition has accumulated, may have a considerable impact on all these aspects. Various studies have reported reductions in macroinvertebrate diversity and the elimination of sensitive groups such as the Ephemeroptera (Harriman & Morrison, 1982; Stoner & Gee, 1985). Slow declines in pH cause skeletal deformities and decreased reproductive success in salmonids, which leads to an unbalanced population structure.

Concentrations of labile monomeric aluminium, known to be toxic to salmonids, have been associated with acidified waters (Baker & Schofield, 1984; Reader & Dempsey, 1989). There are two ways in which aluminium kills fish. Firstly, it is able to reduce the ion exchange through the gills and subsequently causes a salt depletion. Aluminium also precipitates in the gills and interferes with the transport of oxygen and other ions, so that the fish literally dies of suffocation. Secondly, the fish will exude mucus to combat the aluminium in their gills. This mucus builds up and clogs the gills so that oxygen and salt transport is inhibited. Dead fish recovered from acidified streams had low levels of Na^+ and Cl^- in their blood, evidence that they were unable to regulate their body salts.

Small changes in hydrochemical parameters, such as pH may have significant implications for aquatic fauna. The effects of salmonids depend on the stage in the life cycle of the fish and nature of the hydrochemical change. Salmonid eggs and juveniles are the life stages that are most sensitive to low pH values in riverine habitats (Brown &

Sadler, 1989). A relationship between egg survival and the pH of the nursery stream has been demonstrated (Harriman & Morrison, 1982; Muniz & Leivestad, 1980). Declines in salmonid populations have been noted in some afforested systems (Egglishaw *et al*, 1986; Harriman & Morrison, 1982; Ormerod *et al*, 1987; Stoner & Gee, 1985).

Other organisms are affected by acidic water. The decline of the common frog (*Rana temporaria*) has been studied in acidified lakes in Sweden, where in one case extinction took place in six years between the first sighting of dead spawn and the disappearance of the common frog (Hagstrom, 1980). A decline in populations of the Natterjack toad (*Bufo calamita*) have been linked to increased acidification of breeding pools in England (Beebee, 1979).

The acidification not only kills off species, but also alters and decreases the food supply for higher fauna. Acidification can lead to a decline in the benthos (bottom-dwelling organisms) including the number of species of flies, mosquitoes, craneflies, midges and mayflies. This puts a stress on aquatic carnivores such as insect-eating fish.

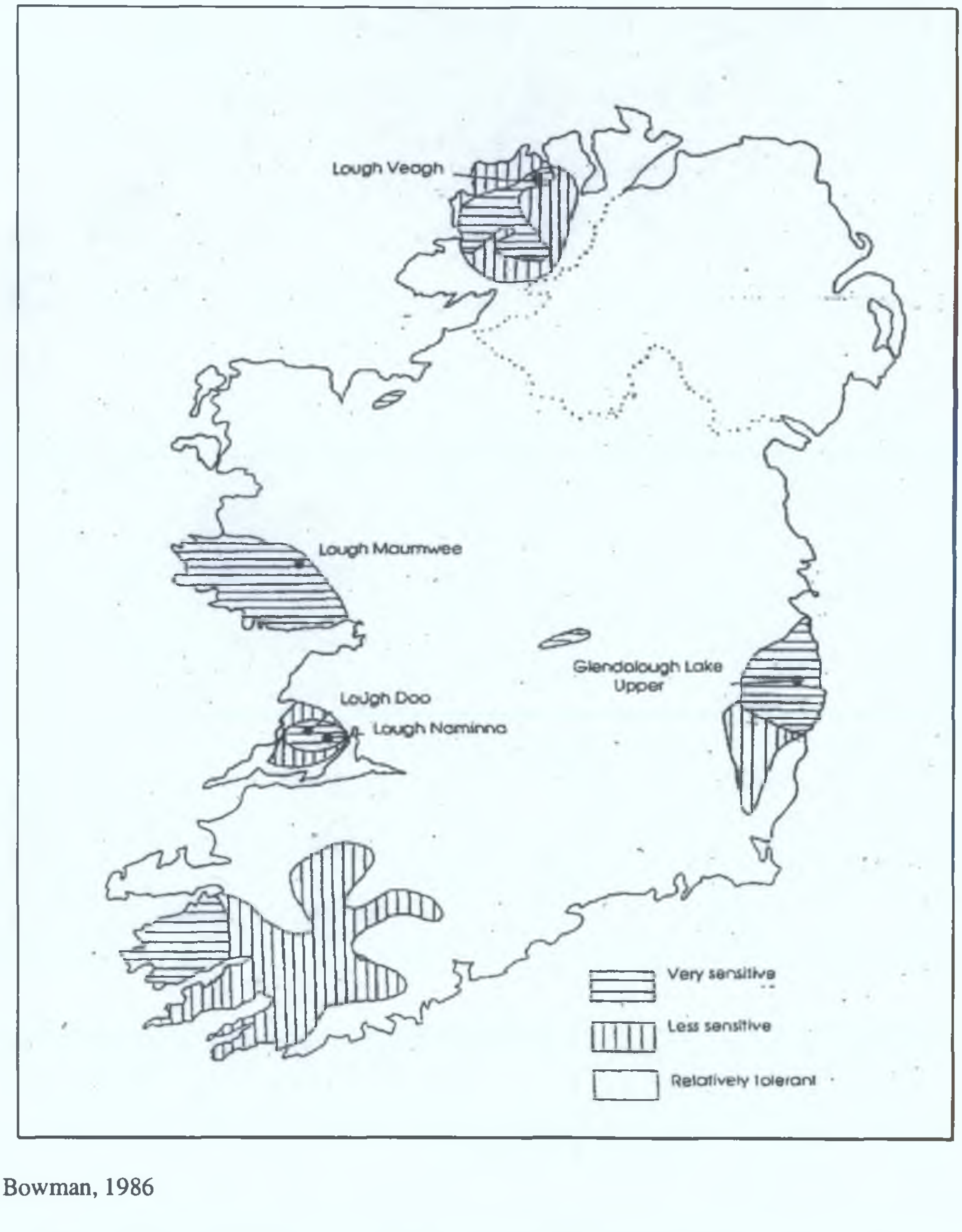
Minnows are the most sensitive to acidification, followed by salmonids. Coarse fish are less sensitive, with eels being fairly resistant (Muniz, 1991). Molluscs and crustaceans are sensitive due to their requirement for calcium, which is depleted in acid waters due to ion exchange with hydrogen at the roots of coniferous trees.

2.1.4 Ireland's vulnerability

Although Ireland has no significant sources of atmospheric pollutants, there is a potential risk of pollution from more industrialised countries such as the UK and mainland Europe though this mainly occurs when the wind direction is from the east. In Ireland the prevailing wind is westerly and the precipitation associated with air masses originating in the Atlantic Ocean is not likely to be artificially acidified. The precipitation borne on easterly winds however, has been shown to be more acidic than that of westerly origin (Bailey *et al*, 1986), and higher concentrations of non-marine sulphate and hydrogen ions have been recorded at east coast compared to west coast sampling sites (Bowman, 1986).

Approximately 50 percent of the sulphur deposition in Ireland is imported while only 25 percent is deposited in the country. More than 80 percent of oxidised nitrogen deposition in Ireland is imported and less than 20 percent of Irish nitrogen oxide emissions are subsequently deposited in the country. In the case of ammonium, however, over 80 percent of total deposition is due to emissions in Ireland even though approximately 50 percent of all such emissions is exported (EPA, 2000). This illustrates the transboundary nature of acid deposition in Europe.

The extensive areas with acid sensitive water bodies in Ireland lie along the western seaboard and in County Wicklow on the east coast (Fig. 2.3). They are underlain by slowly weathering base poor, quartz-bearing bedrock, mostly granite, and have peaty or peaty podzolic soils (Bowman, 1991). These peaty soils would be naturally acidic as they contain many dissolved organic acids. The surface waters in these areas are low in alkalinity and consequently have poor buffering capacity to offset acidification.



Ref: Bowman, 1986

Very sensitive = <10mg/l $CaCO_3$, Less sensitive = 10-15mg/l $CaCO_3$, Relatively tolerant = >15mg/l$CaCO_3$

Fig. 2.3: Acid sensitive areas of Ireland

In Ireland, forestry is located mostly in mountain and upland areas, where the soils tend to be naturally shallow and leached. Calcareous rocks and soils are able to neutralise the acid and prevent its deleterious effects on the ecosystem, whereas impervious soils and unreactive rocks such as granite cannot do this, and the acidity leaches minerals and nutrients from the soil and alters its chemistry (Bache, 1984).

2.2 RESEARCH

2.2.1 Ireland

In 1984-85 a baseline investigation (Bowman, 1986) was carried out to determine the impact of acid precipitation on selected lakes of low buffering capacity in some of the extensive areas of acid-sensitive waters which exist in Ireland. The chemical and biological characteristics of the principal west coast sampling sites used in this study, Lough Maumwee in Co. Galway, did not show evidence of being adversely affected by artificial acidity, whereas several of the biological features of Glendalough Lake Upper on the east coast did show evidence of acid stress. This was attributed to the fact that the Lugduff stream flowing into Glendalough Lake Upper drains an afforested catchment. It was found to be 10 to 100 times more acidic than two other non-forested streams flowing into Glendalough Lake Upper (Bowman, 1991). Recent monitoring of the Lugduff has indicated that its acidity status is unchanged since it was first examined in the late 1980s (EPA, 2002).

In 1987 it was considered desirable to expand the investigation of the water quality of acid-sensitive waters and lakes in Ireland in view of the commissioning of the

Moneypoint coal fired electricity-generating station on the west coast (Bowman, 1991). It provided an opportunity to investigate the impact, if any, of such a sizeable new source of potential acidification on an unimpacted environment. A monitoring schedule of four acid-sensitive areas in Ireland was undertaken: Lough Veagh, Co. Donegal, Glendalough, Co. Wicklow, Maumwee, Co. Galway and Lough Naminna and Doo Lough, Co. Clare (Fig. 2.3).

Overall the investigation showed little evidence that the areas examined were impacted by artificially acidified precipitation. The instances of chronic acidification were confined to those waters containing the run-off from extensive areas of evergreen afforestation.

A study of ten small catchments on granite bedrock in Co. Galway (Allot *et al*, 1990) also concluded that sites in afforested catchments became the most acidic. The AQUAFOR report of 1997 was published by COFORD (National Council For Forest Research and Development) in collaboration with NUI (National University of Ireland) Cork, NUI Dublin and Trinity College Dublin. It was initiated in response to a concern that some forests because of their location might have a negative impact on streamwater and fish populations by exacerbating acidity. The project focused on the interactions between plantation forestry and aquatic ecology. Two poorly buffered areas, west Galway-Mayo and part of the Wicklow Mountains and a less sensitive area of Munster were selected.

The study showed that acid episodes in poorly buffered streams, chiefly on granite, quartzite and schist, at certain Wicklow and Galway-Mayo sites exhibited minimum pH values below that recommended for salmonid fisheries. Most streams were episodically acidic during periods of low flow. Greater deposition rates of sulphur and chloride were recorded during periods of high easterly airflow. Acid episodes were most severe and long lasting, however, in certain afforested catchments and tended to occur in winter and spring when salmonids are at a particularly vulnerable stage in their life cycle.

In the Wicklow region, consistently high levels of acidity and associated toxic levels of inorganic aluminium (>40μg/l) were considered to be responsible for the absence of fish in three afforested river stretches. Twenty-four of the forty six sites sampled in Wicklow had mean labile monomeric aluminium concentrations in excess of the 40μg/l, the maximum concentration recommended for salmonid waters. The Drinking Water Directive (98/83/EC) Mandatory (I) limit for total aluminium is 200μg/l (S.I. 81 of 1988) and the labile monomeric aluminium Critical Limit is 40μg/l (S.I. 293 of 1988). All of these sites were afforested to varying degrees. Eight sites, all afforested, had mean values exceeding twice this limit. The report recommended that levels of inorganic aluminium should be considered in association with pH and buffering capacity in the designation of acid-sensitivity.

Annual monitoring by the EPA of Glendalough catchment highlights the continued acidification of the afforested Lugduff River.

Low pH and alkalinity values were recorded in afforested streams during work conducted by the Eastern Regional Fisheries Board (ERFB) in 1996. Comparison of results showed that afforested streams had lower alkalinity and pH values than those in moorland areas.

Within the Glendalough catchment, the Lugduff River (afforested) was pH 5.1 while the Glenealo River (moorland) recorded pH 6.6. In the King's River catchment, pH of the afforested Ballinagee River was in the range 4.7 to 6.3 and the pH of the Annalecka River (afforested and partial harvesting) was in the range 4.7 to 5.3. In the Vartry catchment, pH results in the range of 5.3 to 6.7 were recorded for streams flowing through afforested areas.

The Three Rivers Project (1999-2002) was a €6 million EU and Government-funded study aimed at identifying pollution sources in Ireland's three most important rivers for abstraction of drinking water, the Liffey, the Suir and the Boyne. Together the three river catchments represent 10.5 percent of the landmass of the country and supports 15 percent of the population. A minor aspect of the study was a focus on surface water acidification in afforested tributaries of the King's River catchment. Weekly analysis of tributaries was undertaken throughout the duration of the project. While there were fluctuations in pH, some very low pH values were recorded for the afforested streams in the King's River catchment under consideration in this study. pH values for the Annalecka Stream were in the range of 3.9 to 6.9, the Glasnadade Stream were in the range pH 4.2 to 7.4 and the Ballinagee Stream in the range pH 4.7 to 7.2.

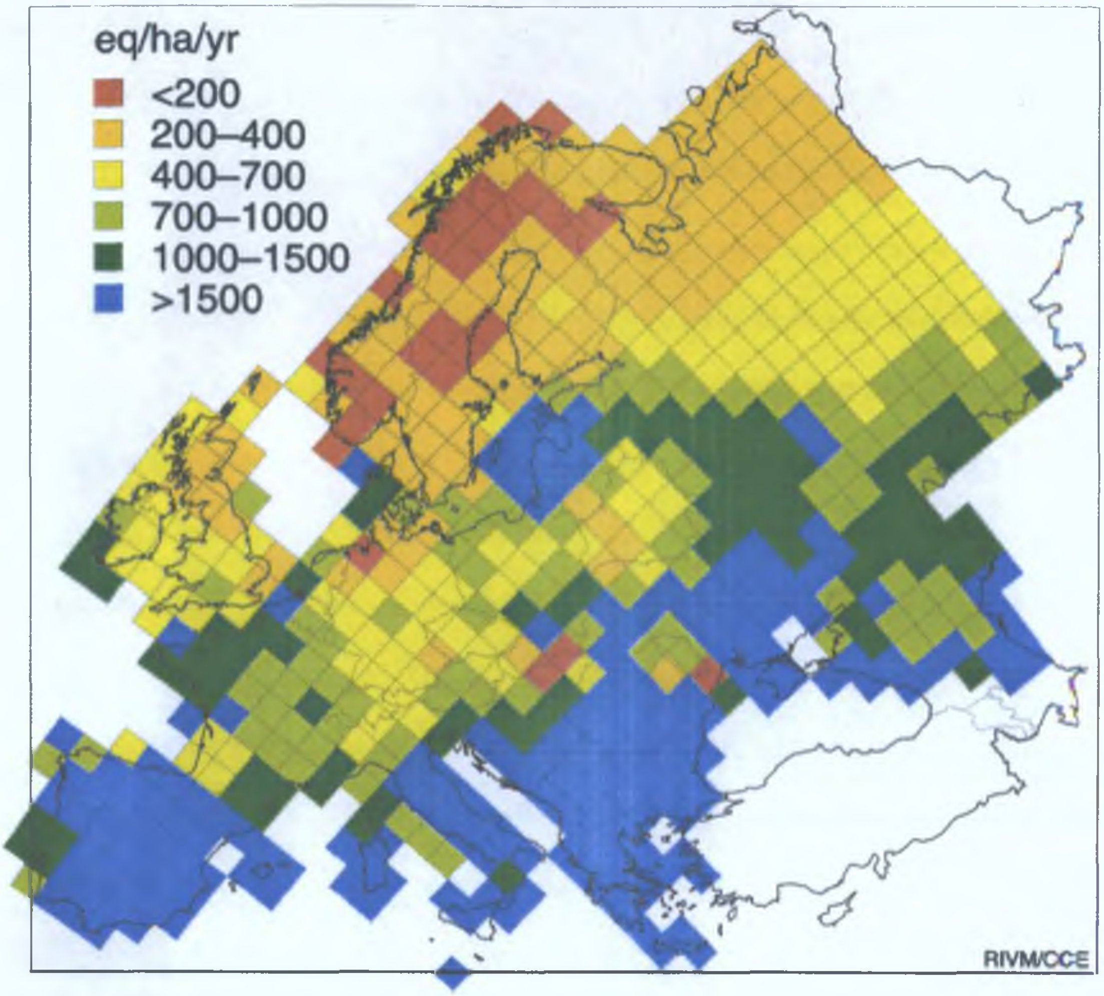
2.2.2 International research on acidification

A critical load is the *quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur according to present knowledge* (UNECE, 1988) i.e. a measure of the damage threshold for pollutants. Critical loads can be set for a range of different habitats and species.

Scientists acting under the auspices of the United Nations Economic Commission for Europe (UNECE) have collated critical load data for sulphur, nitorgen and acidity levels throughout Europe. They have produced maps showing where the tolerance of soils and waters is exceeded, or is likely to be exceeded in the future, (Henriksen, 1992). The critical load for acidification is calculated as the amount of H^+, expressed as equivalents per hectare per year (eq/ha/yr), that the ecosystems are able to neutralise. This sensitivity is illustrated in Figure 2.4 below, where the red areas are the most sensitive and the blue areas the most resistant. The most sensitive ecosystems for acidification (red) are only able to neutralise deposition of <200 eq/ha/yr of H^+ and the most tolerant (blue) ecosystems are able to neutralise >1500 eq/ha/yr of H^+.

'ECOSYSTEM SENSITIVITY FOR ACIDIFICATION, EUROPE'.

Red indicates high sensitivity, blue low.



Source: www.oekodata.com/icpmapping

Fig. 2.4: Critical loads for Europe

The United Kingdom Acid Waters Monitoring Network (UKAWMN) was established in 1988 to monitor the ecological impact of acid deposition in areas of the U.K. believed to be sensitive to acidification. The network consists of 11 lakes and 11 streams located in acid sensitive areas that are monitored chemically and biologically. The UKAWMN contains three sets of 'paired' forest and moorland catchments, two in Scotland and one in Wales. A comparison of the paired moorland and afforested catchments supports the conclusion that afforestation causes increased SO_4 and NO_3 concentrations in runoff, and hence greater acidity (UKAWMN, 2001).

Before the development of intensive industrialisation in Europe, the majority of Swedish lakes and watercourses were only slightly acidic, with pH values around 6.5 or less (highlighted as red and orange areas of critical loads map, see Fig 2.4). But during the 20th century, acid levels have increased significantly in several thousand bodies of water, especially in southern and central Sweden. The primary cause of this development is deposition of acidifying compounds, but it is presumed that modern forestry has also contributed. Sweden conducts many successful liming programmes annually and is committed to the 1979 Convention on Long-Range Transboundary Air Pollution (CLRTAP) and the 'multi-pollutant, multi-effect' protocol of 1999.

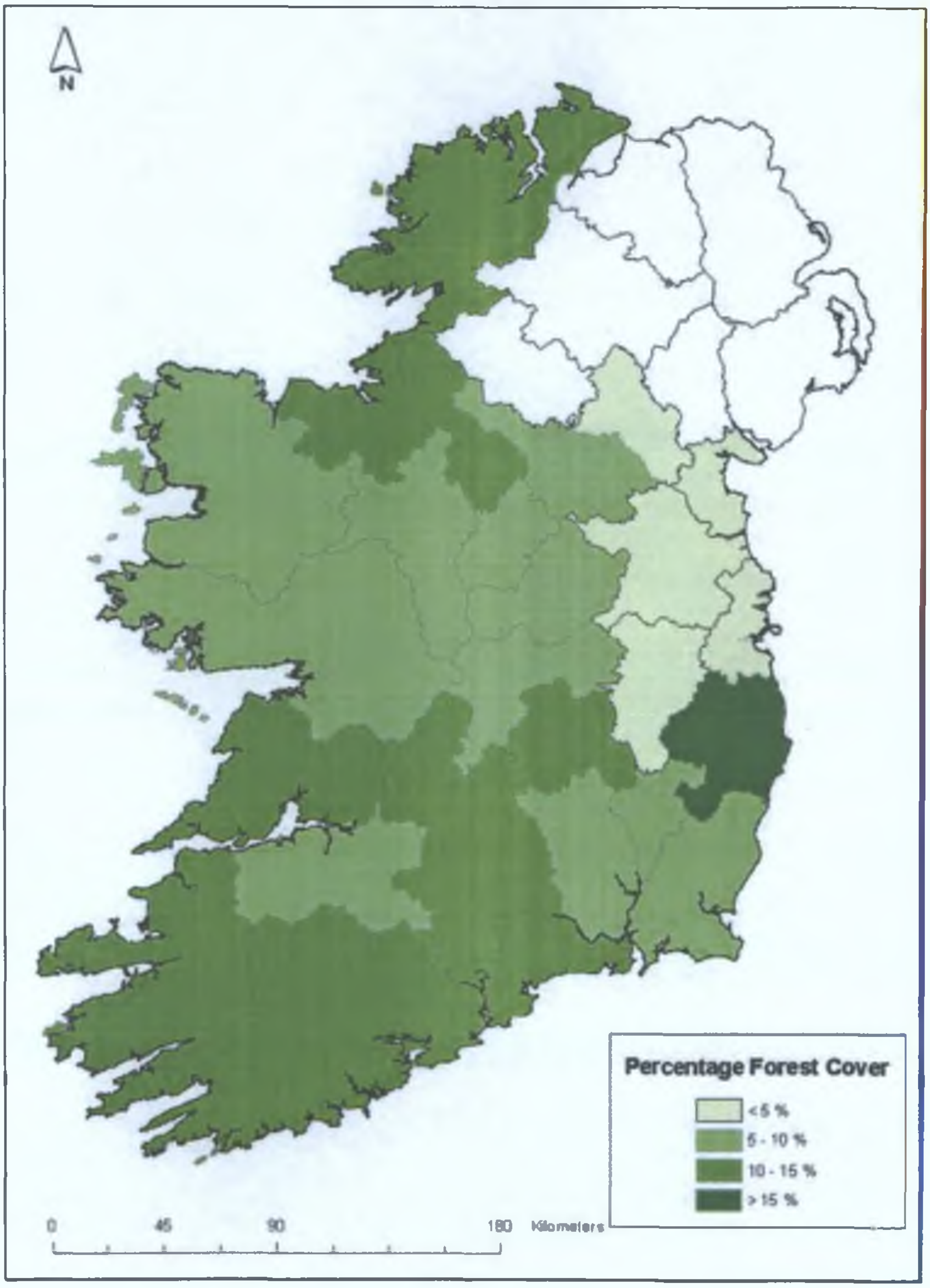
Interest on acid precipitation in Québec, Canada arose at the end of the 1970s after scientific studies showed that southwestern Québec was receiving highly acidic precipitation from the nearby USA. This area was also very sensitive to acidification and in the period of 1986 to 1990 Environment Canada, Québec Region, conducted the first phase of the water quality monitoring programme as part of the Québec Lake Survey. This was a huge project, with 1253 lakes selected randomly from 160,000 lakes scattered throughout the province. Sulphates were considered as a good indicator of the acid deposition intensity. While a large number of lakes in Québec were naturally acidic, those with high concentrations of sulphate were located in the southwest, nearer the more industrialised US, and decreased toward the north and northeast.

2.3 FORESTRY POLICY

2.3.1 Ireland

Ireland is part of the temperate deciduous forest biome. Deciduous woodlands of oak (*Quercus*), elm (*Ulmus*), and ash (*Fraxinus*) once covered extensive areas of lowland Ireland. The decline in the natural forest cover of Ireland was a slow process starting in the Neolithic times, with small scale clearing. As agriculture developed, large areas of forests were burnt or cut down and the land used for grazing and planting crops. Throughout the Medieval period Irish woodlands were increasingly exploited and by the early seventeenth century, the tree cover was decimated as a result of extensive felling for timber export. Felling continued such that 100 years ago only about 1.5 percent of the land was covered.

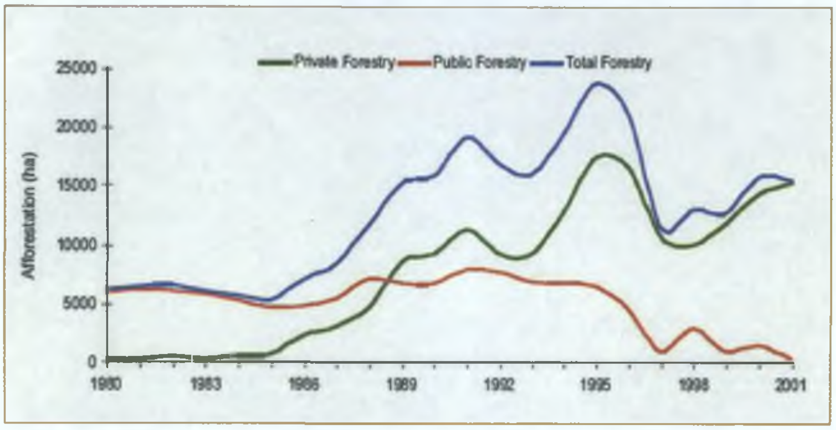
The process of reafforestation began early in the 20th century and has been based almost entirely on the exotic coniferous species. Forest cover is now 9.7 percent of national territory with small units of extensively managed and highly productive coniferous plantations (EPA, 2002a). While Ireland has one of the lowest levels of forest cover in the EU, where the average is 30 percent, the recent planting rate is among the highest in Europe. National planting targets of 20,000 hectares per annum are aimed at doubling forest cover to 17 percent by 2030 (EPA, 2002a). County Wicklow has the highest percentage of land under forestry in Ireland (Fig. 2.5) and a significant amount of this afforestation has occurred on bogland in upland areas.



Ref: EPA, 2002a

Fig. 2.5: Percentage Forest Cover by County

There has been a huge increase in private afforestation since the mid 1950s (Table. 2.1) and at present, about 615,000 ha of Ireland is forested. This is predicted to increase to 1.2 million ha by 2030 (Irish Forest Service, 1996).



Afforestation	1980	1985	1990	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
Private Forestry	268	617	9147	9134	9171	12837	17343	16555	10583	10002	11777	14231	15147
Public Forestry	5922	4625	6670	7565	6827	6622	6367	4426	851	2926	891	1464	317
Total Forestry	6190	5242	15817	16699	15998	19459	23710	20981	11434	12928	12668	15695	15464

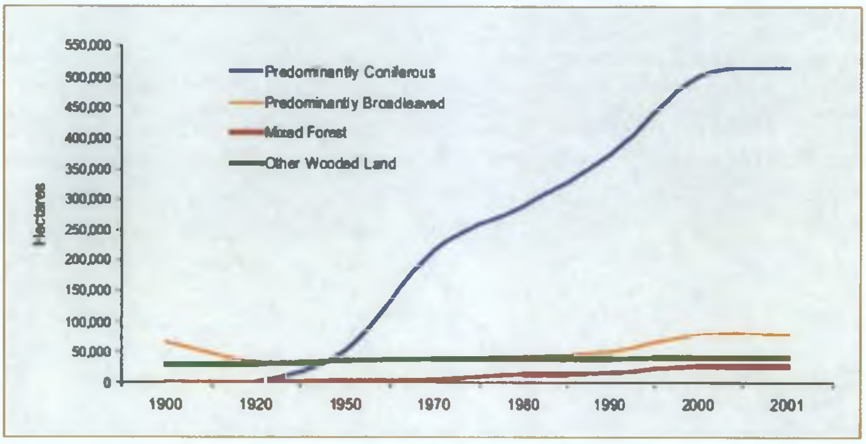
Source: Forest Service

Ref: EPA, 2002a

Table 2.1: Private & Public Afforestation since 1980

Approximately 77 percent of Irish forests consist of coniferous species (Table 2.2) with over 50 percent being of the Sitka Spruce (*Picea sitchensis*) variety. Monoculture plantations of coniferous trees are of limited biological diversity value and can impact adversely on the rural landscape. Alternatively, the inclusion of native and broadleaf species in Irish forests such as beech (*Fagus*), oak (*Quercus*) and sycamore (*Acer*) has particular value in terms of landscape, heritage, amenity and habitats. Annual targets of

20 percent broadleaf afforestation are set under current forest policy (Irish Forest Service, 2000).



	1900	1920	1950	1970	1980	1990	2000	2001
Predominantly Coniferous (ha)	3.000	3.200	52.935	216.665	290.383	373.815	502.035	515577
Predominantly Broadleaved (ha)	65,500	34,300	37.000	39.000	45.000	50.400	78.427	80350
Mixed Forest (ha)	1.500	1,500	5.000	7.500	15.000	17.000	28.350	28350
Other Wooded Land (ha)	30,000	31,000	38,000	39,000	40,000	40.000	41.000	41000

Source: Forest Service

Ref: EPA, 2002a

Table 2.2: Species planted in Irish Forests

Collite Teoranta, the state-owned commercial forestry company, envisages that Sitka Spruce (*Picea sitchensis)* will remain the dominant species in Wicklow but it is proposed to achieve long term reduction to 74 percent and an increase in broadleaves from the present low of 1.8 percent to 10 percent in the county.

Some of this planting has occurred in areas now considered to be acid-sensitive. The Irish Forestry Service processes grant aid applications for afforestation. They require an assessment of acid sensitivity, based on measurements of alkalinity (Gran-Titration

Method), to be conducted in areas considered as acid-sensitive. Sampling and analysis is to be carried out on a minimum of four weeks in the period February to May inclusive. A laboratory, independent of the applicant and participating currently in relevant national or international intercomparison exercises, performs the analysis. Samples are to be taken from and measurements to be made on all watercourses shown on Ordnance Survey 6" Maps, scale 1:10560, within the area of the proposed afforestation. The minimum acid-sensitivity measured in the above manner determines the overall sensitivity of the site. The most recent protocol issued by the Forest Service (Irish Forest Service, 2002) states the following with reference to acidifcation:

> 'There will be no afforestation in areas where the minimum alkalinity of the runoff water, measured in the above manner, is less than 10mg/L as $CaCO_3$'
>
> 'Where the minimum alkalinity of the runoff water, measured in the above manner, is in the range 10-15mg/L as $CaCO_3$, full, partial or no afforestation may be allowed following discussion and agreement between the EPA, the Forest Service of the Department of Communications, Marine and Natural Resources and Regional Fisheries Board'
>
> 'Afforestation will be allowed where the minimum alkalinity of the runoff water is greater than 15mg/L as $CaCO_3$'

The Regional Fisheries Board (RFB) notifies the landowners upon designation of an area as acid-sensitive. Details of the areas affected are also published in *Iris Oifigúil* and in the newspapers circulating in the locality. Landowners may object to the designation of any area as a Fishery Sensitive Area and are entitled to have their views taken into account if they submit an objection within two months of the public notice being issued. Designated Fishery Sensitive Areas are reviewed every five years.

In designated fishery sensitive areas, the RFB must be consulted at least six weeks before beginning planting operations if the planned afforestation is greater than 5 ha. In non-designated areas, the RFB must be consulted at least six weeks before commencement of planting operations if the planned afforestation is greater than 10 ha

However, under the 1946 Felling Act, replanting must take place in existing plantations following felling. This would apply to areas now considered as acid-sensitive. In such cases, derogation must be obtained from the Minister for Communications, Marine and Natural Resources.

Under the National Development Plan, the Irish Government funds the EPA Environmental RTDI Programme 2000-2006. The RTDI water quality research is focused in two main areas: Eutrophication from agriculture and Forestry and water quality. The Forestry Water projects are funded in partnership with COFORD. These projects focus on determining the best practice for forestry plantation and management, particularly with regard to fertiliser application and minimising the threat from acidification. The large-scale projects addressing acidification are listed below:

- Forestry and Environmental Impacts: Addressing Water Quality and Biodiversity – Forestry and the potential for Surface Water Acidification (WaterAc) (Ref: 2000-LS-3.2.1a-M2).
- Forestry and the potential for Surface Water Acidification – Review of Liming Options for Afforested Catchments in Ireland (Ref: 2000-LS-3.2.1b-M2).

Another COFORD co-funded ERTDI project addressing acidification is the BioForest Project: Biodiversity Assessment of Afforestation Sites (Ref: 2000-LS-3.1.1-M2).

The main targets of these projects are:

- Recommended management practices that could prevent and lessen impacts of forest operations on acidification, including the use of buffer strips and liming.
- Development of the Sodium Dominance (or Weathering) Index.
- Assess the efficacy of the current Forestry and Water Quality Guidelines.

Literature reviews of the use of buffer strips and/or liming as mitigation measures against the acidifying effects of afforestation were undertaken (Donnelly *et al*, 2003 & 2003a). This was chiefly an international study as there is little evidence of their use in Ireland. The most commonly adopted indicators of acid-sensitivity, pH and alkalinity, are both extremely variable within any single catchment depending on flow conditions and geology.

The Sodium Dominance (or Weathering) Index attempts to classify/identify acid-sensitive rivers in Ireland by calculating the contribution of sodium to the sum of the major cations in river waters particularly where sea salt inputs, predominantly sodium, dominate the base cation composition of the river water. The extent of sodium dominance provides a quantitative indication of catchment weathering rate, incorporating the effects of diverse geological composition. A value greater than c. 40 percent has been proposed for the more sensitive catchments whereas much lower levels are indicative of well-buffered catchments.

2.3.2 UK Critical Loads Approach

A critical load is defined as the maximum load of a pollutant which a given ecosystem can tolerate without suffering adverse change. For freshwaters, critical loads can be calculated for which, provided they are not exceeded, ensure the maintenance of water chemistry suitable for the protection of populations of fish and other freshwater biota.

The most acidified areas in the UK are in the uplands where catchments with base-poor, slow weathering soils and rocks coincide with high pollutant inputs in the form of large volumes of moderately polluted rainfall. Surface water acidification has been identified as a particular problem in parts of central and south west Scotland, Cumbria, the Pennines and central and north Wales.

In order to reach decisions on forestry proposals the UK Forestry Commission takes into account the effect of scavenging by trees. The UK Forestry Commission developed critical loads maps to identify those areas most susceptible to freshwater acidification. The use of critical loads maps aids the UK Forestry Commission and applicants in understanding where this effect is likely to be important. The Department of Environment, Transport and the Regions (DETR) calculated critical loads for freshwaters in the UK. Having compared these with the non-marine inputs of sulphur, the UK Department of Environment derived maps which indicate where critical loads for acidity for freshwaters are exceeded, and are likely to continue to be exceeded in the year 2010.

The UK critical loads approach maps are similar to the critical loads for Europe (Fig. 2.2) and indicate where additional scavenging by trees could lead to further freshwater acidification. However, because of sampling and scale factors they are not directly useful for determining the susceptibility of running waters in individual catchments. This requires a catchment-based assessment. Catchment-based assessments are likely to be required for new planting proposals within those areas of the map where critical loads are exceeded.

The UK Forestry Commission with the aid of the appropriate water regulatory authority determines assessment. Where insufficient data exists on the area, samples are taken and analysed to determine water chemistry at high and low flows. This enables the calculation of the catchment's freshwater critical load. The additional pollutant capture by the proposed forest is estimated and added to the predicted pollutant depositions for the catchment at the time of canopy-closure (estimates based on the predictions for 2010). Where the combined deposition total exceeds the freshwater critical load, approval of a Woodland Grant Scheme is unlikely to be given.

Catchment assessments are expected to show that where critical load exceedance is currently greatest (*i.e.* by more than 0.5 keq.H^+/ha/yr) and a major part of the proposed planting is at higher altitude, the scavenging effect will result in critical load exceedance at canopy closure (UK Forestry Commission, 2000).

2.3.3 EU Policy - The Water Framework Directive (WFD)

The Water Framework Directive (Directive 2000/60/EC) has recently been adopted by the European Union and transposed into Irish law since December 2003 (S.I. 722 of 2004). It was established with the purpose of creating a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater in the EU (European Parliament and Council for European Union, 2000).

The environmental objective of the WFD in regard to surface waters is that

> *'member states shall protect, enhance, and restore all bodies of surface water…with the aim of achieving good surface water chemical statues at least 15 years after the date of entry into force of the directive'* (Article 4 (a)(II)).

Acidification status is listed in the WFD in the

> *'quality elements for the classification of ecological status of surface waters'* (Annex V).

High status conditions in both rivers and lakes include

> *'levels of salinity, pH, oxygen balance, acid neutralising capacity (ANC), and temperature (which) do not show signs of anthropogenic disturbance and remain within the range normally associated with undisturbed conditions*'.

The range of natural pH values found in fresh waters in Ireland extends from 4.5 in acid peaty upland waters to higher than 10 where there is intense photosynthetic activity by algae (EPA, 2001). The limits for pH outlined in the Freshwater Fish Directive (78/659/EEC) for both salmonid and cyprimid fish are pH 6.0 to 9.0 (EPA, 2001). The UK forests and water guidelines recommend that pH be in the range of 6 to 9 with low levels of dissolved aluminium for the health of salmonid fish (UK Forestry Commission, 2000).

Pollution is defined within the directive as

> *'the direct or indirect introduction as a result of human activity of substances or heat into the air, water or land which may be harmful to human health or to the quality of aquatic systems or terrestrial systems'* (Article 2.33)

and acidification falls within this ambit.

2.3.4 International policy

In Geneva, Switzerland in November 1979, at a time of growing evidence of acidification in Scandinavian lakes, the UNECE (United Nations Economic Commission for Europe) set up the Convention on Long Range Transboundary Air Pollution (CLRTAP). The 'transboundary' nature of acidifying pollutants, where deposition may occur a considerable distance from the emission source, had called for an international response. This was the first multilateral treaty for dealing with air pollutants on a broad regional basis (Fig. 2.6). Aimed initially at reducing the effects of acid rain through control of the emissions of sulphur, its scope was later widened to include nitrogen pollutants, volatile organic compounds (VOCs) and photochemical oxidants. Heavy metals and persistent organic pollutants (POPs) were subsequently added. Since then, the international community has agreed a range of protocols to cut emissions as illustrated in Figure 2.6.

In 1983 the Scandinavian countries put forward a proposal for limiting the emissions of sulphur. The first sulphur protocol was signed in Helsinki, Finland in 1985 and ratified by more than twenty parties to the convention where it came into force in 1987. It required the signatories to reduce their national yearly emissions of sulphur, or its transboundary fluxes, by at least 30 percent by 1993 at the latest, from their 1980 levels. The 30 percent criterion was to be regarded as the first step in a long-term project for reducing emissions. Between 1980 and 1993 total European emissions of sulphur had dropped by 43 percent, according to European Monitoring and Evaluation Programme

(EMEP) data, (Swedish NGO Secretariat on Acid Rain, 2003). The second sulphur protocol was signed in Oslo in 1994 and came into force in 1998. It sets differing requirements for each country – the aim being to attain the greatest possible effect for the environment at the least overall cost. As a result of the countries' commitments under the protocol, total European emissions of sulphur can be expected to have fallen by about 50 percent by 2000, and 58 percent by 2010, as from 1980.

In 1988 in Sofia, Bulgaria, twenty-five nations signed an agreement to limit their emissions of nitrogen oxides. This protocol stipulated that, after 1994, emissions should not exceed their 1987 level. In other words, it did not call for any actual reduction, though it did lay the ground for a second step involving measures to reduce emissions.

While emissions of sulphur and nitrogen increased in association with increased consumption of fossil fuels towards the end of the industrial revolution, emissions of atmospheric pollutants have declined across Europe since the 1980s as a result of the implementation of the CLRTAP.

The most recent is the so-called 'Multi-pollutant, multi-effect' Protocol, signed in Göteburg, Sweden in 1999. This protocol aims at noticeably lessening acidification, eutrophication and the formation of ground-level ozone by setting national ceilings for emissions of the four pollutants that give rise to these effects, namely sulphur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3) and volatile organic compounds (VOCs), to be met from 2010. The protocol also contains binding requirements in the form of emission limit values (ELVs) both for stationary and mobile sources, as well as fuel standards. There is also an annex aimed at bringing down the emissions of ammonia from agricultural sources and although thirty-one countries have signed it, by mid-2003 only five had ratified this protocol as shown in Table 2.3.

Fig. 2.6: Schematic of European legislation to combat acidification

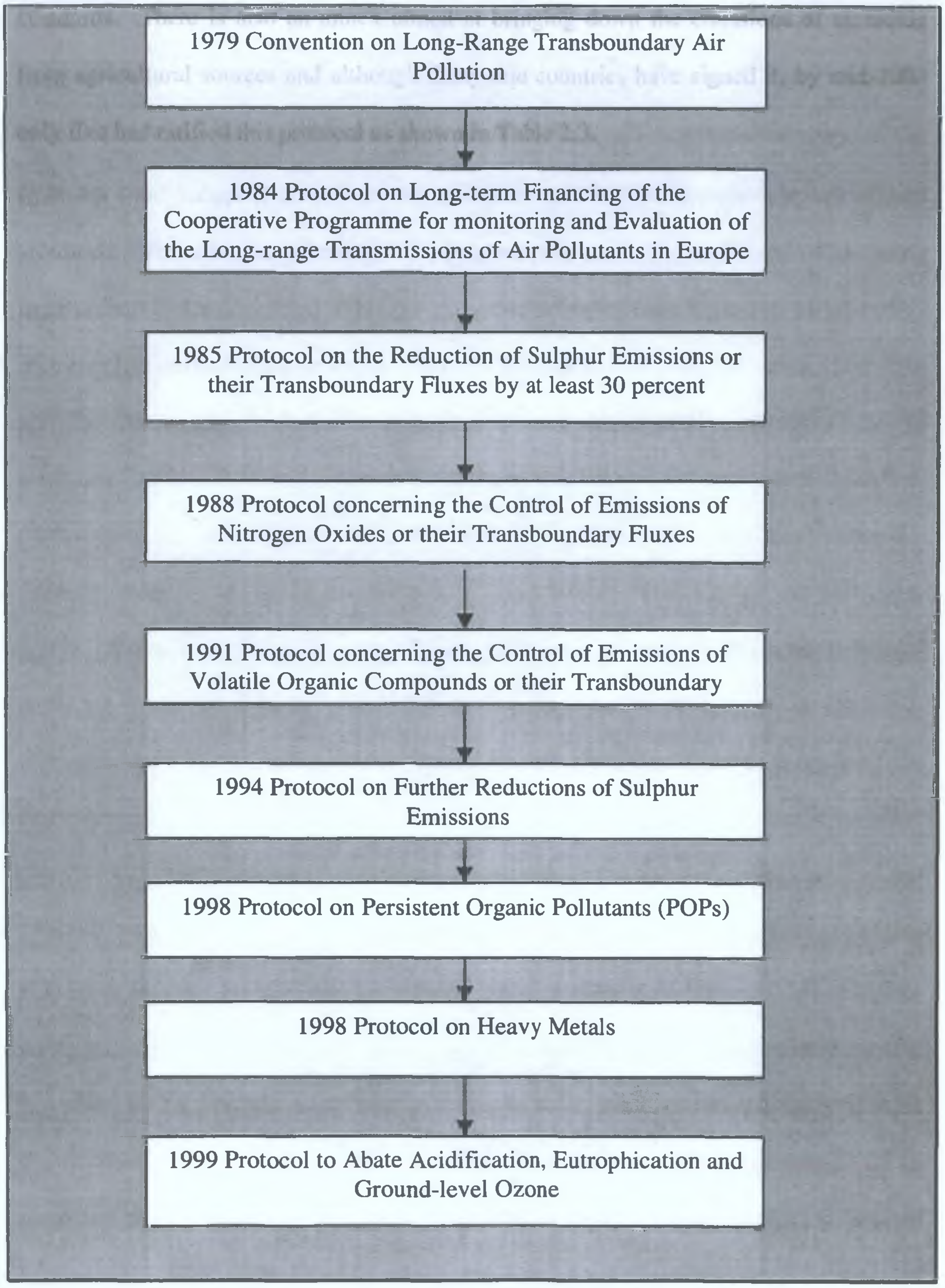


Table 2.3: Status of the Convention in September 2003. S = SIGNED, R = RATIFIED.

	1979 Conv. [a]	1984 EMEP [b]	1985 SO_2 [c]	1988 NO_x [d]		1991 VOCs [e]	1994 SO_2 [f]	1998 POPs [g]	1998 HMs [h]	1999 Multi-eff [i]
Armenia	R							S	S	S
Austria	S+R	R	S+R	S+R		S+R	S+R	S+R	S	S
Azerbaijan	R									
Belarus	S+R	S+R	S+R	S+R						
Belgium	S+R	S+R	S+R	S+R		S+R	S+R	S	S	S
Bosnia & Herz.	R	R								
Bulgaria	S+R	S+R	S+R	S+R		S+R	S	S+R	S	S
Canada	S+R	S+R	S+R	S+R		S	S+R	S+R	S+R	S
Croatia	R	R			R		S+	S	S	S
Cyprus	R	R			S				S	
Czech Rep.	R	R	R	R		R	S+R	S+R	S+R	S
Denmark	S+R	S+R	S+R	S+R		S+R	S+R	S+R	S+R	S+R
Estonia	R	R	R	R		R				
Finland	S+R	S+R	S+R	S+R		S+R	S+R	S+R	S+R	S
France	S+R	S+R	S+R	S+R		S+R	S+R	S+R	S+R	S
Georgia	S+R									
Germany	S+R	S+R	S+R	S+R		S+R	S+R	S+R	S	S
Greece	S+R	R		S+R		S	S+R	S	S	S
Holy See	S									
Hungary	S+R	S+R	S+R	S+R		S+R	S+R	S	S	S
Iceland	S+R		R					S+	S	
Ireland	S+R	S+R		S+R			S+R	S	S	S
Italy	S+R	S+R	S+R	S+R		S+R	S+R	S	S	S
Kazakstan	R									
Kyrgystan	R									
Latvia	R	R			S					
Liechtenstein	S+R	R	S+R	S+R		S+R	S+R	S	S	S
Lithuania	R							S	S	
Luxembourg	S+R	S+R	S+R	S+R		S+R	S+R	S+R	S+R	S+R
Malta	R	R								
Monaco	R	R			R		R			
Netherlands	S+R	S+R	S+R	S+R		S+R	S+R	S+R	S+R	S
Norway	S+R	S+R	S+R	S+R		S+R	S+R	S+R	S+R	S+R
Poland	S+R	R		S			S	S	S	S
Portugal	S+R	R				S		S	S	S
Macedonia[1]	R									
Rep. Moldova	R							S+R	S+R	S
Romania	S+R	R						S	S	S
Russian Feder.	S+R	S+R	S+R	S+R			S			
San Marino	S									
Serbia & Mont.	R	R								
Slovakia	R	R	R	R		R	S+R	S+R	S+R	S
Slovenia	R	R			R		S+	S	S	S
Spain	S+R	R		S+R		S+R	S+R	S	S	S
Sweden	S+R	S+R	S+R	S+R		S+R	S+R	S+R	S+R	S+R
Switzerland	S+R	S+R	S+R	S+R		S+R	S+R	S+R	S+R	S
Turkey	S+R	S+R								
Ukraine	S+R	S+R	S+R	S+R		S	S	S	S	
United Kingd.	S+R	S+R		S+R		S+R	S+R	S	S	S
United States	S+R	S+R		S+R		S		S	S+R	S
Eur. Comm.	S+R	S+R		R		S	S+R	S	S+R	R
Total	33/49	22/40	19/22	25/28		23/21	28/25	36/16	36/14	31/5

[1] The Former Yugoslav Republic of Macedonia.

[a] Covention on Long Range Transboundary Air Pollution (adapted 1979, entry into force 1983).

[b] Protocol on Long-term Financing of the Cooperative Programme for monitoring and Evaluation of the Long-range Transmissions of Air Pollutants in Europe (1984: 1988).

[c] Protocol on the Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30 percent (1985; 1987).

[d] Protocol concerning the Control of Emissions of Nitrogen Oxides or their Transboundary Fluxes (1988: 1991).

[e] Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes (1991: 1997).

[f] Protocol on Further Reductions of Sulphur Emissions (1994; 1998).

[g] Protocol on Persistent organic Pollutants (POPs) (1998).

[h] Protocol on Heavy Metals (1998).

[i] Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (1999).

Ref: Acid News Environmental Factsheet No. 14

2.4 REMEDIATION

2.4.1 International measures

Much research has been focused on recovery and methods to restore acidified surface waters since marked ecological changes were first reported in the 1970s. Causative treatment by reducing acidifying emissions is the primary goal. Symptomatic treatments, however, involving the use of buffer strips or the addition of neutralising agents such as powdered limestone to affected waterbodies or their catchments have become widespread practice in Europe.

2.4.2 Liming

Liming is the generic term for the addition of any base material to neutralise surface water or sediment or to increase the acid neutralising capacity (Olem, 1991). There are four main groups of neutralising agents that have been used in liming: carbonates, oxides, hydroxides and silicates (Olem, 1991). The carbonates are the most widely used.

There are numerous methods of applying lime (crushed or powdered form), such as lake liming, catchment liming, buffer strip and riparian liming, stream liming, doser liming and aquifer liming. Other methods include ditch, road, diversion well and doser liming.

Finely crushed limestone is probably the most common product used in liming. Liming with crushed limestone ensures a gradual increase in water pH up to a level adequate for aquatic organisms. It is cheap, readily available and easily handled. In addition, the risks of harmful effects on the ecology in the event of a high dose are small (Dickson &

Brodin, 1995). Other products can also be used: lime, hydrated lime, caustic soda, *etc.* However, these products are not recommended for liming natural habitats because they are too aggressive and generate a much too rapid increase in pH for aquatic organisms.

Continuous liming is used for streams as the pH varies according to water flow and is generally at its lowest at high flows (Soulsby, 1995). It has also been used for lakes that have a low water renewal time. Due to the constantly changing pH and flow conditions of acid streams, the liming dose should be varied accordingly (White, 2000), *i.e.* continuous liming.

Liming of water directly, however, causes aluminium and other metals to precipitate and fall to the bottom, causing toxicity problems for organisms living on the lake or river bed.

Lime can also be added to the land within a catchment, although this can have an adverse effect on wetland species of plants, *e.g.* bryophytes, lichens and other plant communities (Berggren, 2002). The benefits of liming catchments have been questioned on conservation grounds, as some naturally acidophilic plant communities would be damaged (Farmer, 1992). The advantages, however, are that the effects are longer lasting and metals are prevented from leaching into the lake water from the soil.

In the UK, a number of purpose-built lime dosing units have been installed on the headwaters of rivers. The dosers measure the flow of the river and automatically calculate the amount of lime needed to neutralise the acidic waters. Again, this is a costly measure and there are also issues concerning visual intrusion.

A research group in Wales conducted an assessment of the chemical and biological effects for 10 years after the catchments of three acidified streams were limed in 1987/88. Following single lime applications, acid-base chemistry in treated streams changed significantly. High mean pH (> 6), increased calcium (> 2.5 mg/L) and low aluminium (< 0.1 mg/L) persisted throughout the 10 years following liming. However, the effects on invertebrates were modest. Acid sensitive taxa increased significantly in abundance in limed streams, but only during two years following treatment. Significant effects on richness were more sustained, but on average added only 2-3 acid-sensitive species to the treated streams (Bradley & Ormerod, 2002).

Successful liming programmes to improve the quality of acid waters have been carried out in Sweden, Norway, Finland, the U.K., Canada, U.S.A., Australia, and New Zealand. However, Sweden and Norway have the largest programmes so far. In Nova Scotia limestone gravel bars have been shown to be most effective when flow is low which does not coincide with times when it is needed most (White, 2000).

Acidified lakes in Sweden have been restored in the short term by liming. Ecological impact assessments of limed lakes in Sweden have shown that many species recolonise after treatment (Larsson, 1995, Henrikson *et al*, 1995). Each year thousands of tonnes of limestone are sprayed on Swedish lakes and watercourses, which is an extremely expensive measure. Several years of liming has created a large store of aluminium in the sediment of many Swedish lakes. Some scientists fear that the aluminium store may resolubilise quite rapidly when the liming operations cease (Eriksson, 1998).

In Québec liming is still integral to remediation while the critical loads approach is being taken to reduce emissions in the long term. Liming does not represent an ideal solution to the problem due to the very high number of acidic lakes in the province, the cost involved for liming all these lakes and the liming criteria that are not met for a majority of Québec lakes (not all lakes can be limed). Approximately twenty lakes are limed on a regular basis in the Trois-Rivières area of Québec alone.

As *Sphagnum* mosses are sensitive to even slight change in water chemistry due to the morphology of their leaves, effect of liming in the Loch Fleet catchment area in Scotland on *Sphagnum* communities was deemed detrimental (Bragg and Clymo, 1995). Liming can have varying degrees of effectiveness on plant and communities depending on the dosage and the original species present. The composition of bog species, however, clearly changes as a result of liming mainly by reducing *Sphagnum* species and increasing variety of vascular species (Bragg and Clymo, 1995).

A similar mixture of benefits and problems occur in the case of liming of freshwaters and forest soils.

Table 2.4 below outlines the advantages and disadvantages of liming in freshwater (Henriksen & Brodin, 1995a).

ADVANTAGES	DISADVANTAGES
Recolonisation of species generally takes place.	Vegetation of limed wetlands is often considerably changed/damaged.
Species numbers and diversity increase in most cases.	Species new to the water may appear and occasionally influence natural food webs.
Normalisation of decomposition processes is likely to occur in most cases.	Precipitation of metals may sometimes exert a temporary stress to species.
Re-establishment of natural food webs often occurs.	Algal blooms and mass development of plants may occasionally occur.
Enhanced fish production occurs in most cases.	Disturbances of bird breeding occur on a few occasions.
Re-establishment of functional groups such as shredders is common.	
Elimination of threatened species can often be prevented.	
Decrease or elimination of species favoured by acidification is usual.	

Table 2.4: Advantages and disadvantages of liming aquatic systems

2.4.3 Buffer Strips

The use of buffer strips to ameliorate acidification of surface waters in forested catchments was proposed in the middle to late 1980s by several authors, many associated with the U.K. Forestry Commission. However, in general, no field data was presented to support these suggestions.

Buffer strips have been shown to be effective in filtering out sediments and pollutants, though few specific studies have dealt with the effectiveness of buffer strips to mitigate acidification (Donnelly *et al*, 2003a).

The buffer zone is an area adjacent to an aquatic zone and managed for the protection of water quality and aquatic ecosystems. A buffer zone includes the riparian zone, *i.e.* that area directly adjacent to an aquatic zone, representing the intermediate between the aquatic and terrestrial environments and having its own distinctive hydrological and ecological characteristics. The buffer zone may also occupy adjacent areas beyond the riparian zone. Within the buffer zone, natural ground vegetation is allowed to develop, with additional planting of suitable riparian tree species and ground preparation and other forest operations are curtailed in order to protect water quality. Furthermore, drainage channels leading from the site taper out before entering the buffer zone. This ensures that discharged water gently fans out from the flow by ground vegetation within the zone.

The role of buffer strips in land management is to provide an undisturbed area of land adjacent to streams to act as a filter for sediments and other stream pollutants. They also act to protect the stream from direct insolation when planted with deciduous vegetation and to provide areas of undisturbed habitat, *e.g.* wildlife corridors (Bren, 1998). They may be referred to as vegetated filter strips that control erosion by blocking the flow of sediment, by stabilising banks and by promoting infiltration. The number of studies that have dealt specifically with the effectiveness of buffer strips to mitigate acid water problems is limited. However, none of the studies carried out to date have found that buffer strips are an effective means of mitigating increased acidity in run-off from forested catchments (Donnelly *et al*, 2003a). Buffer strips are commonly recommended to control sediment loss in commercial forestry operations (Irish Forest Service, 2000: UK Forestry Commission, 2000). However, there is no mention in either the Irish or the current UK forestry guidelines of the use of buffer strips to mitigate acid runoff. UK Editions prior to 1993 did include the use of a ‘protective strip’ but this was omitted from later editions (Donnelly *et al*, 2003).

Trials on liming of buffer strips and riparian areas have been carried out in a small number of studies. However, none of these trials have been considered successful.

The application of liming materials to catchments and direct addition of lime to water bodies to mitigate acidification of freshwaters have both been shown to result in negative impacts on both floral and faunal species (Dudley & Stolton, 1995).

2.4.4 Ireland

There is a paucity of research on remediation of acidified surface waters in Ireland. Two studies as part of the WaterAc project (co-funded by EPA/COFORD), however, have investigated international actions to address acidification. These were entitled ‘Effectiveness of buffer strips for the mitigation of acid runoff from afforested catchments’ and ‘Review of liming options in afforested catchments’.

The reports concluded that only three methods appeared to be suitable for further investigation in Ireland. The most promising of these was the stream dosers system, in that it is proven technology, commercially available and the dose rate can be adjusted automatically according to changing stream chemistry.

Other methods include spreading of lime on forest floors and direct addition of limestone to stream beds. Effective remedy depends on the hydrological factors that determine the contact time between lime and runoff water. There is a lack of information in Ireland on both flow paths and residence time in afforested soils. There is also a lack of information on the hydrology of small acid streams in Ireland, particularly those in peatland catchments. Greater understanding of these hydrological factors is required before these two methods can be better assessed.

3. CHARACTERISTICS OF STUDY AREA

3.1 Topography

County Wicklow has a greater percentage (75 percent) of its land over 500 metres above sea level than any other county in Ireland. The Eastern Region of Coillte is divided into five Forestry Management Units (FMUs). The three study sites are located in one of these FMUs, the Wicklow-Dublin Uplands FMU.

The central north/south axis of this FMU traverses mountain summits and high moorland from which a number of major steep-sided glens radiate forming significant river catchments and sub-catchments.

The central part of the Wicklow Mountains consists of rounded granite uplands with summits of 457-610 metres in the north, with 610 metres achieved regularly in the south and a high of 926 metres at Lugnaquilla.

The Pollaphuca dam on the River Liffey was built in the late 1930s and is the principal means of flood control in the Liffey catchment through storage and controlled discharge of upper catchment inflow, which generates electricity for the National Grid. The dam is served by an upper catchment area of 308 km^2 consisting mainly of blanket bog overlying granite. The large storage available, at approximately 50 percent of the average annual inflow, is such that it is rarely necessary to use the spillway gates. The Liffey flood of November 2001 is estimated to have had a return period in excess of fifty years. The flood was stored in Pollaphuca until the peak of the storm was passed and then discharged in a controlled manner *via* the generating station. At its peak, the hourly inflow was estimated at over 420 m/s while the maximum discharge is 73 m/s.

The catchments studied in this project are all located in the central part of the Wicklow Mountains. This area consists of wide-open valleys with rounded granite uplands 400 to 600 metres in altitude. Ordovician shales and associated mixed drift material cover the other remaining hills and wide open valleys (Glendalough Upper Lake catchment). To the east of the mountain belt lays the Vartry river catchment sloping from 300 to 150 metres. The Blessington Lake basin lies to the west, encompassing both the glavifluvial lakes and the Poulaphuca reservoir. The River Liffey and the King's River and its tributaries (Annalecka, Ballinagee and Glasnadade) flow into this reservoir. The geology is base poor and the aquatic zones are part of recognised fisheries. The streams in these catchments are also spawning, nursery and angling areas.

3.2 Study sites

Four catchments in County Wicklow with surface waters regarded as being sensitive to acidification were selected as appropriate for investigation (Fig. 3.1). The three Cloghoge River tributaries were all completely moorland sites and the other three catchments contained afforested, partially afforested and harvested sites. Afforested sites varied as to the extent of mature closed canopy forest.

Fig. 3.1: Location of study area in County Wicklow (circled)

The sites were situated on the headwaters of the Cloghoge River, King's River and the Glenealo River as well as the feeder streams of the Vartry Reservoir (Fig. 3.2, OSI). These waters are typical trout nursery streams and are characterised by short riffle-glide-pool sequences.

Each site was given a code that was either a mnemonic of the catchment (*e.g.* SG1 for Sally Gap #1, V4 for Vartry Reservoir Inflow #4) or a shortened version of the actual name (*e.g.* GLEN for Glenealo River). The physical characteristics of the individual sampling sites are illustrated in Table 3.1 below.

Site code	Site Catchment	Grid Reference	Altitude (m)	Forested (F) Partial Forestry (PF) Moorland (M) Harvested (H)	Predominant Substrate	Geology	Soil
SHEEP	Cloghoge	O 154 095	420	M	R+ST+SA	G	3
SG1	River	O 149 092	240	M	B+ST+SA	G	1+2
SG2	Tributaries	O 144 099	400	M	B+ST+SA	G	1+2
V3	Vartry	O 192 058	250	F+H	R+C+SL	P	3
u/s V3	Reservoir	O 183 059	290	F	R+G+SI	P	3
V4	Feeder	O 188 070	275	F	R+SA+SI	P	2+3
V5	Streams	O 200 085	290	PF	R+ST+G	P	2+3
V6		O 206 091	275	PF	R+ST+SA	P	3
GLEN	Glendalough	T 087 962	140	M	R+B+ST+SA	G	3
LUG	Lake Upper	T 112 961	130	F	ST+SA	P	3
ANNA	King's	O 067 027	355	F+H	B+ST+SA	G	2+4
B'GEE	River	O 036 042	320	PF	B+ST+SA	G	2+4
GLAS	Catchment	O 037 042	270	F	B+ST	G	2+4

Where: **Substrate:** R = Bedrock, B = Boulders (>30cm), ST= Stones (6-30cm), G = Gravel (2-6cm), SA = Sand, SI = Silt.

Geology: G = Granite, P = Palaeozoic Sediments (incl. Metamorphic rocks).

Soils: 1 = Deep Mountain Peat, 2 = Peaty Podzols with some Peaty Gleys and Pockets of Peat, 3 = Brown Podzolics with some Gleys, 4 = Lithosols and Brown Podzolics, 5 = Gleys and Peaty Gleys.

Ref: Aquafor Report 1997

Table 3.1: Catchment characteristics

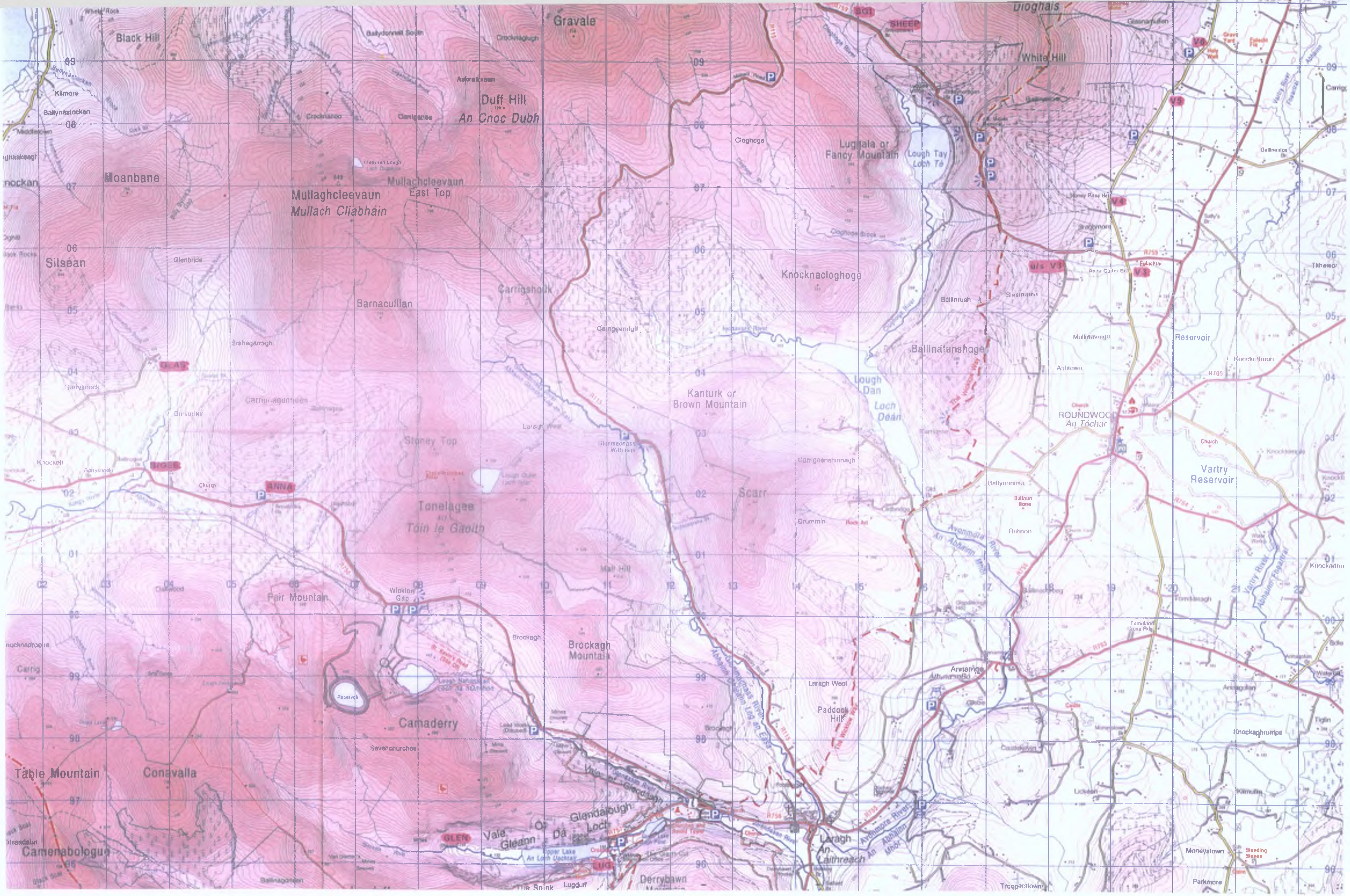


Fig. 3.2 Map of Sampling Sites

OSI Permit No. 003704

3.3 Geology and soils

The Wicklow-Dublin Uplands are part of the Leinster mountain chain. These mountains are a product of the Caledonian mountain-building episode, which left its mountains and hills configured in a northeast to southwest direction (Fig. 3.3, GSI 1994). Into the great uplifts of these mountains, which then had a surface geology of shales, a core of granite was emplaced. The granite core has been exposed in many places through erosion of surface geology, leaving behind uplands characterized by smooth and peat covered surfaces. The Caledonian batholith, which was emplaced into country rocks, has five separate dome-like units surrounded by Paleozoic sediments (Brindley, 1973). Glaciation affected most of these uplands, being mostly responsible for smoothing the granite hills and giving the valleys their characteristic U-shape.

The glacial deposits west of the Wicklow Mountains were deposited by ice that originated in the midlands. This ice pushed eastward and southeast ward across the area and up into many of the western valleys of the Wicklow Mountains. The Wicklow Mountains ice cap was generally confined to the Wicklow district although at one time it did extend into County Kildare. The ice cap carved very fine corries (*e.g.* Lough Bray and Lough Nahanagan) and spectacular glaciated valleys (*e.g.* Glendalough and Glenmalure). It also deposited locally derived till and gravel in the valleys and lower ground. In addition, large erratics were carried both east and west of their source and indicate the former extent of this ice body (GSI, 1994).

After the ice had melted and large ice-marginal lakes had drained, extensive depressions surrounded by glacial deposits remained. These retained shallow lakes in whose basins the great raised bogs of the midlands developed in the postglacial period (*e.g.* the nearby Bog of Allen). Likewise, the great spreads of blanket bog that cover extensive upland areas of the district formed in the 10,000 years following the end of the Ice Age. The alluvial deposits of the rivers, including the Liffey and Barrow, were also deposited during this period.

Soils in the Wicklow-Dublin Uplands are climatic in nature, yielding deep peats, peaty podsolics and lithosols at the highest elevations and brown podsolics and acid brown earths at the lower elevations. Glacial activity resulted in moderately deep mineral soil in the eastern part of the county (GSI, 1994)

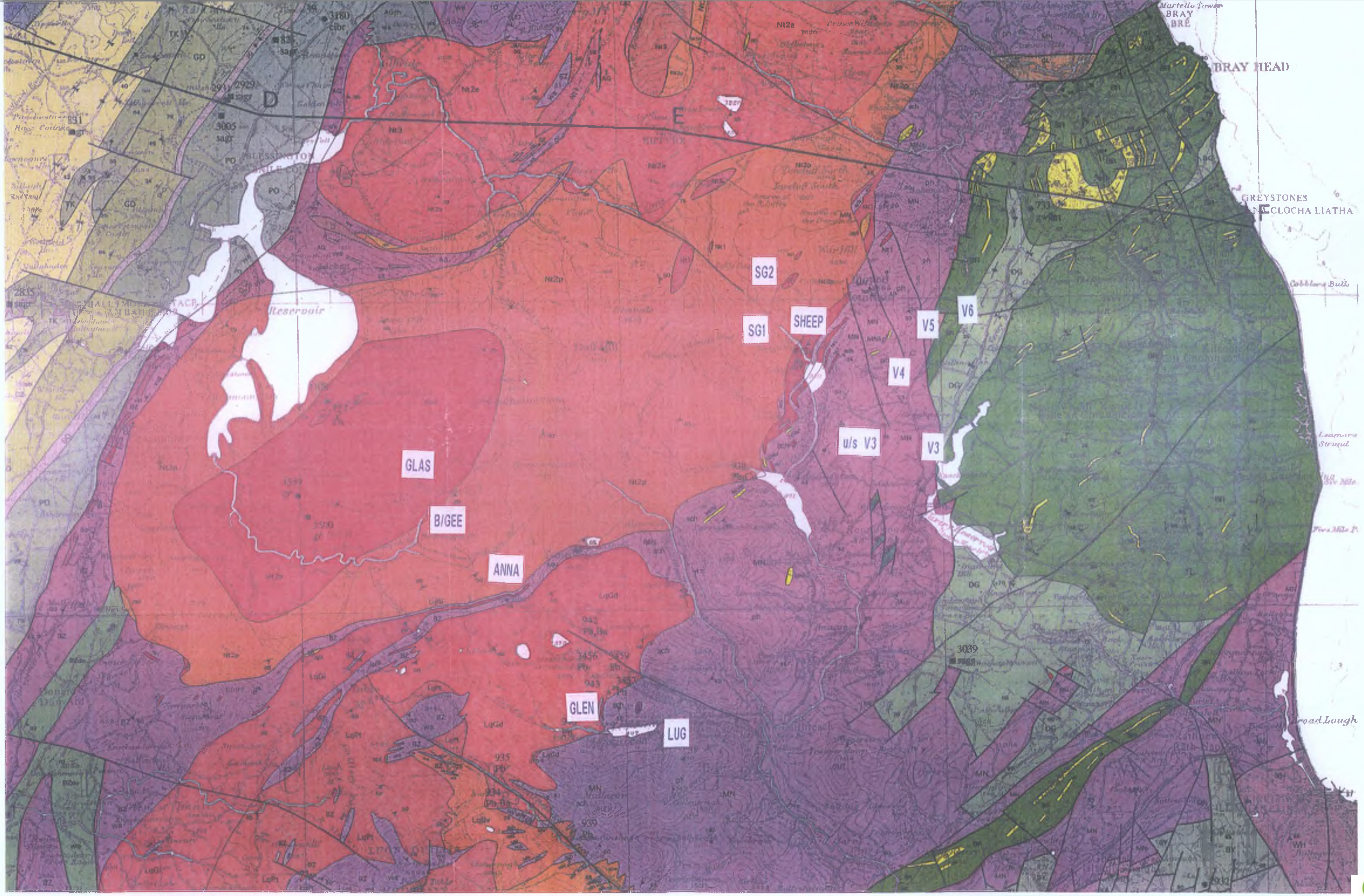


Fig. 3.3 Map of Geology of Survey Area

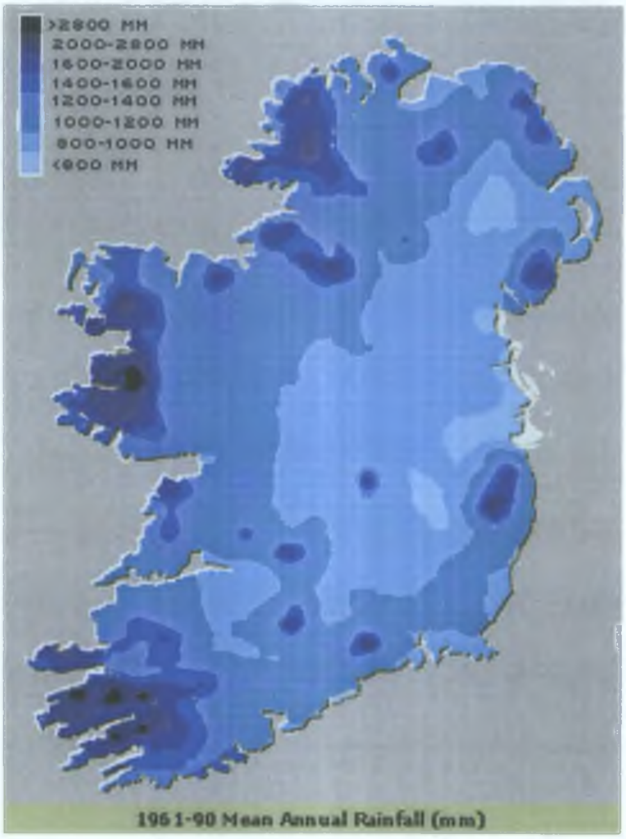
Red/Orange Granites

Purple Ordovician Rocks

Green Cambrian Rocks

3.4 Climate and weather

The dominant influence on Ireland's climate is the Atlantic Ocean. Consequently, it does not suffer from the extremes of temperature experienced by many other countries at similar latitude. Mean daily temperature ranges from 4.4°C in January to 14.9°C in July. Average annual temperature is about 9°C. In the centre and east of the country temperatures tend to be somewhat more extreme than in other parts of the country. For example, summer mean daily maximum is about 19°C and winter mean daily minimum is about 2.5°C in these areas. Sunshine duration is highest in the southeast of the country. Average rainfall varies between about 800 and 2800mm (Fig. 3.4).



Source: www.metéireann.ie

Figure 3.4: Mean annual rainfall (mm) from 1961-1991

With southwesterly winds from the Atlantic dominating, rainfall figures are highest in the northwest, west and southwest of the country, especially over the highest ground. Rainfall accumulation tends to be highest in winter and lowest in early summer. The annual number of days with more than 1mm of rain varies between about 150 in the drier parts and over 200 in wetter parts of the country. Fortnightly rainfall at Cronykerry and Kilcoole Weather Stations in County Wicklow are represented in Table 3.2 with Fig. 3.5 showing a corresponding graph.

		Rainfall (mm)	
Sample Run #	**Date**	**Cronykerry/mm**	**Kilcoole/mm**
1	28/12/03 – 11/01/04	73.1	62
2	11/01/04 – 25/01/04	42.6	36.6
3	25/01/04 – 08/02/04	58.8	45.2
4	08/02/04 – 23/02/04	1	2.5
5	23/02/04 – 07/03/04	12.5	12.9
6	07/03/04 – 21/03/04	78.5	65.5
7	21/03/04 – 04/04/04	16.1	19.4
8	04/04/04 – 18/04/04	25	24.3
9	18/04/04 – 04/05/04	10.7	13.5
10	04/05/04 – 18/05/04	10.9	9.2

Source: Met Éireann, *pers. comm.*

Table 3.2: Rainfall data from Cronykerry and Kilcoole

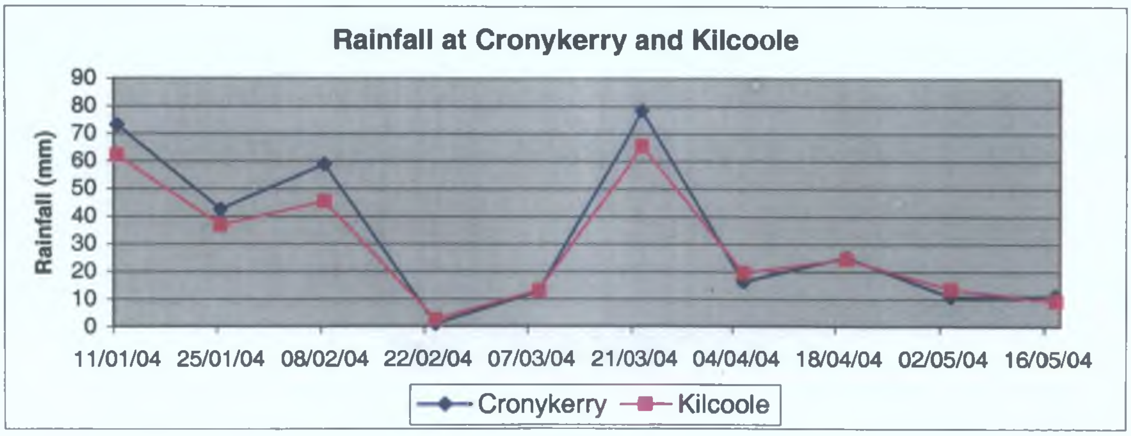
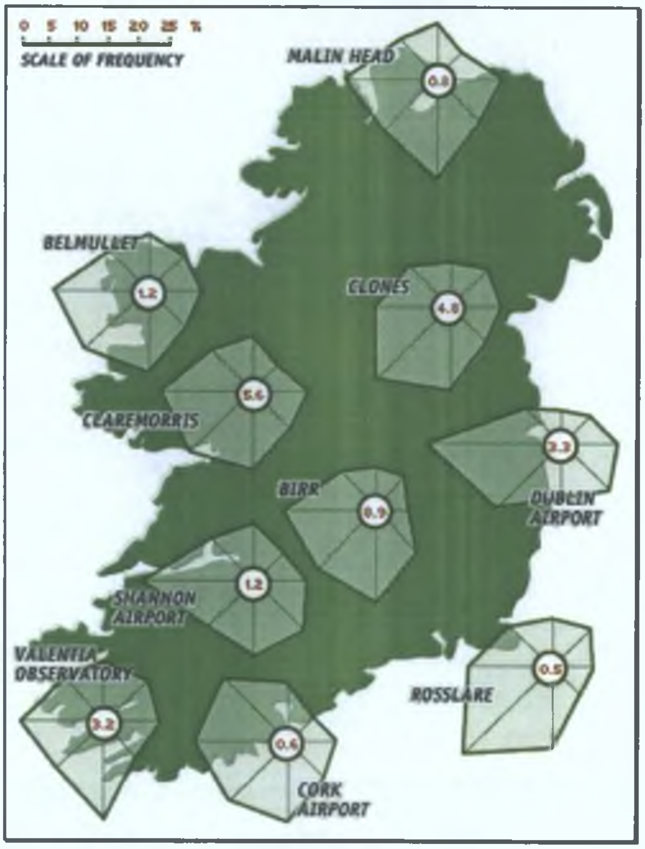


Fig. 3.5: Rainfall at Cronykerry and Kilcoole

Due to Ireland's geographical position, winds are predominantly southwesterly or westerly (Fig. 3.6). Mean annual wind speed varies between about 4m/s in the east midlands and 7m/s in the northwest. Strong winds tend to be more frequent in winter than in summer.

WIND DIRECTION (percentage frequency of wind direction)

O : Circled number = %CALM



Source: www.metéireann.ie

Figure 3.6: Percentage frequency of wind direction in Ireland

The monthly totals of easterly airflow from three angles at Casement Aerodrome (Easterly = 90^{o}) during the study period are illustrated in Table 3.3 and Figure 3.7 below. Easterly winds would be expected to have a higher polluting load than westerlies originating from the Atlantic Ocean (see section 2.1.4). Higher rainfall during easterly airflows would be expected to exacerbate surface water acidification in acid-sensitive areas (Fig. 3.8).

Month	**Number of hours with wind direction:**		
	>50 and <130° E	**>70 and <110° E**	**>80 and <100° E**
December '03	19	16	9
January '04	22	8	4
February '04	117	58	38
March '04	168	87	53
April '04	64	46	33
May '04	73	52	40

Source: Met Éireann, *pers. comm.*

Table 3.3: Monthly totals of Easterly airflow at Casement Aerodrome

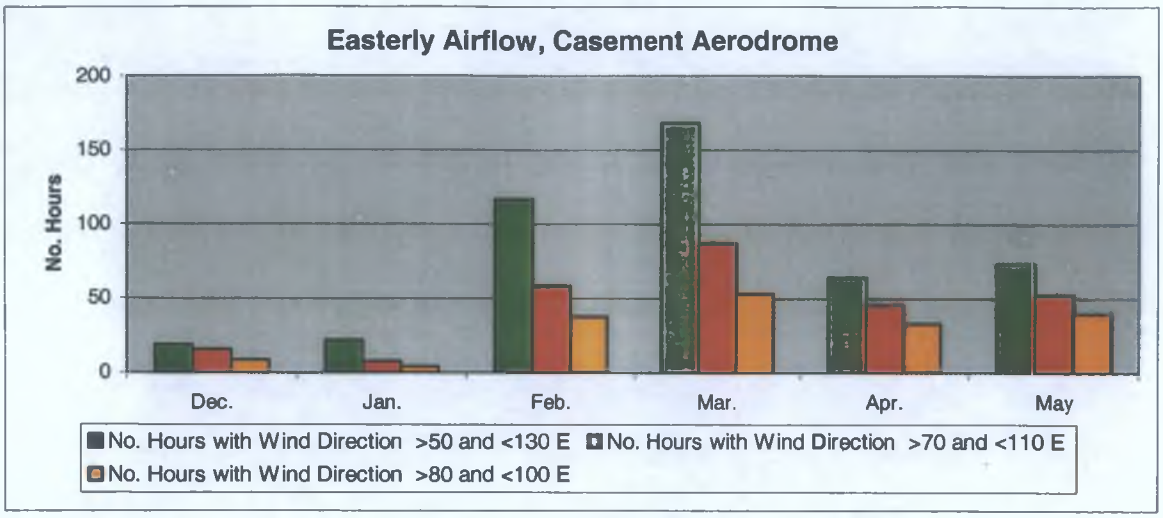


Figure 3.7: Graph of Easterly airflow at Casement Aerodrome

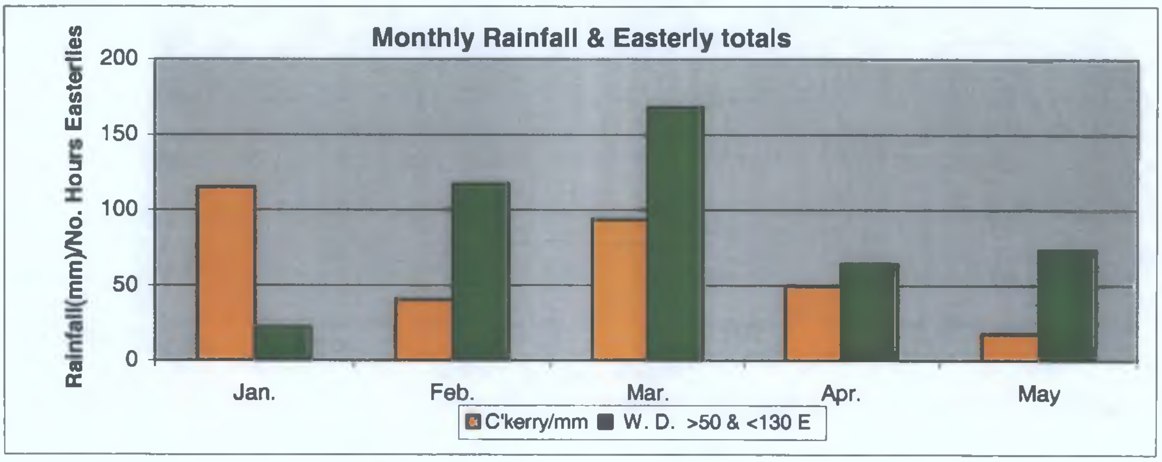


Figure 3.8: Easterly Airflow (Casement) and Rainfall (C'kerry)

3.5 Sampling and Analysis

Sampling of the study sites was performed every fortnight from January to May 2004 inclusive. Temperature and Dissolved Oxygen (as mg/L and % Saturation) were recorded *in situ* and samples were analysed at EPA Dublin Regional Inspectorate laboratories within twenty-four hours. Samples for metal analysis were preserved on site with 0.25ml of HNO_3.

Parameter	Method of Analysis
pH	WTW Inolab Level 3
Conductivity	WTW Inolab Level 3
Colour	Lovibond Nessleriser 2150 Unit
Temperature	WTW Oxi Meter (Oxi 196)
Dissolved Oxygen	WTW Oxi Meter (Oxi 196)
Alkalinity	Gran-Titration Method
Ortho-Phosphate	Thermo Electron Corp. Konelab Aqua30
Total Oxidised Nitrogen (TON)	Thermo Electron Corp. Konelab Aqua30
Ammonia	Thermo Electron Corp. Konelab Aqua30
Sulphate	Thermo Electron Corp. Konelab Aqua30
Chloride	Thermo Electron Corp. Konelab Aqua30
Calcium	Elan 6000 PE SCIEX ICP-MS
Magnesium	Elan 6000 PE SCIEX ICP-MS
Sodium	Elan 6000 PE SCIEX ICP-MS
Potassium	Elan 6000 PE SCIEX ICP-MS
Manganese	Elan 6000 PE SCIEX ICP-MS
Iron	Elan 6000 PE SCIEX ICP-MS
Zinc	Elan 6000 PE SCIEX ICP-MS
Total Aluminium	Elan 6000 PE SCIEX ICP-MS

(ICP-MS: Inductively Coupled Plasma/Mass Spectrometer)

Table 3.4: List of Parameters Measured and Methodologies Used

4. HYDROMETRIC MEASUREMENTS

The EPA Hydrometric Division has gauging stations on the Annalecka Stream and the Ballinagee stream. Water levels were monitored at the two sites for the duration of the study. Velocity data was also calculated for the Ballinagee stream using the Area Water Velocity Method as per BS 3680. Hydrological data was calculated and flood graphs were constructed with the assistance of the EPA Hydrometric Division.

4.1 Results

Ballinagee Stream has a larger catchment than the Annalecka Stream and as expected has higher flow rates. Table 4.1 below shows the flow rates calculated at the exact time of sampling at the Annalecka and Ballinagee rivers throughout the project.

Date	Annalecka R. Flow (m^3/s)	Ballinagee R. Flow (m^3/s)
11/0104	0.4161	0.9438
25/01/04	0.1239	0.3080
08/02/04	0.1058	0.2813
23/02/04	0.0540	0.1427
07/03/04	0.0992	0.1887
21/03/04	0.9176	1.7501
04/04/04	0.1539	0.3939
18/04/04	0.3233	1.1266
04/05/04	0.1481	0.4265

Table 4.1: Flow Rates (Q) at Annalecka & Ballinagee Rivers

The two hydrographs are very similar which presumably reflects the close proximity of the two catchments. During periods of high flows the pH dropped by over one unit on both sites (Fig. 4.1 & 4.2 below).

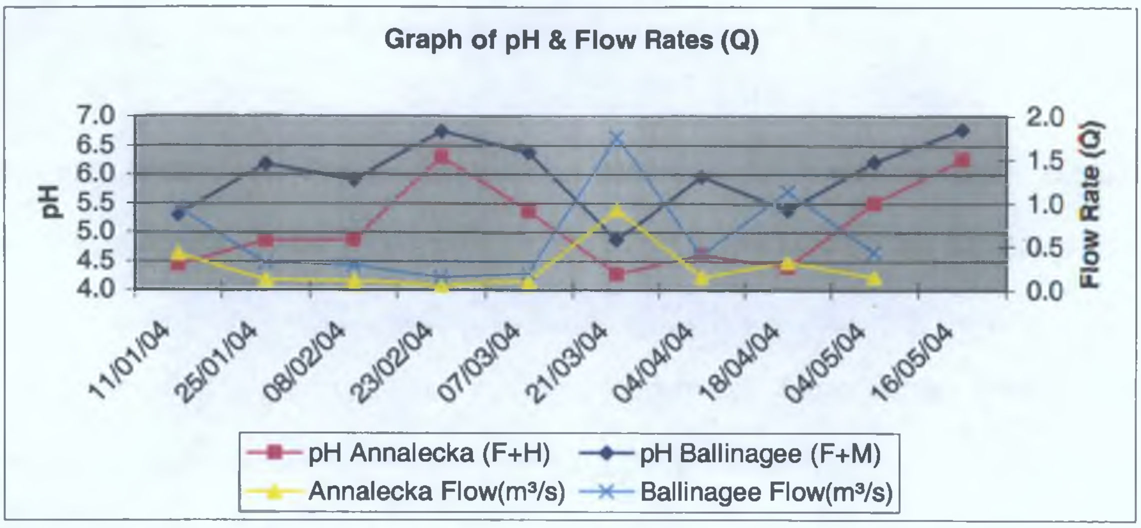


Fig. 4.1: pH and fortnightly flows at Annalecka & Ballinagee Rivers

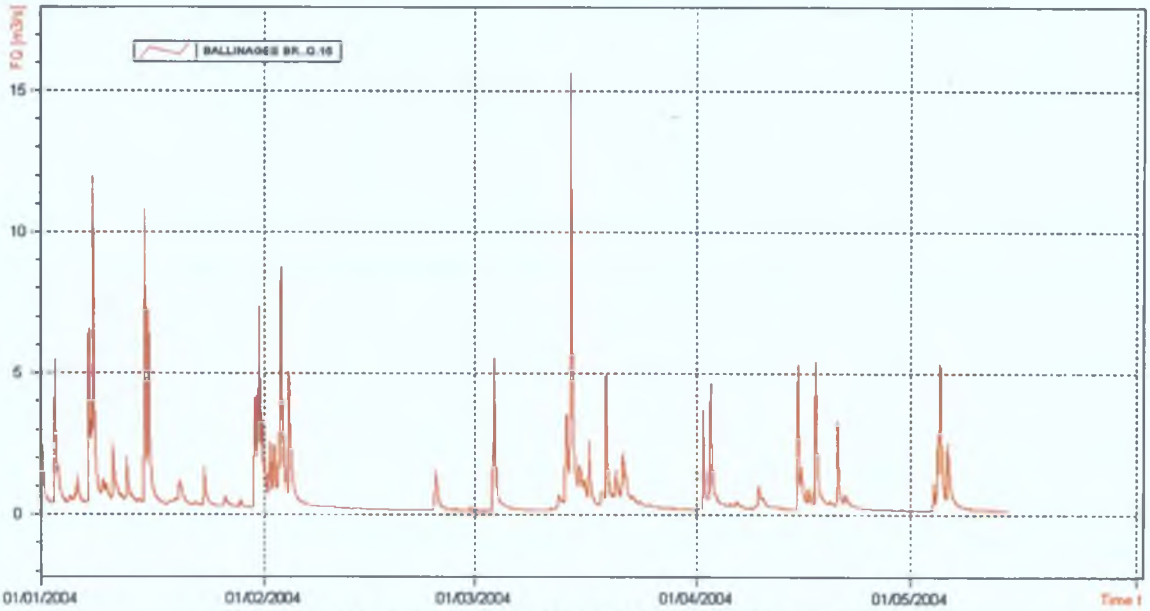


Fig. 4.2: Graph of Flow Rate (Q) at Ballinagee River

Note: Graph of Flow Rate (Q) at Annalecka River unavailable

The 'spaty' nature of the two streams is evident as water levels may increase several fold over a short space of time (Fig 4.3 & 4.4 below). During periods of low flow, export of water from both catchments was similar, though Ballinagee had the higher flow rate of the two. This could be due to the larger catchment area of the Ballinagee stream or retention of water by the afforested Annalecka stream or both factors combined.

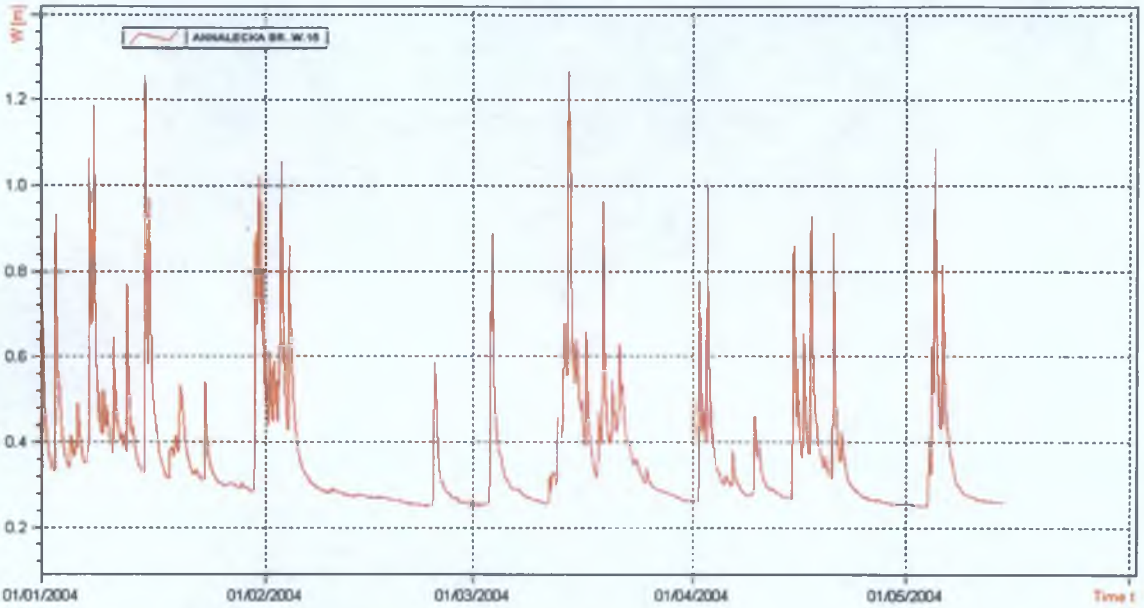


Fig. 4.3: Water Level (W) Graph at the Annalecka River

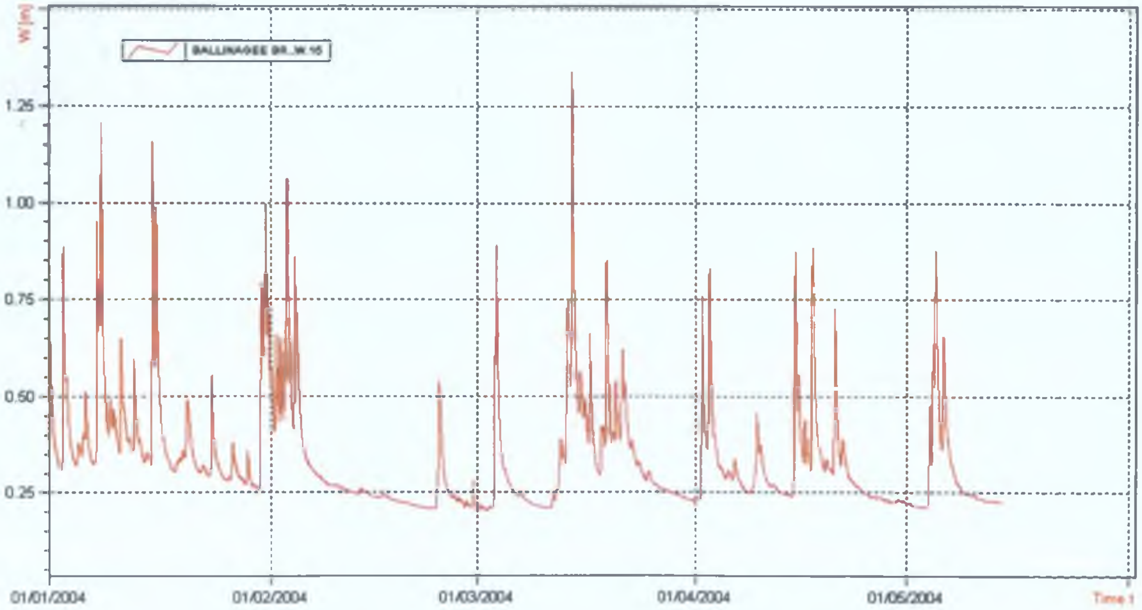


Fig. 4.4: Water Level (W) Graph at the Ballinagee River

The two principal rivers in the King's River catchment, the Annalecka and Ballinagee Rivers, were the only sites with available flow data and consequently were the only sites where correlations between rainfall, flow and chemical parameters (*e.g.* pH, alkalinity, aluminium *etc.*) could be calculated (Appendix A).

Correlation refers to a measure of how strongly two or more variables are related to each other and a correlation coefficient refers to a number between –1 and +1 and states how strongly a correlation is. If the coefficient is close to +1 then there is a positive correlation (high values of one variable are associated with high values of the other). If the number is close to –1 then there is a negative correlation (high values of one variable are associated with low values of the other). If the number is close to 0 then the variables are uncorrelated. Correlations are very good for showing possible relationships between variables although they cannot demonstrate a cause and effect.

5. SURFACE WATER CHEMISTRY

5.1 Results

Levels of Dissolved Oxygen (D.O.) were satisfactory at all sites during the investigation. Very low levels of ammonia (NH_3) and ortho phosphate (PO_4^{3-}) were also recorded at all sites.

Colour values in the Vartry Catchment ranged from 10 to 35 Hazen Units (HU), typical of surface waters on Palaeozoic sediments. High values were recorded on the moorland catchment of the Cloghoge River (~160 HU). Elevated colour values coincided with higher rainfall, presumably due to increased humic acid runoff. In the Glendalough Upper Lake Catchment there was a marked difference between the moorland and afforested streams. While the moorland Glenealo River (GLEN) had a median colour value of 50 HU, the afforested Lugduff River (LUG) had a median value of <10 HU. The King's River tributaries (Annalecka, Ballinagee and Glasnadade Streams) also had high colour readings as afforestation here is planted on blanket bog.

On one sampling occasion however, conductivities in all streams increased by several factors above normal. This coincided with the lowest colour readings and highest pH and alkalinity (Fig. 5.1). Correspondingly, the lowest total aluminium values of the entire study period were recorded on these dates.

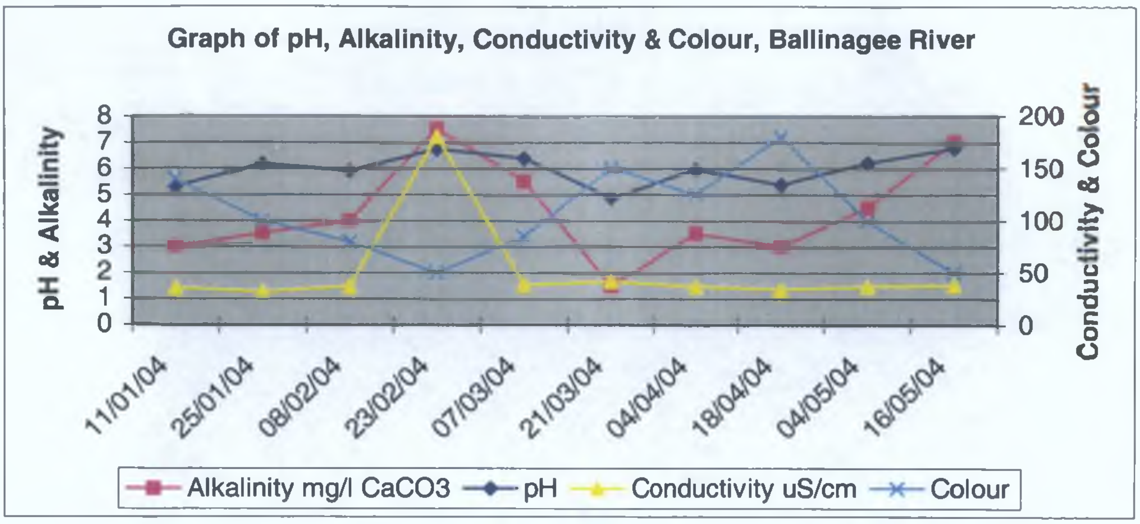


Fig. 5.1: pH, Alkalinity, Conductivity & Colour, Ballinagee River

The surface waters examined in this study are of low ionic strengths, with conductivities typical of soft water systems. Conductivity values on granite were usually less than 80µS/cm and less than 65µS/cm on Palaeozoic sediments.

The results for the principal chemical parameters used in determining acid sensitivity are listed in Table 5.1 below. Afforested sites within each catchment have lower pH, lower alkalinity and consequently higher total aluminium concentrations than corresponding moorland sites (Table 5.1). The summary results including ranges and median values for the chemical parameters measured during the five-month investigation are listed in Tables 5.2 to 5.14.

Values presented are ranges with medians in brackets underneath.

Site	pH	Alk. mg/L $CaCO_3$	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^+ mg/L	Cl^- mg/L	SO_4^{2-} mg/L	TON mg/L	Total Al µg/L
Vartry Reservoir Inflows									
V3	6.09-6.47 (6.38)	3.5-5.5 (5.0)	1.78-2.02 (1.89)	1.63-3.70 (1.99)	6.13-9.12 (7.53)	12.8-14.5 (13.5)	3.19-4.83 (3.75)	0.93-1.42 (1.16)	62-151 (96)
u/s V3	5.71-6.15 (5.86)	2.0-3.0 (2.5)	1.10-1.38 (1.15)	1.20-2.80 (1.47)	5.84-8.53 (7.25)	12.1-13.2 (12.3)	2.75-8.6 (3.25)	0.60-1.05 (0.78)	53-95 (70)
V4	5.59-6.07 (5.89)	1.0-3.5 (3)	1.42-1.78 (1.65)	1.16-2.90 (1.36)	5.35-7.17 (6.27)	10.7-12.3 (11.2)	3.96-6.35 (4.5)	0.56-0.87 (0.74)	52-134 (82)
V5	5.89-6.45 (6.30)	1.0-3.5 (3.0)	1.56-2.46 (2.04)	1.01-2.90 (1.46)	3.40-6.25 (5.05)	8.7-10.1 (9.2)	2.52-4.36 (3.24)	0.54-0.98 (0.77)	19-121 (39)
V6	6.03-6.51 (6.40)	3.5–5 (4.5)	1.11-1.47 (1.3)	0.88-2.50 (1.3)	3.75-6.28 (5.15)	7.7-10.8 (8.6)	2.42-4.07 (2.75)	0.38-0.76 (0.53)	21-100 (58)
Cloghoge River Catchment									
SHEEP	4.51-7.10 (6.49)	0.5-6.5 (6)	0.85-3.52 (1.09)	0.51-2.87 (1.09)	3.01-6.90 (4.99)	7.1-9.2 (8.1)	<0.05-0.72 (<0.05)	<0.01-0.03 (<0.01)	69-177 (150)
SG1	4.60-7.27 (6.50)	0-19 (10)	1.14-4.70 (3.04)	0.53-3.30 (1.10)	2.93-7.10 (4.74)	6.9-9.5 (8.1)	<0.05-0.02 (<0.05)	<0.01-0.05 (<0.01)	66-159 (142)
SG2	4.31-7.06 (5.92)	0-10 (4)	0.52-1.77 (1.30)	0.40-1.78 (0.7)	2.69-6.7 (4.43)	6.9-9.0 (7.6)	<0.05-0.55 (<0.05)	<0.01-0.11 (<0.01)	96-170 (114)
Glendalough Lake Upper Catchment									
GLEN	5.47-6.73 (6.21)	2.5-8.5 (3.8)	1.00-2.00 (1.31)	0.43-1.70 (0.7)	2.45-4.80 (3.56)	4.9-8.2 (5.4)	0.34-4.89 (1.87)	<0.01-0.16 (<0.01)	40-148 (113)
LUG	4.95-5.62 (5.16)	1.0-3.0 (1.8)	0.49-0.72 (0.6)	0.55-2.03 (0.74)	3.47-6.19 (4.57)	7.2-8.7 (8.1)	2.82-3.55 (3.13)	0.06-0.23 (0.16)	109-345 (211)
King's River Catchment									
ANNA	4.27-6.25 (4.86)	0-3.5 (1.3)	0.84-1.50 (1.15)	0.59-2.00 (0.78)	3.59-6.74 (4.8)	6.6-10.8 (9.0)	<0.05-2.28 (0.87)	0.04-0.15 (0.01)	152-287 (254)
B'GEE	4.86-6.76 (6.06)	1.5-7.5 (3.8)	1.13-2.00 (1.56)	0.50-2.00 (0.78)	2.72-5.5 (4.01)	4.9-8.1 (6.4)	<0.05-2.58 (1.74)	<0.01-0.24 (0.12)	83-220 (197)
GLAS	4.48-6.67 (5.49)	0-6.5 (2)	0.67-1.40 (0.92)	0.48-2.20 (0.76)	2.76-6.47 (4.80)	5.2-9.4 (7.3)	<0.05-1.31 (0.50)	<0.01-0.19 (0.07)	107-264 (209)

Where; F = Afforested, PF = Partially Afforested, C = Clearfelled Areas, M = Moorland

Table 5.1: Summary statistics for principal chemical parameters

VARTRY RESERVOIR INFLOWS

V3		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	5	6.32	68.3	40	<0.01	<5	1.25
25/01/04	#2	5.8	95.7	11.55	4	6.38	67	40	<0.01	17.25	1.41
08/02/04	#3	5.6	99.6	12.3	3.5	6.09	70	30	<0.01	NM	1.29
23/02/04	#4	4.4	100.8	12.84	5	6.33	324	30	<0.01	<5	1.42
07/03/04	#5	5.8	100.5	12.38	5	6.37	79.5	30	<0.01	<5	1.40
21/03/04	#6	6.5	99.2	11.69	5	6.38	79	40	<0.01	<5	0.93
04/04/04	#7	7	100.3	11.74	5	6.47	74.7	40	<0.01	19.27	1.06
18/04/04	#8	7.9	108	11	5	6.35	75.6	35	<0.01	<5	1.02
04/05/04	#9	NM	NM	NM	5.5	6.42	73.7	25	<0.01	44.81	0.98
16/05/04	#10	11.7	105	11.26	5.5	6.43	70.8	20	NM	NM	1.05
RANGE					3.5-5.5	6.09-6.47	67-324	20-40			0.93-1.42
MEDIAN					5	6.38	74.2	33			1.16

V3		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	Total Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	12.71	4.19	7.31	2.05	104.92	0.37	1.97	157.61	51.54	9.93
25/01/04	#2	13.18	3.30	9.12	2.44	107.01	0.39	1.81	71.36	53.28	2.75
08/02/04	#3	12.82	3.30	7.42	1.77	100.85	0.43	1.87	150.02	55.18	11.36
23/02/04	#4	13.94	3.76	7.23	1.91	63.25	0.35	1.80	99.93	52.56	7.03
07/03/04	#5	14.15	4.23	7.54	2.17	62.12	0.38	1.99	102.32	57.98	7.82
21/03/04	#6	14.14	4.83	8.33	1.93	150.74	0.46	2.02	224.65	72.69	9.94
04/04/04	#7	13.76	3.95	7.51	1.92	94.45	0.40	1.82	138.05	49.57	6.52
18/04/04	#8	13.45	3.73	6.13	1.63	89.05	0.42	1.90	161.68	56.42	7.89
04/05/04	#9	13.47	3.26	7.60	3.70	97.50	0.80	1.90	248.40	53.00	5.80
16/05/04	#10	12.87	3.19	7.72	3.65	65.25	0.64	1.78	200.01	36.38	5.96
RANGE		12.71-14.15	3.19-4.83	6.13-9.12	1.63-3.70	62-151	0.35-0.80	1.78-2.02	71.36-248.40	36.38-72.69	2.75-11.36
MEDIAN		13.46	3.75	7.53	1.99	96	0.41	1.89	153.82	53.14	7.43

Table 5.2: Principal chemical parameters measured for V3 (F+C)
NM = Not Measured; F = Afforested; C = Clearfelled

VARTRY RESERVOIR INFLOWS

u/s V3		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
25/01/04	#2	5.8	95.2	11.42	2	5.76	57.2	20	<0.01	<5	0.95
08/02/04	#3	5.8	100.3	12.28	2.5	5.73	63	30	<0.01	NM	1.05
23/02/04	#4	4.3	99.9	12.75	2.5	5.86	274	10	<0.01	<5	0.83
07/03/04	#5	6.3	101.5	12.32	2	5.86	65.4	20	<0.01	<5	0.62
21/03/04	#6	6.5	99.2	11.61	2	5.71	66.8	10	<0.01	<5	0.76
04/04/04	#7	7.6	98.4	11.29	2.5	5.84	64.6	20	<0.01	20.40	0.75
18/04/04	#8	8.3	98	10.7	2.5	5.86	64	10	<0.01	<5	0.61
04/05/04	#9	NM	NM	NM	3	6.13	61.5	10	<0.01	<5	0.60
16/05/04	#10	13.4	103.4	10.73	3	6.15	59.9	5	NM	NM	0.80
RANGE					2.0-3.0	5.71-6.15	57.2-274	5-30			0.60-1.05
MEDIAN					2.5	5.86	64	10			0.78

u/s V3		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	Total Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
25/01/04	#2	12.30	2.91	8.53	1.84	94.94	0.20	1.24	120.11	71.45	3.51
08/02/04	#3	12.12	2.75	6.89	1.38	93.07	0.25	1.38	157.65	64.32	5.27
23/02/04	#4	12.88	8.60	6.61	1.29	72.96	0.21	1.16	250.02	77.89	5.51
07/03/04	#5	13.19	3.93	6.91	1.43	60.75	0.20	1.15	256.78	98.86	5.11
21/03/04	#6	12.28	4.94	7.50	1.50	88.30	0.20	1.15	197.90	79.60	5.60
04/04/04	#7	13.16	3.63	7.25	1.47	70.33	0.17	1.15	148.00	75.58	4.77
18/04/04	#8	12.55	3.25	5.84	1.20	52.98	0.18	1.11	169.04	82.26	4.77
04/05/04	#9	12.17	3.21	7.30	2.80	63.30	0.40	1.10	392.90	87.40	4.40
16/05/04	#10	12.06	3.07	7.92	2.80	57.97	0.41	1.14	429.44	75.08	6.08
RANGE		12.06-13.19	2.75-8.6	5.84-8.53	1.20-2.80	53-95	0.17-0.41	1.10-1.38	120.11-429.44	64.32-98.86	4.40-6.08
MEDIAN		12.30	3.25	7.25	1.47	70	0.20	1.15	197.90	77.89	5.11

Table 5.3: Principal chemical parameters measured for u/s V3 (F)
NM = Not Measured; F= Afforested

VARTRY RESERVOIR INFLOWS

V4		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	3	5.75	56.4	10	<0.01	<5	0.83
25/01/04	#2	6.5	94.9	11.22	3	5.83	57.3	10	<0.01	<5	0.87
08/02/04	#3	6.4	101.3	12.18	1	5.59	59	20	<0.01	NM	0.78
23/02/04	#4	5.2	101.1	12.54	3	5.88	273	10	<0.01	<5	0.86
07/03/04	#5	5.3	100.5	12.45	3	5.89	65	10	<0.01	<5	0.76
21/03/04	#6	6.6	100.8	11.77	2.5	5.68	59.6	20	<0.01	<5	0.63
04/04/04	#7	7.4	99.1	11.46	3	6	62.4	10	<0.01	22.40	0.71
18/04/04	#8	8.4	100	10.9	3	6.04	62	5	<0.01	<5	0.63
04/05/04	#9	NM	NM	NM	2.5	6.07	60.4	5	<0.01	<5	0.56
16/05/04	#10	11.2	105.9	11.45	3.5	5.94	58.5	5	NM	NM	0.61
RANGE					1.0-3.5	5.59-6.07	56.4-273.0	5-20			0.56-0.87
MEDIAN					3.0	5.89	60.00	10			0.74

V4		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	Total Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	10.71	3.96	6.04	1.35	133.97	0.33	1.55	76.77	56.87	10.59
25/01/04	#2	11.16	6.35	7.56	1.70	113.33	0.42	1.78	<50	56.50	6.86
08/02/04	#3	10.93	6.01	6.21	1.20	125.98	0.37	1.58	54.81	53.49	10.78
23/02/04	#4	11.64	4.48	5.90	1.24	79.70	0.35	1.70	<50	55.70	11.47
07/03/04	#5	11.75	5.06	6.20	1.40	80.66	0.35	1.78	51.26	60.48	13.05
21/03/04	#6	12.28	4.94	6.63	1.28	128.97	0.27	1.42	56.90	58.14	10.36
04/04/04	#7	11.59	4.51	6.33	1.36	84.18	0.32	1.63	<50	53.15	10.76
18/04/04	#8	11.19	4.35	5.35	1.16	61.56	0.33	1.66	<50	56.80	14.62
04/05/04	#9	11.20	4.22	6.90	2.90	74.30	0.60	1.70	52.00	58.20	11.30
16/05/04	#10	11.01	4.19	7.17	2.79	52.46	0.52	1.59	<50	51.74	10.41
RANGE		10.71-12.28	3.96-6.35	5.35-7.17	1.16-2.9	52-134	0.27-0.60	1.42-1.78	<50-76.77	51.74-60.48	6.86-14.62
MEDIAN		11.20	4.50	6.27	1.36	82	0.35	1.65	50.63	56.65	10.77

Table 5.4: Principal chemical parameters measured for V4 (F)
NM = Not Measured; F= Afforested

VARTRY RESERVOIR INFLOWS

V5		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L CaCO$_3$	pH	Cond. μS/cm	Colour Hazen Units	NH$_3$ mg/L	PO4^{3-} μg/L	TON mg/L
11/01/04	#1	NM	NM	NM	5.5	6.45	52.7	20	<0.01	<5	0.93
25/01/04	#2	5.9	94.2	11.27	4	6.28	50	20	<0.01	7.99	0.98
08/02/04	#3	5.8	100.8	12.32	2.5	5.89	50	20	<0.01	NM	0.86
23/02/04	#4	3.8	99.7	12.9	5	6.14	238	10	<0.01	<5	0.86
07/03/04	#5	5.6	101.8	12.53	6	6.31	59.2	10	<0.01	<5	0.71
21/03/04	#6	6.7	99.2	11.53	5	6.45	57.1	30	<0.01	<5	0.77
04/04/04	#7	7	98.3	11.44	5	6.45	56.8	20	<0.01	20.96	0.77
18/04/04	#8	7.7	98	10.8	6.5	6.43	58.4	10	<0.01	<5	0.68
04/05/04	#9	NM	NM	NM	5	6.25	51.4	5	<0.01	<5	0.57
16/05/04	#10	11.8	113.5	12.17	4.5	6.21	49.5	5	NM	NM	0.54
RANGE					2.5-6.5	5.89-6.45	49.5-238	5-30			0.54-0.98
MEDIAN					5.0	6.30	54.80	15			0.77

V5		Cl$^-$ mg/L	SO$_4^{2-}$ mg/L	Na$^+$ mg/L	Mg^{2+} mg/L	Total Al μg/L	K$^+$ mg/L	Ca^{2+} mg/L	Fe μg/L	Mn^{2+} μg/L	Zn^{2+} μg/L
11/01/04	#1	8.65	3.13	4.78	1.41	60.30	0.44	2.10	36.10	29.93	6.60
25/01/04	#2	9.40	3.21	6.25	1.76	46.94	0.37	1.98	<50	29.36	2.90
08/02/04	#3	8.95	2.52	4.98	1.19	56.86	0.37	1.56	<50	31.72	8.75
23/02/04	#4	10.09	3.26	4.77	1.29	23.80	0.30	1.85	<50	27.23	5.32
07/03/04	#5	9.92	4.36	4.91	1.48	19.26	0.35	2.20	<50	21.80	4.74
21/03/04	#6	9.66	3.58	5.18	1.44	121.44	0.55	2.46	58.17	29.98	6.07
04/04/04	#7	9.53	3.48	5.11	1.47	41.35	0.35	2.14	<50	24.89	4.87
18/04/04	#8	8.95	3.41	3.40	1.01	36.99	0.40	2.46	<50	24.52	4.51
04/05/04	#9	9.05	2.88	5.50	2.90	26.40	0.70	1.80	<50	20.20	5.30
16/05/04	#10	8.66	2.75	5.64	2.62	19.60	0.49	1.67	<50	15.80	4.57
RANGE		8.65-10.09	2.52-4.36	3.40-6.25	1.01-2.90	19-121	0.30-0.70	1.56-2.46	<50-58.17	15.80-31.72	2.90-8.75
MEDIAN		9.23	3.24	5.05	1.46	39	0.39	2.04	<50	26.06	5.09

Table 5.5: Principal chemical parameters measured for V5 (PF)
NM = Not Measured; PF = Partially Afforested

VARTRY RESERVOIR INFLOWS

V6		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	5	6.33	49.4	30	<0.01	<5	0.64
25/01/04	#2	5.3	95.3	11.61	4	6.38	46.4	30	<0.01	5.56	0.76
08/02/04	#3	5.2	101	12.62	3.5	6.03	47	20	<0.01	NM	0.66
23/02/04	#4	3.7	100.9	13.04	5	6.31	229	10	0.02	<5	0.66
07/03/04	#5	5.3	99.6	12.37	4.5	6.51	54.7	10	<0.01	<5	0.53
21/03/04	#6	6.4	100.3	11.77	3.5	6.27	56	30	<0.01	<5	0.42
04/04/04	#7	7.3	100.3	11.64	4.5	6.49	50.5	30	<0.01	18.01	0.52
18/04/04	#8	8	99	11	4.5	6.41	52.9	35	<0.01	<5	0.43
04/05/04	#9	NM	NM	NM	4	6.44	44.9	5	<0.01	<5	0.38
16/05/04	#10	13.2	104.3	10.84	5	6.51	45.4	5	NM	NM	0.39
RANGE					3.5-5	6.03-6.51	44.9-229	5-35			0.38-0.76
MEDIAN					4.5	6.40	50.00	25			0.53

V6		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	Total Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	7.79	2.71	4.76	1.21	66.99	0.33	1.11	75.43	32.27	8.68
25/01/04	#2	8.36	2.73	5.98	1.60	50.31	0.27	1.31	<50	29.51	2.76
08/02/04	#3	8.38	2.59	4.98	1.16	59.99	0.31	1.20	75.46	28.58	8.65
23/02/04	#4	9.08	3.28	4.89	1.29	28.21	0.33	1.47	71.78	32.48	8.99
07/03/04	#5	9.33	4.07	5.04	1.42	21.15	0.25	1.44	77.50	39.66	10.17
21/03/04	#6	10.79	3.16	6.28	1.30	100.14	0.35	1.37	122.90	40.76	9.78
04/04/04	#7	9.28	3.09	5.28	1.29	57.00	0.24	1.28	119.39	35.29	7.64
18/04/04	#8	8.89	2.76	3.75	0.88	74.51	0.26	1.34	234.51	45.76	8.56
04/05/04	#9	8.03	2.42	5.30	2.50	58.10	0.50	1.20	190.50	30.60	7.20
16/05/04	#10	7.72	2.60	5.47	2.47	40.90	0.46	1.21	191.19	28.53	7.76
RANGE		7.72-10.79	2.42-4.07	3.75-6.28	0.88-2.50	21-100	0.24-0.50	1.11-1.47	71.78-234.51	28.53-45.76	2.76-10.17
MEDIAN		8.64	2.75	5.15	1.30	58	0.32	1.30	98.45	32.38	8.61

Table 5.6: Principal chemical parameters measured for V6 (PF)
NM = Not Measured; PF = Partially Afforested

SHEEP		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
25/01/04	#2	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
08/02/04	#3	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
23/02/04	#4	2.9	102.2	13.3	16	7.1	248	80	<0.01	64.19	0.03
07/03/04	#5	6.4	102.5	12.19	10.5	7.08	51.1	140	<0.01	<5	<0.01
21/03/04	#6	5.6	100.8	11.91	0.5	4.51	50.1	160	0.01	<5	0.01
04/04/04	#7	6.5	100.1	11.64	3	6.49	41.9	180	<0.01	14.82	<0.01
18/04/04	#8	7.6	101	11.1	2	4.95	42.7	260	<0.01	<5	<0.01
04/05/04	#9	NM	NM	NM	6	6.44	42.9	190	<0.01	<5	<0.01
16/05/04	#10	14.3	104.3	10.45	16.5	7.05	56.1	90	NM	NM	<0.01
RANGE					0.5-16.5	4.51-7.1	41.9-248	90-260			<0.01-0.03
MEDIAN					6	6.49	50.1	160			<0.01

SHEEP		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	Total Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
25/01/04	#2	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
08/02/04	#3	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
23/02/04	#4	7.18	0.72	5.39	1.19	69.41	0.34	3.31	422.72	154.95	3.26
07/03/04	#5	7.68	0.31	4.99	1.09	93.88	0.31	2.60	430.81	136.92	4.86
21/03/04	#6	9.18	0.22	4.59	0.76	160.62	0.29	0.85	251.22	111.16	13.33
04/04/04	#7	8.63	<0.05	4.54	0.77	157.69	0.20	1.23	356.86	110.61	7.99
18/04/04	#8	8.10	<0.05	3.01	0.51	150.02	0.19	1.03	379.97	115.88	11.45
04/05/04	#9	8.66	<0.05	5.50	2.10	176.90	0.90	2.20	579.10	149.60	7.90
16/05/04	#10	7.10	<0.05	6.90	2.87	90.95	0.77	3.52	604.35	129.50	3.92
RANGE		7.1-9.18	<0.05-0.72	3.01-6.90	0.51-2.87	69-176	0.19-0.90	0.85-3.52	251.22-604.35	110.61-154.95	3.26-13.33
MEDIAN		8.10	<0.05	4.99	1.09	150	0.31	2.20	422.72	129.50	7.90

Table 5.7: Principal chemical parameters measured for Sheepbanks Br. (M)
NM = Not Measured; M = Moorland

CLOGHOGE RIVER CATCHMENT

SG1		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
25/01/04	#2	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
08/02/04	#3	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
23/02/04	#4	2.1	105.1	14	19	7.21	277	80	<0.01	<5	0.04
07/03/04	#5	6.2	105.5	12.59	11	7.08	50.5	160	<0.01	<5	0.02
21/03/04	#6	5.7	100.8	11.9	0	4.6	47.3	180	<0.01	<5	<0.01
04/04/04	#7	6.5	101.5	11.81	4	5.87	40.7	200	<0.01	16.28	<0.01
18/04/04	#8	7.6	101	11.1	2	4.99	41.2	200	<0.01	<5	<0.01
04/05/04	#9	NM	NM	NM	10	6.5	46.7	135	0.012	<5	0.05
16/05/04	#10	14.6	109.5	10.78	17.5	7.27	61.1	80	NM	NM	<0.01
RANGE					0-19	4.6-7.21	47.3-277	80-200			<0.01-0.05
MEDIAN					10	6.5	47.3	160			<0.01

SG1		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	Total Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
25/01/04	#2	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
08/02/04	#3	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
23/02/04	#4	6.96	0.62	5.02	1.28	66.30	0.29	4.63	247.67	54.94	3.51
07/03/04	#5	7.75	0.08	4.74	1.10	111.15	0.25	3.04	288.57	49.85	5.43
21/03/04	#6	9.52	<0.05	4.37	0.74	146.70	0.24	1.14	205.05	71.03	11.98
04/04/04	#7	8.62	<0.05	4.50	0.80	158.82	0.17	1.73	249.46	62.69	9.09
18/04/04	#8	8.07	0.17	2.93	0.50	141.64	0.15	1.31	276.69	76.32	11.36
04/05/04	#9	8.70	<0.05	5.60	2.20	143.60	0.60	3.30	335.60	51.00	5.40
16/05/04	#10	6.92	<0.05	7.1	3.3	73.1	0.6	4.7	239.0	26.2	2.9
RANGE		6.92-9.52	<0.05-0.62	2.93-7.10	0.50-3.30	66-158	0.15-0.60	1.14-4.70	205.05-335.60	26.2-76.32	2.9-11.98
MEDIAN		8.07	<0.05	4.74	1.10	142	0.25	3.04	249.46	54.94	5.43

Table 5.8: Principal chemical parameters measured at SG1 Tributary (M)
NM = Not Measured; M = Moorland

CLOGHOGE RIVER CATCHMENT

SG2		**Temp. °C**	**D.O. % Sat.**	**D.O. mg/l**	**Alk. mg/L $CaCO_3$**	**pH**	**Cond. µS/cm**	**Colour Hazen Units**	**NH_3 mg/L**	**$PO4^{3-}$ µg/L**	**TON mg/L**
11/01/04	#1	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
25/01/04	#2	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
08/02/04	#3	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
23/02/04	#4	2.4	102.1	13.53	10	7.06	183.5	120	<0.01	<5	0.11
07/03/04	#5	6.5	103.3	12.26	4.5	6.49	40	160	<0.01	<5	0.02
21/03/04	#6	5.6	100.2	11.86	0	4.31	54.1	180	0.011	<5	<0.01
04/04/04	#7	6.6	97.8	11.32	1	4.61	45.6	200	<0.01	17.05	<0.01
18/04/04	#8	7.6	101	11.1	0	4.44	45.6	220	<0.01	<5	<0.01
04/05/04	#9	NM	NM	NM	4	5.92	37.1	185	0.014	<5	<0.01
16/05/04	#10	15.5	108	10.49	8	7.05	42.6	100	NM	NM	<0.01
RANGE					0-10	4.31-7.06	37.1-183.5	100-200			<0.01-0.11
MEDIAN					4	5.92	45.6	180			<0.01

SG2		**Cl^- mg/L**	**SO_4^{2-} mg/L**	**Na^+ mg/L**	**Mg^{2+} mg/L**	**Total Al µg/L**	**K^+ mg/L**	**Ca^{2+} mg/L**	**Fe µg/L**	**Mn^{2+} µg/L**	**Zn^{2+} µg/L**
11/01/04	#1	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
25/01/04	#2	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
08/02/04	#3	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
23/02/04	#4	7.06	0.55	4.68	0.75	96.16	0.28	1.77	310.15	28.76	3.67
07/03/04	#5	7.64	0.10	4.43	0.70	147.98	0.26	1.31	262.14	41.46	7.60
21/03/04	#6	8.98	<0.05	4.14	0.66	110.45	0.21	0.52	160.92	22.60	10.31
04/04/04	#7	8.57	0.24	4.26	0.70	125.21	0.17	0.74	237.04	34.39	9.90
18/04/04	#8	7.38	0.43	2.69	0.40	101.13	0.13	0.53	216.46	25.36	8.97
04/05/04	#9	8.13	<0.05	5.40	1.70	170.10	0.60	1.30	311.20	31.50	8.40
16/05/04	#10	6.89	<0.05	6.73	1.78	113.64	0.58	1.58	212.11	18.69	4.04
RANGE		6.89-8.98	<0.05-0.55	2.69-6.7	0.40-1.78	96-170	0.13-0.60	0.52-1.77	160.92-311.2	18.69-41.46	3.67-10.31
MEDIAN		7.64	0.10	4.43	0.70	114	0.26	1.30	237.04	28.76	8.40

Table 5.9: Principal chemical parameters measured at SG2 (M)
NM = Not Measured; M = Moorland

GLENDALOUGH LAKE UPPER CATCHMENT

GLEN		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L CaCO$_3$	pH	Cond. µS/cm	Colour Hazen Units	NH$_3$ mg/L	PO4^{3-} µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	3	6.11	32.9	60	<0.01	<5	0.15
25/01/04	#2	3.5	99.3	12.9	4	6.5	28.8	60	<0.01	<5	0.13
08/02/04	#3	3.5	100.4	13.34	3.5	6.24	31	50	<0.01	NM	0.12
23/02/04	#4	2.1	103.1	14.15	8	6.73	164.4	30	<0.01	<5	0.16
07/03/04	#5	5.6	102.3	12.86	5.5	6.73	36	40	<0.01	<5	0.16
21/03/04	#6	6.5	98.8	11.83	2.5	5.47	38.3	50	<0.01	<5	0.08
04/04/04	#7	7.1	99.1	11.74	3.5	6.17	34.3	60	<0.01	12.41	0.04
18/04/04	#8	7.8	100	11.3	3	5.97	29.3	75	<0.01	<5	0.05
04/05/04	#9	NM	NM	NM	4.5	6.16	35.6	75	0.012	60.62	0.07
16/05/04	#10	17.2	92.7	8.94	8.5	6.68	37.3	30	NM	NM	<0.01
RANGE					2.5-8.5	5.47-6.73	28.8-164.4	30-75			<0.01-0.16
MEDIAN					3.8	6.21	34.9	55			0.01

GLEN		Cl$^-$ mg/L	SO$_4^{2-}$ mg/L	Na$^+$ mg/L	Mg^{2+} mg/L	Total Al µg/L	K$^+$ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	5.17	2.06	3.30	0.64	112.55	0.26	1.21	58.72	15.01	10.42
25/01/04	#2	4.91	1.53	3.87	0.79	113.24	0.22	1.32	<50	8.46	6.13
08/02/04	#3	4.94	4.31	3.31	0.57	94.20	0.28	1.29	80.97	7.09	9.43
23/02/04	#4	5.13	2.17	3.50	0.72	39.70	0.23	1.97	55.56	3.89	5.04
07/03/04	#5	5.56	2.13	3.26	0.63	65.02	0.26	1.53	54.04	5.35	6.75
21/03/04	#6	8.16	4.89	4.07	0.73	145.80	0.34	1.22	155.94	24.33	14.38
04/04/04	#7	6.90	0.34	3.62	0.67	124.29	0.22	1.14	67.51	14.33	10.20
18/04/04	#8	5.71	0.80	2.45	0.43	117.21	0.21	1.00	72.32	16.41	10.98
04/05/04	#9	6.44	0.89	4.16	1.67	148.29	0.67	1.87	122.40	18.40	36.20
16/05/04	#10	5.07	1.68	4.8	1.7	44.6	0.50	2.0	72.0	4.8	5.0
RANGE		4.91-8.16	0.34-4.89	2.45-4.80	0.43-1.70	40-148	0.21-0.67	1.00-2.00	<50-155.94	3.89-24.33	5.04-36.20
MEDIAN		5.37	1.87	3.56	0.70	113	0.26	1.31	72.16	11.40	9.82

Table 5.10: Principal chemical parameters measured at Glenealo River (M)
NM = Not Measured; M = Moorland

GLENDALOUGH LAKE UPPER CATCHMENT

LUG		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	3	5.1	45	20	<0.01	<5	0.22
25/01/04	#2	5.6	95.7	11.79	2	5.21	40.4	20	<0.01	<5	0.23
08/02/04	#3	5.6	101.3	12.72	1.5	4.99	43	20	<0.01	NM	0.17
23/02/04	#4	4.2	101.3	13.07	2	5.51	177.4	5	<0.01	<5	0.18
07/03/04	#5	5.6	103.2	12.95	1.5	5.45	42.5	10	<0.01	58.67	0.20
21/03/04	#6	6.3	126.2	13.31	1	4.95	44.5	10	<0.01	<5	0.10
04/04/04	#7	7.2	99.2	11.71	1.5	5.09	42.6	5	<0.01	16.16	0.12
18/04/04	#8	6.7	102	11.9	1	4.99	46	5	<0.01	44.56	0.14
04/05/04	#9	NM	NM	NM	2	5.54	41	5	<0.01	<5	0.12
16/05/04	#10	12.5	96.7	8.94	2	5.62	40.5	5	NM	NM	0.06
RANGE					1.0-3.0	4.95-5.62	40.4-177.4	5-20			0.06-0.23
MEDIAN					1.8	5.16	42.8	8			0.16

LUG		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	TotaL Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	7.20	3.29	4.40	0.77	275.46	0.14	0.53	51.27	65.16	9.56
25/01/04	#2	8.08	3.55	5.44	0.92	205.62	0.12	0.60	<50	68.91	2.79
08/02/04	#3	7.95	2.93	4.54	0.68	239.98	0.16	0.60	53.35	64.18	10.63
23/02/04	#4	8.44	3.09	4.40	0.68	109.36	0.14	0.64	<50	57.75	5.69
07/03/04	#5	8.67	3.17	4.54	0.74	128.59	0.16	0.67	<50	67.00	6.67
21/03/04	#6	8.67	3.20	4.75	0.72	344.59	0.14	0.49	67.27	61.06	8.56
04/04/04	#7	8.55	3.21	4.60	0.74	216.03	0.10	0.57	<50	65.20	6.50
18/04/04	#8	8.12	3.09	3.47	0.55	244.85	0.13	0.52	<50	69.38	8.00
04/05/04	#9	8.14	2.85	6.19	2.03	173.15	0.32	0.72	<50	63.70	6.30
16/05/04	#10	8.09	2.82	5.96	1.70	111.45	0.29	0.69	<50	54.95	5.94
RANGE		7.2-8.67	2.82-3.55	3.47-6.19	0.55-2.03	109-345	0.10-0.32	0.49-0.72	<50-67.27	54.95-69.38	2.79-10.63
MEDIAN		8.13	3.13	4.57	0.74	211	0.14	0.60	<50	64.67	6.58

Table 5.11: Principal chemical parameters measured at Lugduff River (F)
NM = Not Measured; F = Afforested

KING'S RIVER CATCHMENT

ANNA		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	1	4.43	52.20	240	0.01	15.00	0.09
25/01/04	#2	3.9	98.5	12.3	1.5	4.85	41.00	160	<0.01	14.26	0.14
08/02/04	#3	4	102.1	13.05	1	4.86	45.00	120	0.01	NM	0.10
23/02/04	#4	2.7	101.1	13.31	3.5	6.29	182.60	80	<0.01	<5	0.11
07/03/04	#5	5.4	102.8	12.64	2.5	5.35	46.00	120	<0.01	8.80	0.12
21/03/04	#6	4.7	NM	NM	0	4.27	63.30	250	0.03	9.08	0.04
04/04/04	#7	7.2	98.8	11.37	0.5	4.60	56.90	150	<0.01	17.41	0.07
18/04/04	#8	6.3	101	11.7	0	4.39	60.30	200	<0.01	12.44	0.08
04/05/04	#9	NM	NM	NM	2	5.5	46	135	<0.01	<5	0.10
16/05/04	#10	15.6	96.7	9.38	3.5	6.25	42.2	70	NM	NM	0.15
RANGE		2.7-15.6	96.7-102.8	9.38-13.31	0-3.5	4.27-6.25	41.0-182.6	70-250			0.04-0.15
MEDIAN		5.1	101	12.3	1.3	4.86	49.1	145			0.10

ANNA		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	TotaL Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	6.57	2.22	4.19	0.70	287.15	0.20	0.86	273.79	78.81	10.06
25/01/04	#2	8.26	0.53	5.34	0.86	279.28	0.18	1.05	310.70	118.68	2.91
08/02/04	#3	8.74	1.20	4.79	0.64	247.27	0.23	1.10	300.33	124.88	7.65
23/02/04	#4	8.63	2.28	4.77	0.62	152.38	0.20	1.23	232.42	114.23	3.39
07/03/04	#5	9.61	1.79	4.58	0.71	206.34	0.18	1.20	267.71	122.70	6.13
21/03/04	#6	10.10	<0.05	4.81	0.85	275.42	0.19	0.84	204.49	63.20	7.65
04/04/04	#7	10.77	<0.05	5.43	0.85	270.04	0.19	1.21	278.89	110.25	7.73
18/04/04	#8	9.29	0.40	3.59	0.59	259.81	0.16	0.94	281.17	87.72	8.29
04/05/04	#9	9.62	0.40	6.50	2.00	227.40	0.50	1.50	375.80	113.00	6.30
16/05/04	#10	8.40	1.68	6.79	1.49	165.65	0.42	1.22	239.91	90.91	3.70
RANGE		6.57-10.77	<0.05-2.28	3.59-6.79	0.59-2.00	152-287	0.16-0.5	0.84-1.5	204.49-375.8	63.2-124.88	2.91-10.06
MEDIAN		9.02	0.87	4.80	0.78	254	0.20	1.15	276.34	111.63	6.98

Table 5.12: Principal chemical parameters measured at Annalecka River (F+C)
NM = Not Measured; F = Afforested; C = Clearfelled

KING'S RIVER CATCHMENT

B'GEE		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	3	5.3	36	140	<0.01	<5	0.07
25/01/04	#2	4	100.2	12.69	3.5	6.17	32.4	100	<0.01	6.47	0.14
08/02/04	#3	4.7	102	12.93	4	5.89	37	80	<0.01	NM	0.14
23/02/04	#4	3.4	104.9	13.64	7.5	6.73	180.4	50	<0.01	<5	0.24
07/03/04	#5	6.9	104.6	12.53	5.5	6.37	39.1	85	<0.01	<5	0.05
21/03/04	#6	6.2	129.3	15.44	1.5	4.86	41.9	150	<0.01	<5	<0.01
04/04/04	#7	8.1	101.4	11.5	3.5	5.95	37.2	125	<0.01	<5	<0.01
18/04/04	#8	8.3	103	11.3	3	5.38	34.6	180	<0.01	<5	<0.01
04/05/04	#9	NM	NM	NM	4.5	6.2	36.9	100	0.01	<5	<0.01
16/05/04	#10	NM	NM	NM	7	6.76	38.3	50	NM	NM	<0.01
RANGE					1.5-7.5	4.86-6.76	32.4-180.4	50-180			<0.01-0.24
MEDIAN					3.8	6.06	37.1	100			0.12

B'GEE		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	TotaL Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	4.98	1.81	3.27	0.69	216.19	0.41	1.13	164.03	50.05	5.91
25/01/04	#2	5.97	1.21	4.36	0.87	196.94	0.34	1.51	98.60	35.97	<1
08/02/04	#3	6.16	2.09	3.88	0.66	160.82	0.49	1.61	113.60	35.01	3.83
23/02/04	#4	6.49	2.47	4.06	0.81	83.47	0.28	2.00	87.94	29.87	2.39
07/03/04	#5	6.96	2.58	3.78	0.73	134.03	0.28	1.60	102.91	29.70	3.48
21/03/04	#6	8.09	<0.05	3.99	0.81	220.84	0.34	1.14	139.31	53.02	8.83
04/04/04	#7	7.70	1.87	4.03	0.75	211.70	0.24	1.37	127.82	41.13	4.72
18/04/04	#8	6.33	0.32	2.72	0.50	208.51	0.20	1.14	150.96	46.51	6.14
04/05/04	#9	6.77	0.34	4.90	2.00	196.40	0.60	1.80	182.00	26.90	3.00
16/05/04	#10	5.89	1.66	5.52	1.77	94.14	0.48	1.89	113.99	12.70	1.99
RANGE		4.98-8.09	<0.05-2.58	2.72-5.5	0.50-2.00	83-221	0.20-0.60	1.13-2.00	87.94-182.00	12.7-53.02	<1-8.83
MEDIAN		6.41	1.74	4.01	0.78	197	0.34	1.56	120.90	35.49	3.66

Table 5.13: Principal chemical parameters measured at Ballinagee River (PF)
NM = Not Measured; PF = Partially Afforested

KING'S RIVER CATCHMENT

GLAS		Temp. °C	D.O. % Sat.	D.O. mg/l	Alk. mg/L $CaCO_3$	pH	Cond. µS/cm	Colour Hazen Units	NH_3 mg/L	$PO4^{3-}$ µg/L	TON mg/L
11/01/04	#1	NM	NM	NM	2	4.75	39.5	200	<0.01	<5	0.05
25/01/04	#2	4.5	93.5	11.48	2	5.31	31.6	160	<0.01	7.54	0.13
08/02/04	#3	4.5	100	12.54	2	5.47	37	120	<0.01	NM	0.18
23/02/04	#4	2.2	102.4	13.81	6.5	6.67	175.9	70	<0.01	<5	0.19
07/03/04	#5	5.3	101.8	12.55	4	6.17	37	120	<0.01	<5	0.13
21/03/04	#6	5.4	113.2	13.51	0	4.48	48.7	180	<0.01	<5	<0.01
04/04/04	#7	6.4	98.6	11.53	2	5.95	39	150	<0.01	<5	0.02
18/04/04	#8	6.5	101	11.5	1.5	4.89	36.6	180	<0.01	<5	0.04
04/05/04	#9	NM	NM	NM	3	5.5	38.4	125	0.015	<5	0.03
16/05/04	#10	12.3	106.3	11.07	6	6.6	39.3	65	NM	NM	0.09
RANGE					0-6.5	4.48-6.67	31.6-175.9	65-200			<0.01-0.19
MEDIAN					2	5.49	38.7	138			0.07

GLAS		Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	Mg^{2+} mg/L	TotaL Al µg/L	K^+ mg/L	Ca^{2+} mg/L	Fe µg/L	Mn^{2+} µg/L	Zn^{2+} µg/L
11/01/04	#1	5.19	1.31	3.32	0.65	217.36	0.15	0.67	100.27	20.84	6.46
25/01/04	#2	6.93	0.42	4.85	0.82	263.79	0.13	0.88	74.50	17.07	<1
08/02/04	#3	7.30	0.72	4.48	0.60	220.82	0.19	0.89	82.95	12.88	4.12
23/02/04	#4	7.20	1.09	4.58	0.79	106.48	0.14	1.38	51.75	2.55	2.30
07/03/04	#5	7.43	0.42	4.10	0.65	189.27	0.14	1.07	82.87	4.60	3.42
21/03/04	#6	9.35	0.38	4.10	0.82	193.23	0.15	0.81	81.80	23.18	6.12
04/04/04	#7	8.03	<0.05	4.31	0.73	234.10	0.12	0.94	92.23	15.24	4.01
18/04/04	#8	6.93	0.52	2.76	0.48	200.08	0.12	0.80	91.43	18.42	4.35
04/05/04	#9	7.59	0.48	5.10	2.20	222.30	0.30	1.40	125.30	11.00	3.10
16/05/04	#10	7.19	0.66	6.47	1.78	114.77	0.43	1.24	<50	2.10	2.41
RANGE		5.19-9.35	<0.05-1.31	2.76-6.47	0.48-2.20	106-264	0.12-0.43	0.67-1.40	<50-125.3	2.10-23.18	<1-6.46
MEDIAN		7.25	0.50	4.40	0.76	209	0.15	0.92	82.91	14.06	3.72

Table 5.14: Principal chemical parameters measured at Glasnadade Brook(F)

NM = Not Measured; F = Afforested

5.2 pH

The highest pH values in all streams during the investigation were recorded during the exceptionally dry two weeks preceding 23/02/04. Correspondingly, the lowest pH values were recorded after the wettest two-week period and at the time of maximum easterly airflow, on 21/03/04 (Table 5.15).

Site	Land Use	Median pH (Range)	11/01	25/01	08/02	23/02	07/03	21/03	04/04	18/04	04/05	16/05
Rainfall (mm)			73.1	42.6	58.8	1	12.5	78.5	16.1	25	10.7	10.9
Vartry Catchment												
V3	F+C	6.38 (6.09-6.47)	6.32	6.38	6.09	6.33	6.37	6.38	6.47	6.35	6.42	6.43
u/s V3	F	5.86 (5.71-6.15)	-	5.76	5.73	5.86	5.86	5.71	5.84	5.86	6.13	6.15
V4	F	5.89 (5.59-6.07)	5.75	5.83	5.59	5.88	5.89	5.68	6.00	6.04	6.07	5.94
V5	PF	6.30 (5.89-6.45)	6.45	6.28	5.89	6.14	6.31	6.45	6.45	6.43	6.25	6.21
V6	PF	6.40 (6.03-6.51)	6.33	6.33	6.33	6.33	6.33	6.33	6.33	6.33	6.33	6.33
Cloghoge River Catchment												
SHEEP	M	6.49 (4.51-7.10)	-	-	-	7.10	7.08	4.51	6.49	4.95	6.44	7.05
SG1	M	6.50 (4.60-7.27)	-	-	-	7.21	7.08	4.60	5.87	4.99	6.5	7.27
SG2	M	5.92 (4.31-7.06)	-	-	-	7.06	6.49	4.31	4.61	4.44	5.92	7.05
Glendalough Lake Upper Catchment												
GLEN	M	6.21 (5.47-6.73)	6.11	6.50	6.24	6.73	6.73	5.47	6.17	5.97	6.16	6.68
LUG	F	5.16 (4.95-5.62)	5.1	5.21	4.99	5.51	5.45	4.95	5.09	4.99	5.54	5.62
King's River Catchment												
ANNA	F+C	4.86 (4.27-6.25)	4.43	4.85	4.86	6.29	5.35	4.27	4.60	4.39	5.50	6.25
B'GEE	PF	6.06 (4.86-6.76)	5.30	6.17	5.89	6.73	6.37	4.86	5.95	5.38	6.20	6.76
GLAS	F	5.49 (4.48-6.67)	4.75	5.31	5.47	6.67	6.17	4.48	5.95	4.89	5.50	6.60

Where; F = Afforested, PF = Partially Afforested, C = Clearfelled Areas, M = Moorland

Table 5.15: Summary of pH values measured

The lowest pH recorded during the entire project was that for the afforested Annalecka stream (ANNA) at 4.27 and the highest was for a moorland tributary (SG1) of the Cloghoge River at pH 7.21. Only two sites (V3 & V6) recorded values above pH 6.0 on all sampling dates.

Most sites within the Vartry system regularly exhibited values above pH 6.0, except for two afforested sites, V4 and upstream of V3 (u/s V3), where pH values were usually less than pH 6.0 but always greater than pH 5.5 (Fig. 5.2). The inflows to the Vartry reservoir are of gentle gradients underlain by Palaeozoic sediments. The pH of all sites within the Vartry catchment did not vary by greater than 0.5 pH units throughout the entire investigation. Statistical analysis (ANOVA) of all five sites within the Vartry catchment indicates there are no significant differences (F < F Critical) in pH among the afforested, partially afforested and clearfelled sites (Appendix B-1). However, t-tests performed between V4 (heavily afforested) and V6 (the least afforested site within Vartry) point to significant differences (t stat > t Critical) between the mean pH values of the two streams (Appendix B-1).

A block of forestry was harvested between sites V3 and upstream of V3 (u/s V3) in 2003. The site upstream of V3 (u/s V3) was consistently more acidic than site V3, and this is emphasised by t-test analysis indicating significant differences between the two means.

The most variable pH values were recorded in the three tributaries of the Cloghoge River (SHEEP, SG1 & SG2). This is illustrated well in Figure 5.2. These sampling sites were located in non-forested (moorland) sites on peaty podsolic soils underlain with granite bedrock. High colour readings (higher still during acidic episodes) were observed due to the high amount of humic and fulvic acids. Variations of up to 2 pH units within a fortnight of sampling were observed at all three systems.

The most acidic site within this catchment was SG2 (median pH 5.9) while sites SG1 and Sheepbanks Bridge (SHEEP) had mean pH values of 6.5. The ranges for the Sheepbanks Bridge (SHEEP) site were pH 4.51 to 7.1 and for the SG1 site the range was pH 4.6 to 7.21, both streams recording values less than pH 5.5 on two out of the seven sampling dates. The range at site SG2 was pH 4.31 to 7.06, with three out of seven sampling dates less than pH 5.5.

The wide pH ranges on each stream within this moorland site, with peaty soils on granite bedrock, highlight the sensitivity of this catchment to acidification. Statistical analysis (ANOVA) demonstrates there is no significant difference between the means of the pH values at the sites within the Cloghoge River catchment (Appendix B-2). However, t-test analysis points to significant differences in the mean pH values of SHEEP (brown podsolic soils with some gleys) and SG1 (deep mountain peat) (Appendix B-2).

Within the Glendalough Upper Lake catchment area, the afforested Lugduff River (LUG) was consistently more acidic than the moorland Glenealo River (GLEN) (Fig. 5.2). On eight of the ten sampling dates the pH values in the Lugduff were one pH unit less (*i.e.* 10 times more acidic) than the Glenealo River.

Palaeozoic sediments underlie the Lugduff River and granite bedrock underlies the Glenealo river catchment. The Lugduff River was the second most acidic site of the study with a median pH of 5.16 (pH range 4.95 to 5.62). Seven of the ten sampling dates had pH values less than 5.5. The Glenealo River drains moorland and recorded a median pH of 6.21 (pH range 5.47 to 6.73) with the pH less than 5.5 on only one occasion, that after the wettest period of the investigation. Statistical analysis (both ANOVA and t-test) indicates highly significant differences in the mean pH values of the afforested and moorland sites within this catchment (Appendix B-3).

There was a greater variation in pH values within individual sites (up to two units) recorded in the tributaries of the King's River (Fig. 5.2). Within this extensively afforested catchment are also sections of harvested forest and recently planted blocks. The afforested Annalecka stream (ANNA) had a median value of pH 4.86 (range pH 4.27 to 6.27), the most acidic site of the project. This afforested site recorded values greater than pH 5.5 on only two occasions. The most acidic episode of the whole project was noted at the Annalecka Bridge, where a value of pH 4.27 was recorded on 23/02/04. The Glasnadade stream (GLAS), an afforested tributary of the Ballinagee River, had a median of pH 5.49 and (range pH 4.47 to 6.67) recorded values less than pH 5.5 on five occasions. The Ballinagee River (B'GEE), the least afforested stream within the King's River catchment,), had the highest median of pH 6.06 (range pH 4.86 to 6.76) but on three occasions the pH was less than 5.5. ANOVA statistical analysis of the mean pH values pointed to significant differences among the three sites (F > F Critical) (Appendix B-4).

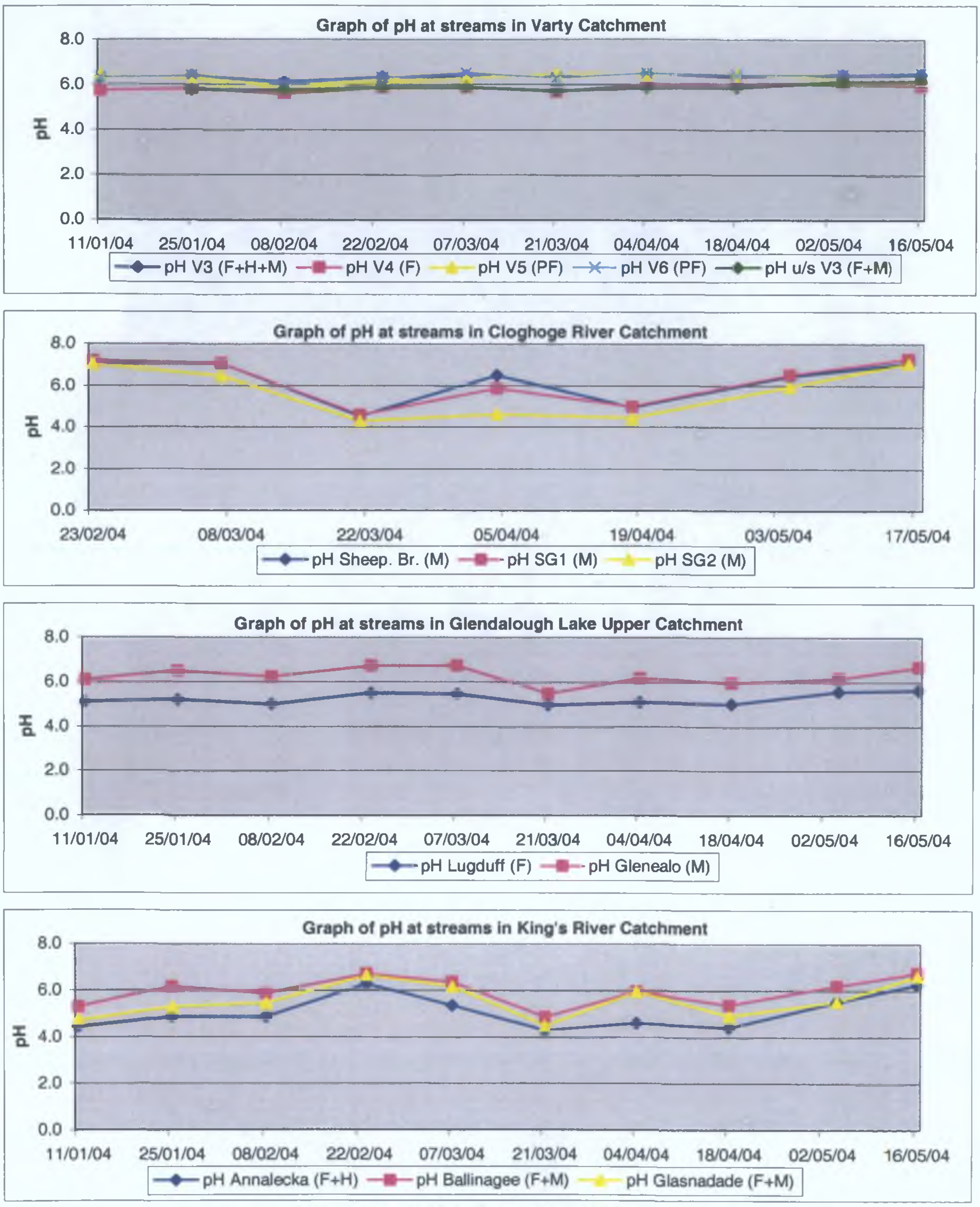


Fig. 5.2: pH at Sampling Sites

5.3 Alkalinity

Most sites recorded alkalinity values well below 10mg/L $CaCO_3$ and would therefore be considered as highly sensitive to acidification.

Sites within the Vartry catchment exhibited alkalinities less than 5mg/L $CaCO_3$, though none of the sites had pH less than 5.5 (Fig. 5.3 & 5.4). The two most afforested sites within this catchment (V4 and u/s V3) recorded the lowest alkalinities and the least afforested site, V6, had the highest median pH and alkalinity values of the catchment. Statistical analysis (ANOVA) denoted significant differences in mean alkalinity values in the Vartry inflows (Appendix B-1) . Highly significant differences were noted for mean alkalinity values at V4 (heavily afforested) and V5 (partially afforested).

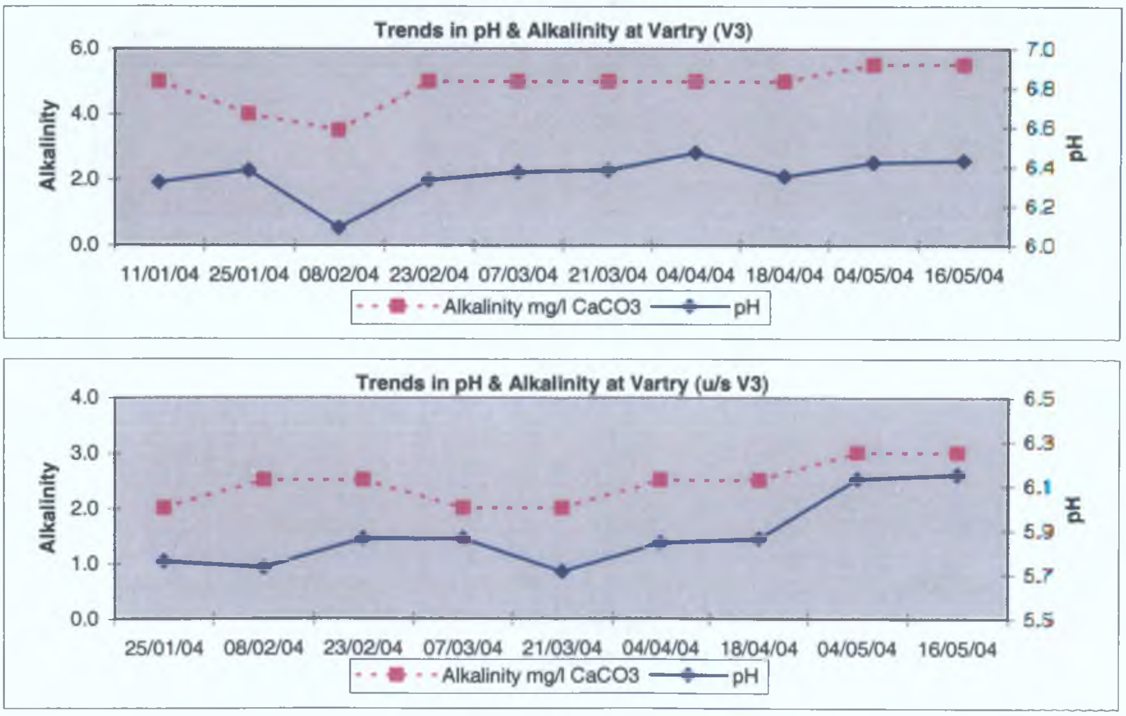
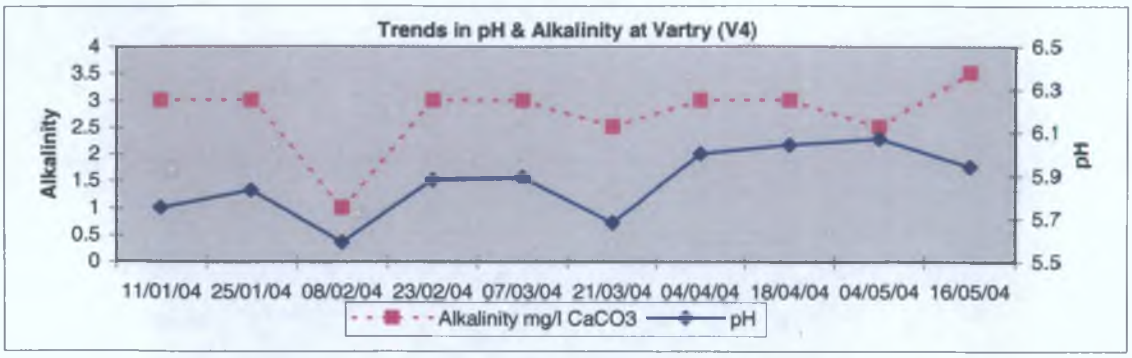
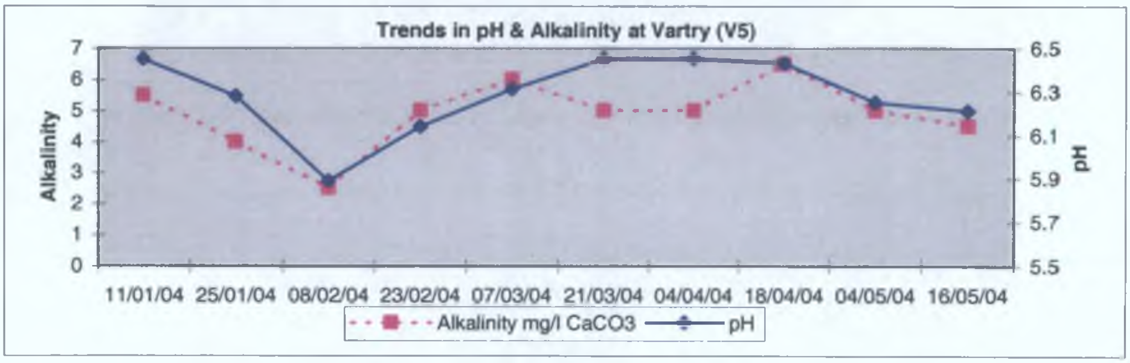


Fig. 5.3: pH & Alkalinity at V3 & u/s V3





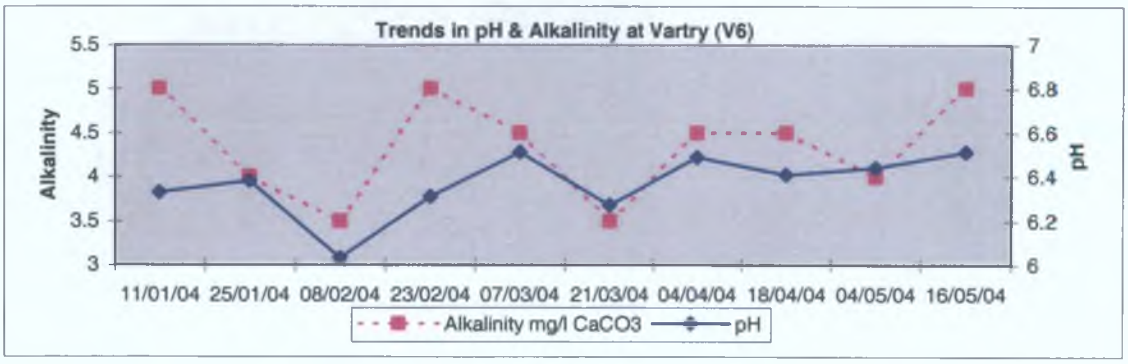


Fig. 5.4: pH & Alkalinity at V4, V5 & V6

The moorland tributaries of the Cloghoge River (SHEEP, SG1 and SG2) exhibited wide fluctuations in alkalinity. In terms of buffering capacity, all three tributaries seemed to respond to wet and dry deposition in a very similar fashion (Fig. 5.5 below). Easterly airflows were greater during February and especially March, the wettest occasion of the study.

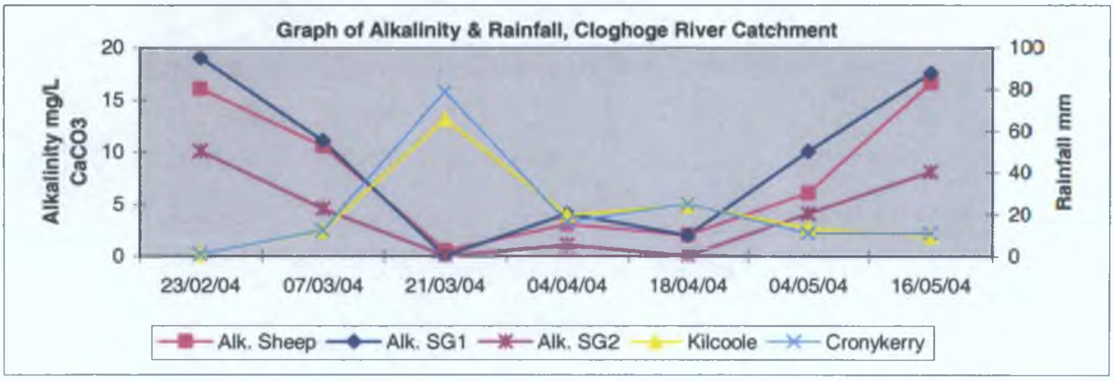


Fig. 5.5: Alkalinity and Rainfall, Cloghoge River Catchment

The highest alkalinities of the entire project (up to 19mg/L $CaCO_3$) were recorded in this catchment during drier periods. Alkalinity increased with low rainfall but decreased to zero during wetter periods. The occasions of low alkalinities were associated with low pH values and high colour values, suggesting high concentrations of humic and fulvic acids. This close relationship is apparent from Figure 5.6 overleaf.

Statistical analysis (ANOVA) of the three tributaries of the Cloghoge River (SHEEP, SG1 & SG2) indicated no significant differences in buffering capacity (Appendix B-2). ANOVA analysis between sites of different soils (SHEEP; brown podsolic soils with some gleys and either sites at SG1 or SG2; deep mountain peat) within this catchment showed no significant differences in mean alkalinities.

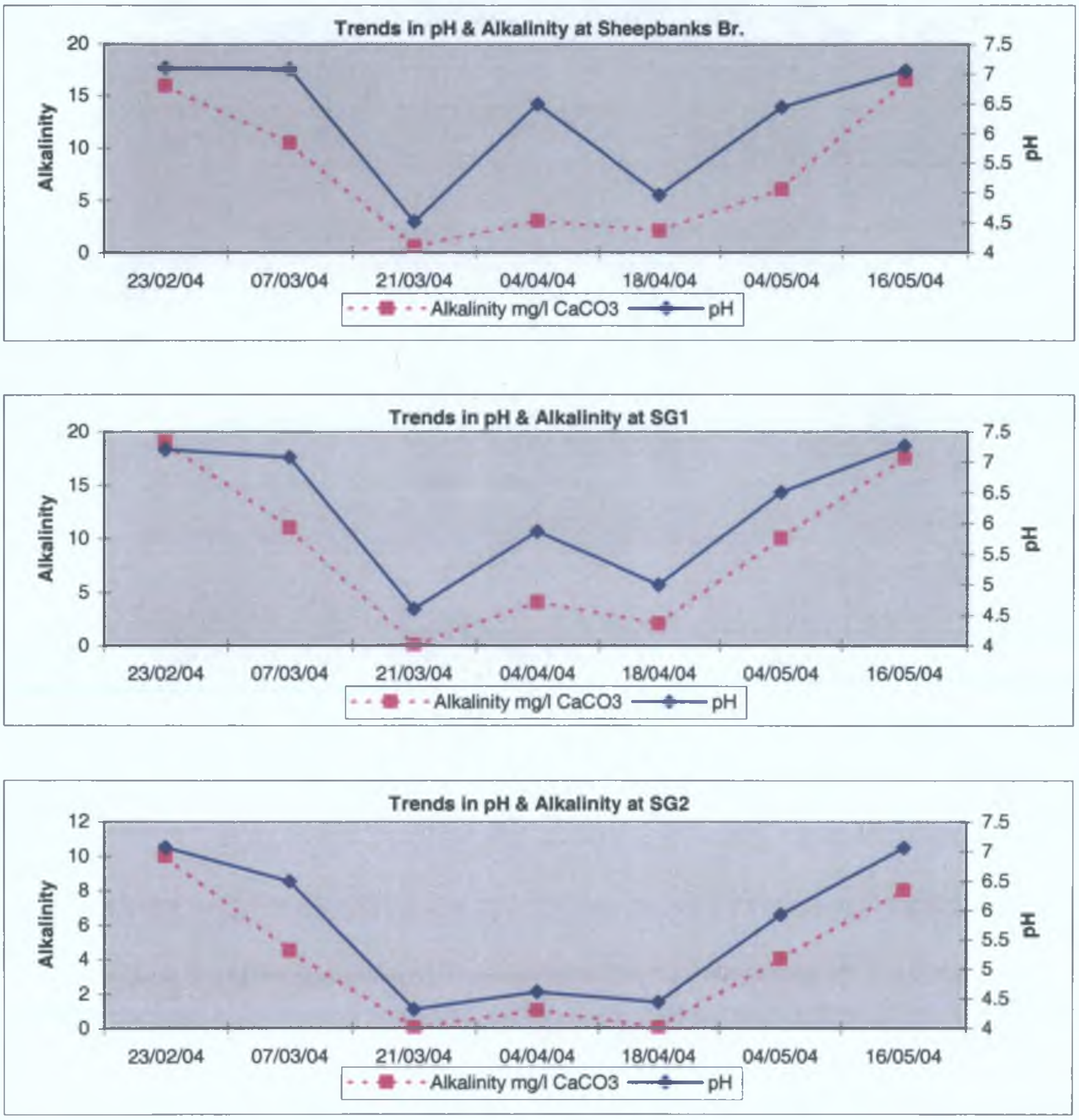


Fig.5.6: pH & Alkalinity in Cloghoge River Tributaries

The afforested Lugduff River had lower alkalinity (as well as pH) values than the comparable moorland Glenealo River (Granite bedrock) on each of the ten sampling dates (Fig. 5.7). It did not record an alkalinity value greater than 3mg/L as $CaCO_3$ on any of the sampling dates. T-Test analysis of the heavily afforested Lugduff and the moorland Glenealo rivers testified to very significant differences in mean alkalinity (Appendix B-3).

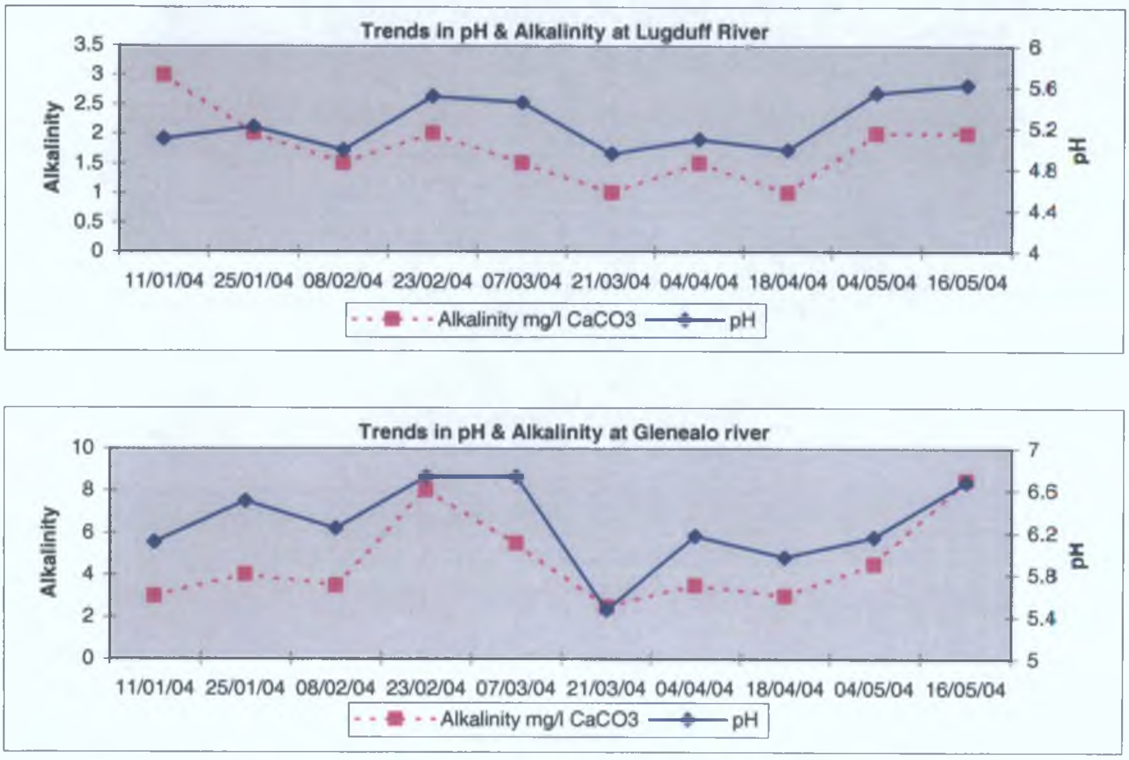


Fig. 5.7: pH & Alkalinity at Glendalough

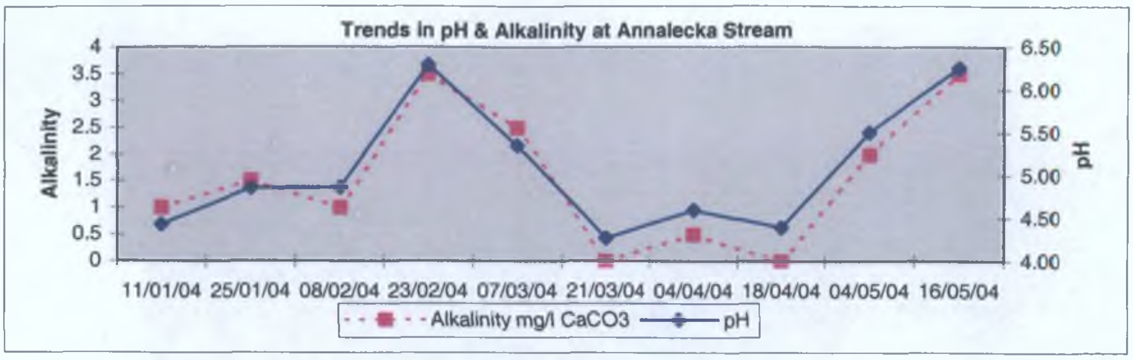
Alkalinity values in the King's River catchment were very low, none of the sites recording values greater than 10mg/L $CaCO_3$. Similar to the tributaries in the Cloghoge River catchment, all three rivers in the King's River catchment recorded lowest pH and alkalinity values during periods of higher precipitation (Fig. 5.8).

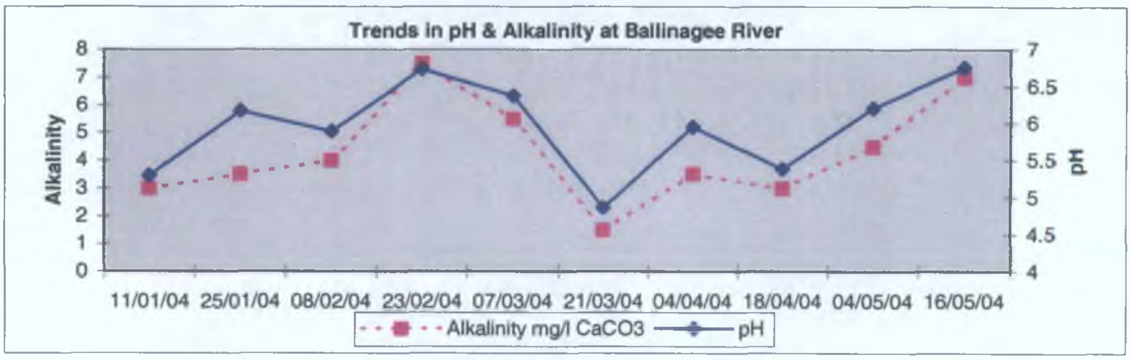
The afforested Annalecka River (ANNA), the most acidic site within this catchment and indeed the whole project, recorded alkalinity values less than 5mg/L $CaCO_3$ on all ten sampling occasions. The median alkalinity value was 1.3mg/L $CaCO_3$.

The afforested Glasnadade Brook (GLAS) shows similar trends in pH and alkalinity (median 2.0mg/L CaCO3) to the Annalecka River. Alkalinity decreased to zero during times of greater precipitation, and increased during drier spells.

The partially forested Ballinagee River (B'GEE) had the highest median alkalinity values (3.8mg/L CaCO3) and highest median pH (6.06) within the King's River catchment. This sub-catchment would have the lowest proportion of afforestation of the three rivers within the King's River catchment. The lowest alkalinity value at the Ballinagee River coincided with the same date as those of the Annalecka River and Glasnadade Stream.

Statistical analysis (ANOVA) showed significant differences among the three sites in this catchment with regard to buffering capacity (Appendix B-4). A significant difference in alkalinity values was noted between the afforested and clearfelled Annalecka River and the partially afforested Ballinagee River. The Ballinagee River and the Glasnadade Brook (a tributary of the Ballinagee) and showed no significant difference between them (T-Test).





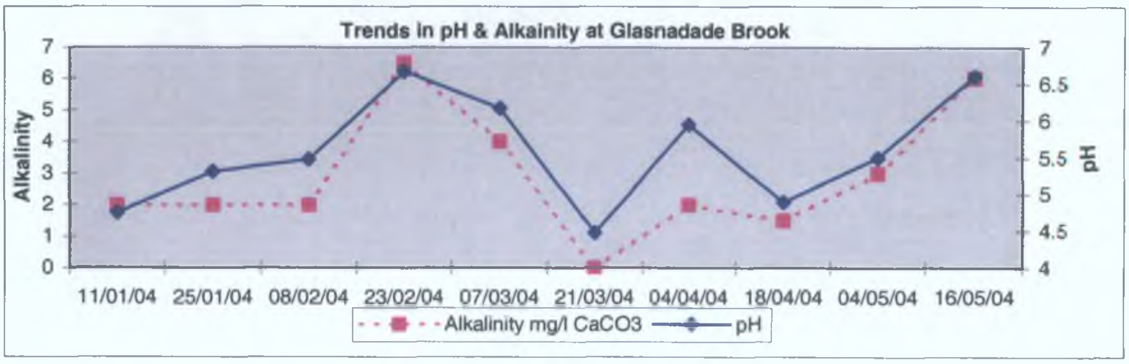


Fig. 5.9: pH & Alkalinity at King's River Catchment

5.4 Total Aluminium

Associated with increasing stream acidity was an increase in the concentration of total aluminium. All sites had higher concentrations of total monomeric aluminium during periods of higher rainfall and therefore winter figures were generally higher than summer values. As aluminium solubility is closely associated with pH, concentrations rose as the pH dropped during the wetter months. Four sites, all afforested to some degree, had median total aluminum values greater than 200µg/L, the Drinking Water Directive (98/83/EC) Mandatory (I) limit for total aluminum (S.I. 81 of 1988). The highest total aluminium value recorded during the investigation was 345µg/L for the afforested Lugduff River.

None of the sites in the Vartry Catchment recorded total aluminium values greater than 200µg/L (Fig. 5.9). Statistical analysis (ANOVA and t-test) pointed to highly significant differences in mean total aluminium between the heavily afforested V4 site and the slightly afforested V5 site and among all the sites within the Vartry catchment (Appendix B-1).

The tributaries (SHEEP, SG1 and SG2) of the moorland Cloghoge River Catchment recorded medium values for total aluminium. However, values did not exceed 200µg/L on any date (Fig. 5.9). Statistical analysis (ANOVA and t-test) of the mean total aluminium values demonstrated no significant differences among the three moorland sites (Appendix B-2). No significant differences were observed for t-test analysis of SHEEP (brown podsolic soils with some gleys) or either SG1 or SG2 (deep mountain peat).

The Lugduff River in the Glendalough Catchment had a median total aluminum concentration of 211µg/L Al. On six of the ten sampling dates values greater than 200µg/L were recorded here (Fig. 5.9). There were significantly greater concentrations of aluminium in the afforested Lugduff than the comparable moorland Glenealo River. The Glenealo did not exceed 200µg/L Al on any of the sampling dates. Highly significant differences (ANOVA and t-test) in mean total aluminium were demonstrated between the heavily afforested Lugduff and non-forested Glenealo River (Appendix B-3).

The heavily afforested King's River Catchment recorded the highest median total aluminum values of the four catchments. The three rivers monitored in this catchment had median total aluminium values greater than 200µg/l Al (Fig. 5.9). The Annalecka River, the most afforested of the three rivers, had the highest median value of the investigation at 259µg/L and greater than 200µg/L on eight of the ten dates. Statistical analysis (ANOVA and t-test) between the afforested and clearfelled Annalecka River and the partially afforested Ballinagee and Glasnadade streams indicated significant differences in mean total aluminum (Appendix B-4). There was no significant difference between the Ballinagee River and the Glasnadade Brook (a tributary of the Ballinagee) in terms of total aluminium.

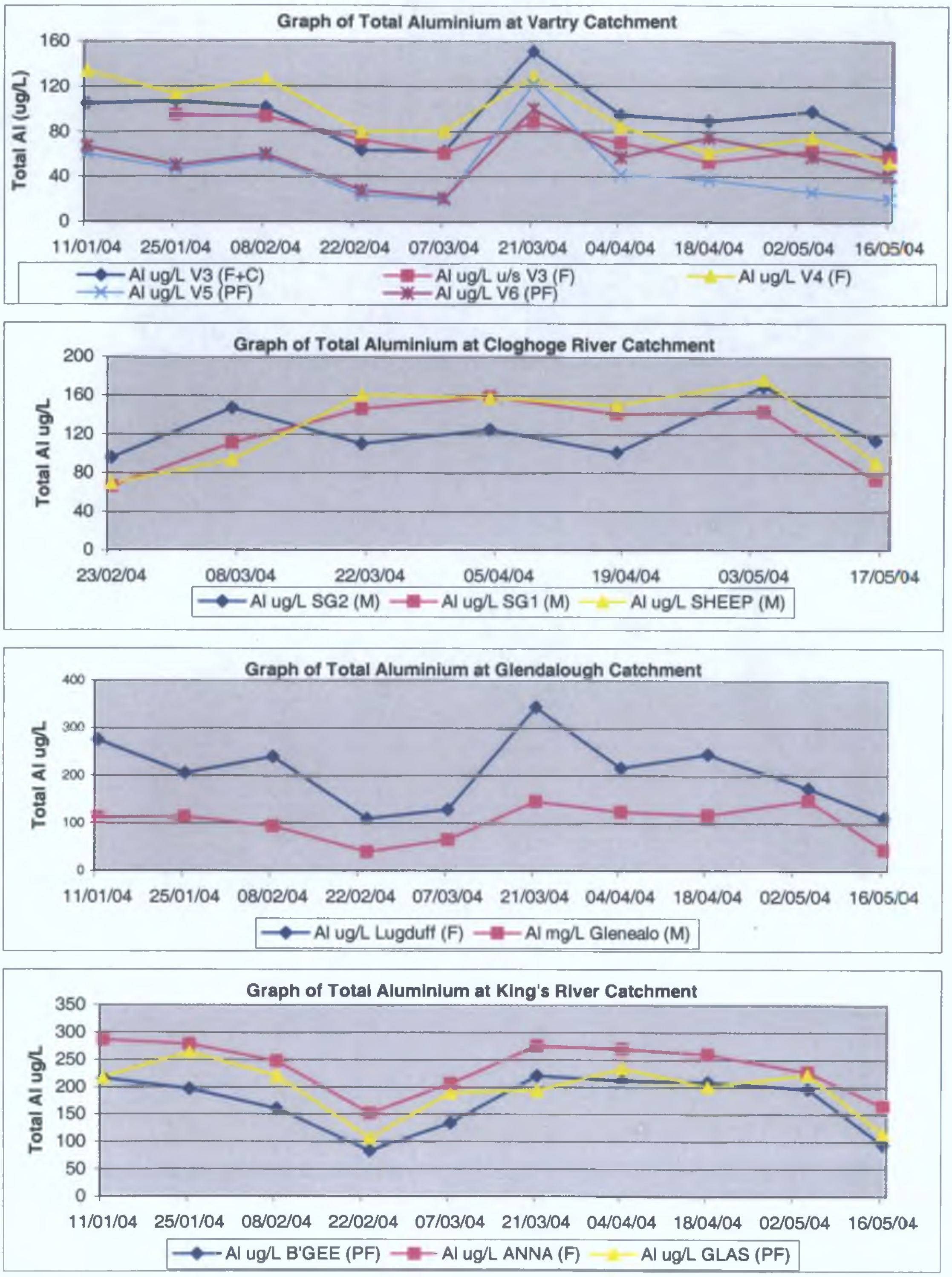


Fig. 5.9: Total Aluminium at Sampling Sites

5.5 Chloride

The concentration of chloride in the surface waters examined was generally low. Chloride values were higher in the Vartry catchment where the solid geology is marine sediments. On both granite and Palaeozoic sediments, however, higher concentrations of chloride ion were associated with heavily afforested sites (Fig.5.10). This probably reflects scavenging by the forest canopy.

Within the Vartry catchment, statistical analysis of mean chloride concentrations indicated highly significant differences among the sites, all afforested to varying degrees (ANOVA) (Appendix B-1). Very significant differences were observed for t-test analysis between one of the most afforested sites (V3) and the least afforested site (V6) in the catchment. A significant difference was also noted between the afforested site upstream of V3 (u/s V3) and the afforested and clearfelled V3 (ANOVA and t-test).

Significant differences were not observed for statistical analysis (ANOVA) of the three tributaries of the Cloghoge River (SHEEP, SG1 and SG2) (Appendix B-2). However, t-test analysis did highlight a significant difference in mean chloride values between SHEEP (brown podsolic soils with some gleys) and SG2 (deep mountain peat).

Chloride concentrations at the two sites in the Glendalough Lake Upper catchment highlighted the scavenging effects of mature forest canopy. The afforested Lugduff River had consistently higher chloride values than the moorland Glenealo River. Statistical analysis (ANOVA and t-test) pointed to highly significant differences in mean chloride values between the afforested and moorland sites within this catchment (Appendix B-3).

ANOVA analysis of the three systems in the King's River catchment indicated a significant difference among the sites in terms of mean chloride concentrations (Appendix B-4). There were significant differences (ANOVA and t-test) between the afforested and clearfelled Annalecka River and the less afforested Ballinagee River and its tributary, the Glasnadade Brook.

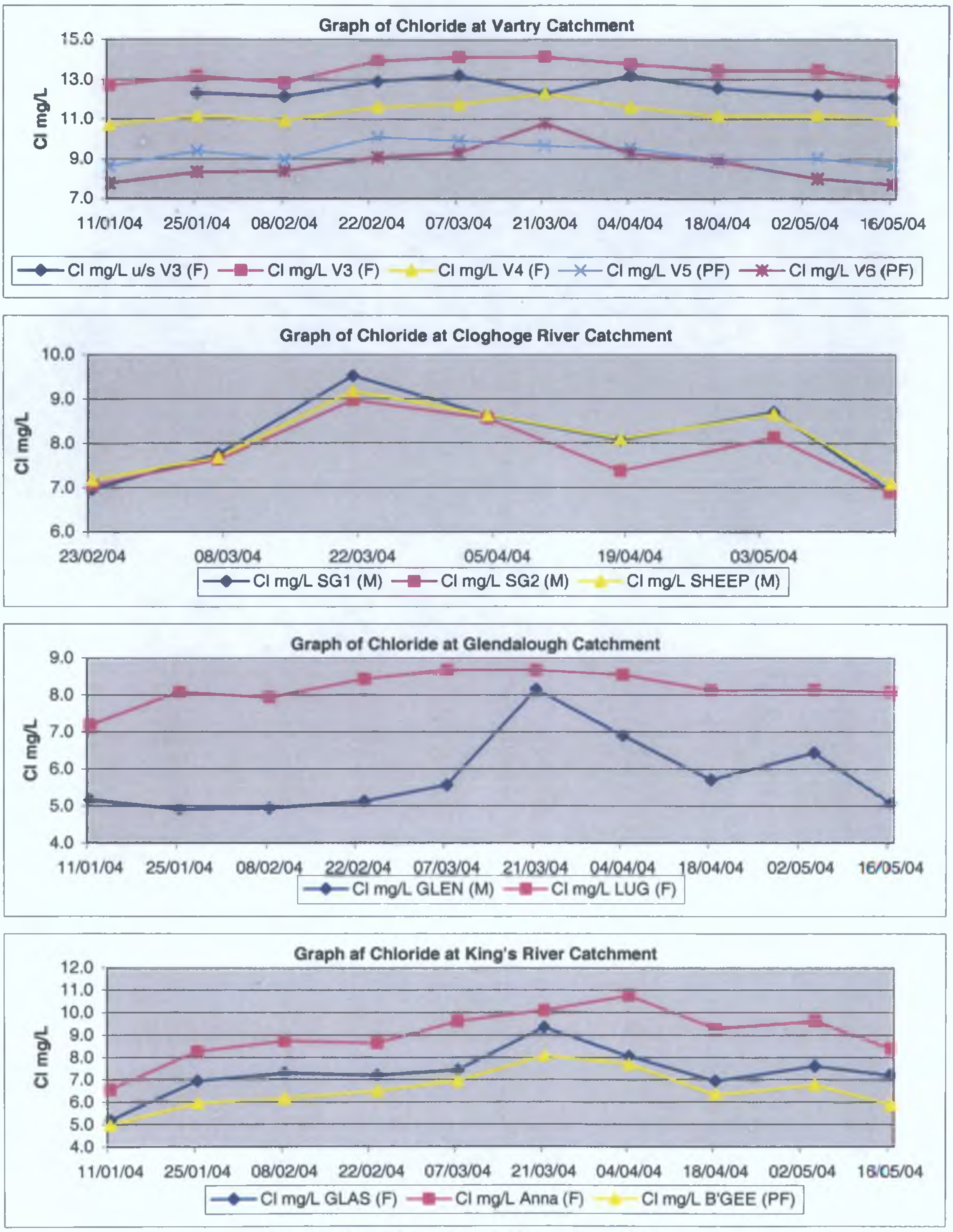


Fig.5.10: Chloride at Sampling Sites

5.6 Sulphate

The most important anion associated with acidification of surface waters is sulphate (section 2.1.1). There is considerable marine influence in Ireland, particularly on the western seaboard, and it is necessary to take account of that fraction of the sulphate of marine origin and consider only the non-marine or 'excess' sulphate.

Median concentrations of sulphate and non-marine sulphate were higher in streams in afforested catchments than streams draining moorland areas (Fig. 5.11). This is presumably due to the scavenging capacity of the forest canopy, the greater the percentage of mature canopy the greater the scavenging effect. The sulphate may have arisen from wet deposition or resulted from the flushing of dry deposition into the streams.

ANOVA statistical analysis indicated that there were significant differences among mean sulphate concentrations at the Vartry sites (Appendix B-1). T-test analysis pointed to significant differences between the heavily afforested V4 site and the partially afforested V6 site. No significant differences were observed between the afforested u/s V3 site and the afforested and clearfelled V3 site. No significant differences were observed at the moorland tributaries of the Cloghoge River (ANOVA) (Appendix B-2) or at Glendalough Lake Upper (t-test) between the afforested Lugduff and the moorland Glenealo rivers(Appendix B-3). ANOVA analysis indicated there were no significant differences among the systems in the King's River catchment or between the Annalecka and either of the Ballinagee or Glasnadade streams. However, t-test analysis pointed to a significant difference in the mean sulphate concentration between the partially afforested Ballinagee River and its afforested tributary, the Glasnadade Brook (Appendix B-4).

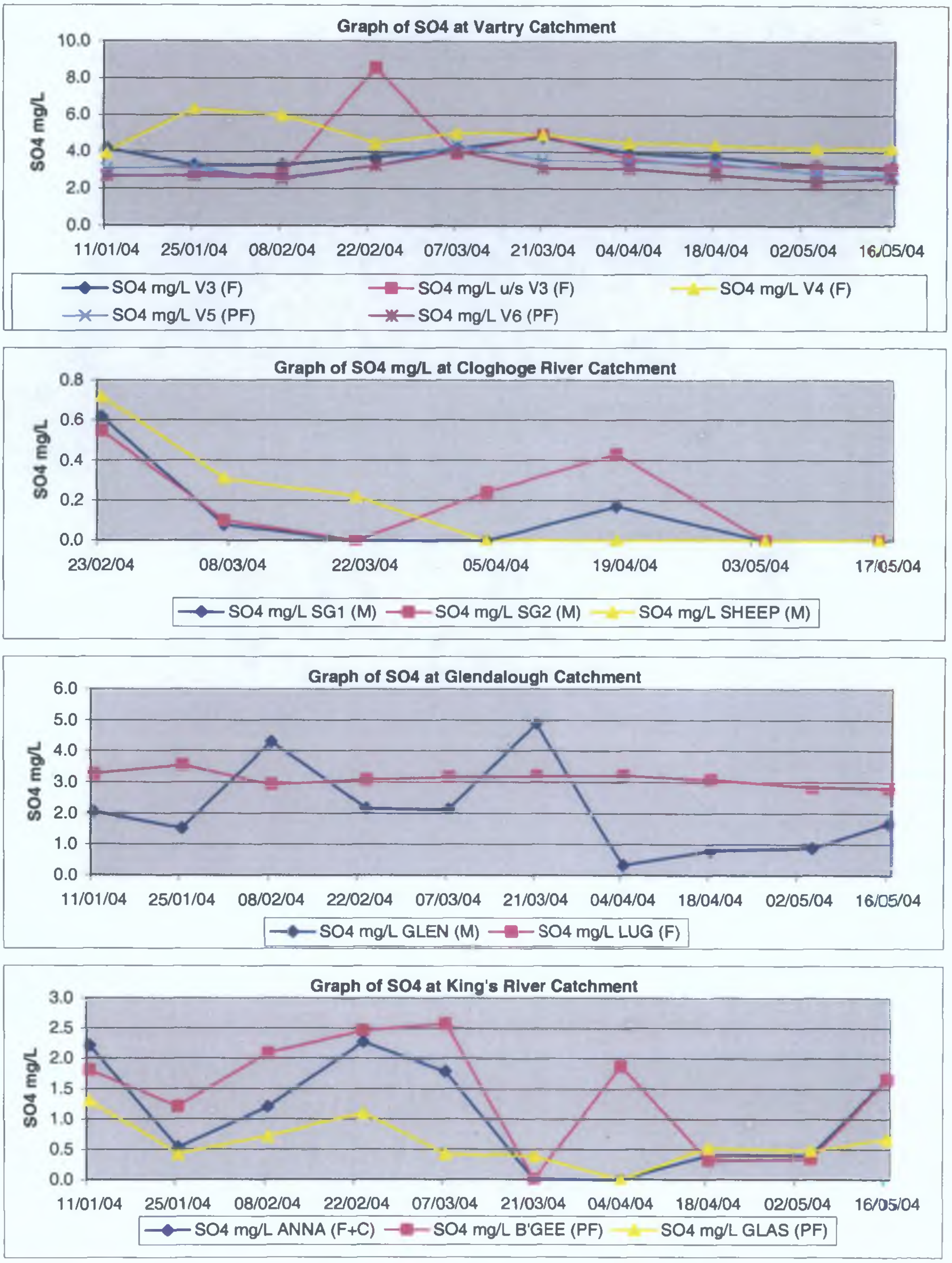


Fig. 5.11: Sulphate at Vartry, Cloghoge, Glendalough & King's River Catchments

No clear seasonal pattern is evident in the concentrations of non-marine sulphate in the streams and the levels recorded may be closely related to sulphate deposition in the days immediately prior to or coinciding with the sampling date. Tables 5.16 to 5.19 document the non-marine values for SO4 at each of the catchments. Figure 5.12 illustrates the trends of this data.

	NM SO4 mg/L V3 (F+C)	NM SO4 mg/L u/s V3 (F)	NM SO4 mg/L V4 (F)	NM SO4 mg/L V5 (PF)	NM SO4 mg/L V6 (PF)
11/01/04	2.89	NM	2.86	2.24	1.91
25/01/04	1.95	1.65	5.21	2.25	1.87
08/02/04	1.99	1.51	4.89	1.60	1.73
23/02/04	2.33	7.28	3.29	2.23	2.35
07/03/04	2.78	2.58	3.86	3.34	3.11
21/03/04	3.38	3.68	3.68	2.59	2.05
04/04/04	2.54	2.28	3.32	2.50	2.14
18/04/04	2.35	1.96	3.20	2.49	1.85
04/05/04	1.88	1.96	3.07	1.95	1.60
16/05/04	1.87	1.83	3.06	1.86	1.81

Table 5.16: Non-Marine Sulphate at Vartry Catchment

	NM SO4 mg/L SG1 (M)	NM SO4 mg/L SG2 (M)	NM SO4 mg/L SHEEP (M)
23/02/04	-0.09	-0.17	-0.02
07/03/04	-0.71	-0.68	-0.48
21/03/04	<-0.93	<-0.87	-0.72
04/04/04	<-0.83	-0.64	<-0.83
18/04/04	-0.66	-0.33	<-0.78
04/05/04	<-0.84	<-0.78	<-0.84
16/05/04	<-0.66	<-0.66	<-0.68

Table 5.17: Non-Marine Sulphate at Cloghoge River Catchment

	NM SO4 mg/L LUG (F)	NM SO4 mg/L GLEN (M)
11/01/04	2.55	1.53
25/01/04	2.72	1.03
08/02/04	2.12	3.80
23/02/04	2.22	1.64
07/03/04	2.28	1.56
21/03/04	2.31	4.05
04/04/04	2.33	-0.37
18/04/04	2.26	0.21
04/05/04	2.02	0.23
16/05/04	1.99	1.16

Table 5.18: Non-Marine Sulphate at Glendalogh Lake Upper Catchment

	NM SO4 mg/L ANNA (F+C)	NM SO4 mg/L GLAS (F)	NM SO4 mg/L B'GEE (PF)
11/01/04	1.55	0.78	1.30
25/01/04	-0.32	-0.29	0.60
08/02/04	0.30	-0.03	1.46
23/02/04	1.40	0.35	1.80
07/03/04	0.80	-0.34	1.87
21/03/04	-0.99	-0.58	0.78
04/04/04	-1.06	-0.77	1.08
18/04/04	0.55	-0.19	-0.33
04/05/04	0.59	-0.30	-0.35
16/05/04	0.82	-0.08	1.06

Table 5.19: Non-Marine Sulphate at King's River Catchment

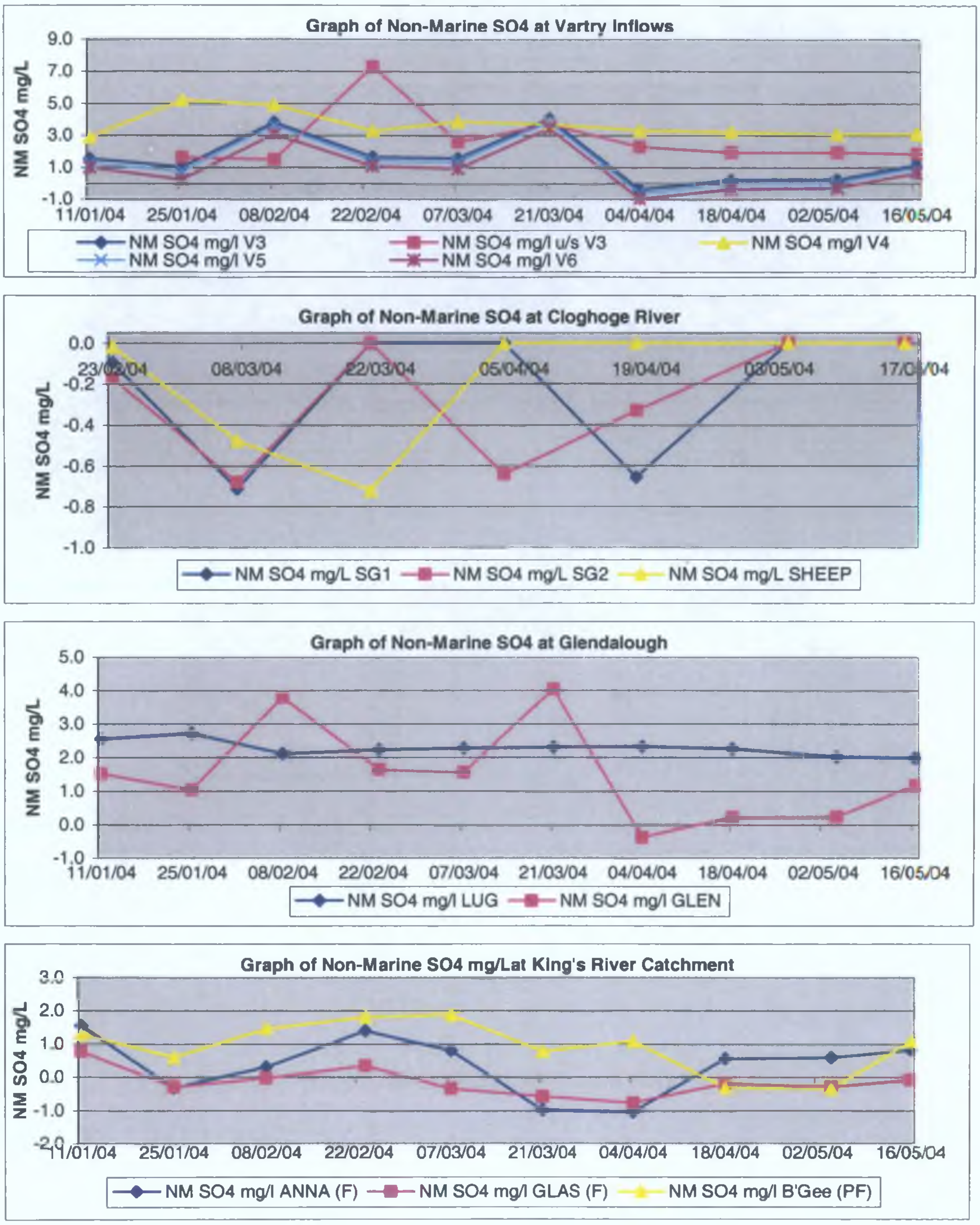


Fig. 5.12: Non-Marine Sulphate at Sampling Sites

5.7 TON

Concentrations of Total Oxidised Nitrogen (NO_3^- & NO_2^-) were very low in all sites except for the surface waters within the Varty Reservoir Catchment where median TON values ranged from 0.5 to 1.2mg/L (Fig. 5.13). Elevated levels at the afforested Vartry Inflows are indicative of nitrogen saturation in the catchment soil and may be as a result of increased nitrification due to the conifer plantations or due to the spreading of artificial fertiliser. ANOVA statistical analysis indicated highly significant differences in mean TON concentrations between the sites within the Vartry system (Appendix B-1). Significant differences (t-test) were noted between the afforested V4 site and the partially afforested V6 site.

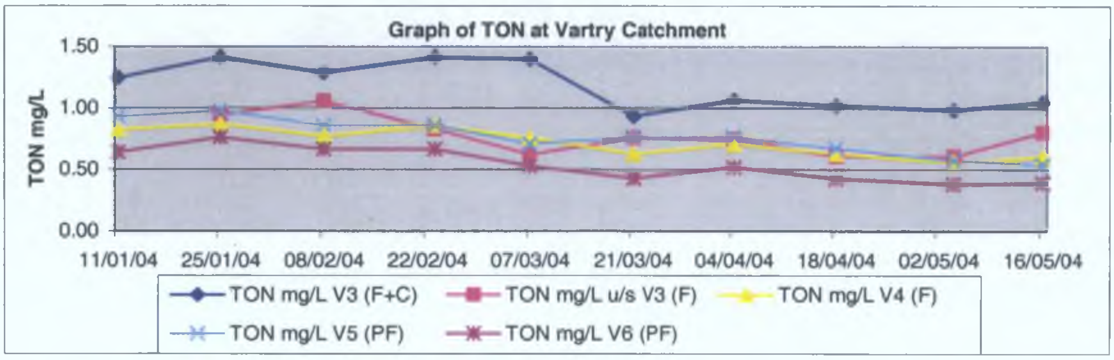


Fig. 5.13: Total Oxidisable Nitrogen (TON) at Vartry Catchment

There was a difference in TON values on V3 and upstream of V3 on the Vartry system. Between the two sampling sites are both afforested and clearfelled land. Significant differences were also observed (t-test) between the afforested upstream of V3 (u/s V3) and the afforested and clearfelled V3 site (Fig. 5.14).

At Glendalough Lake Upper Catchment, there was a significant difference (t-test) in the TON values between the afforested Lugduff River and the moorland Glenealo River (Fig. 5.14) (Appendix B-3). TON concentrations at the King's River tributaries were generally low while values at the Cloghoge River tributaries were very low, generally less than the detection limits of 0.01 mg/L TON.

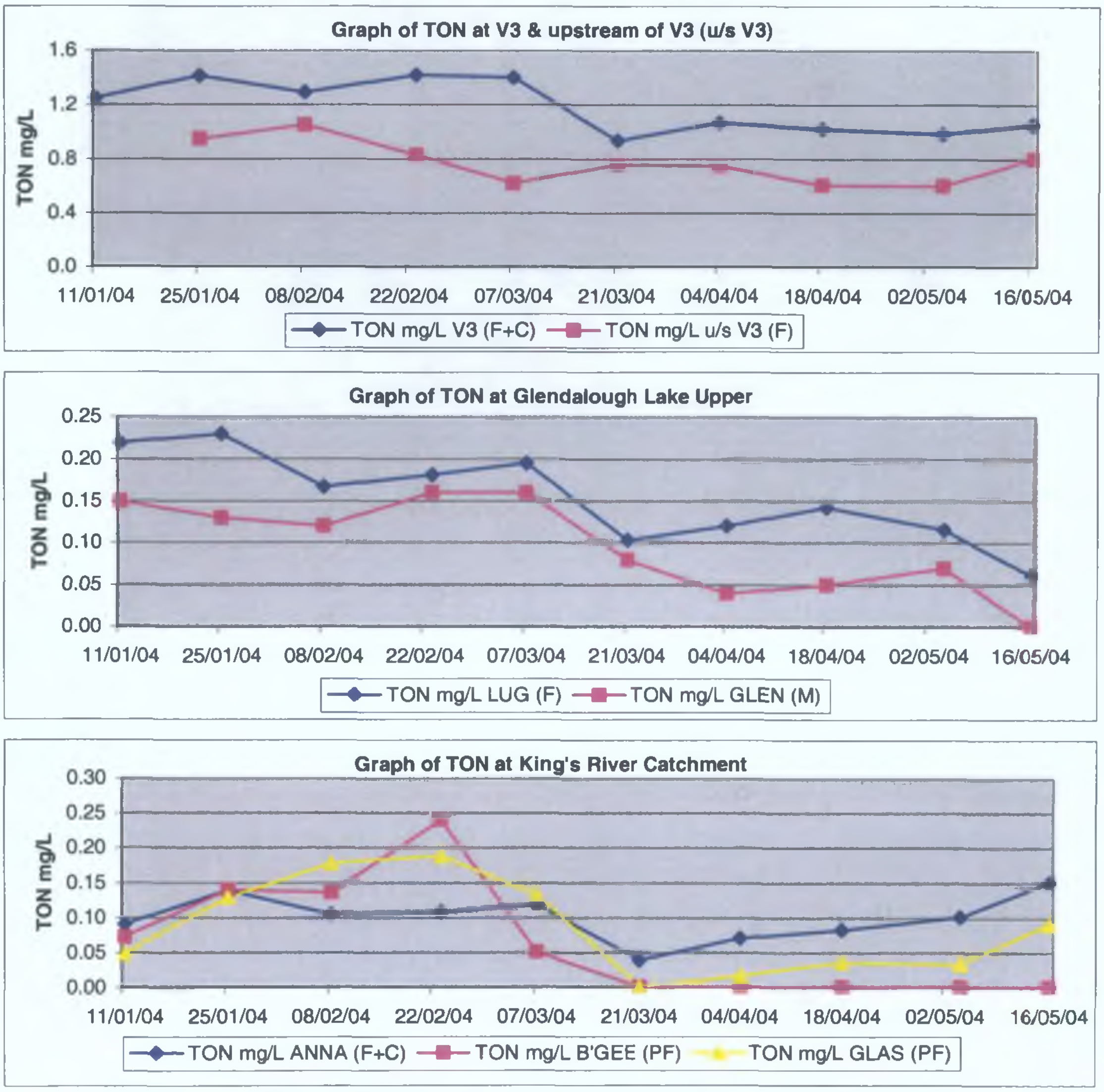


Fig. 5.14: Total Oxidisable Nitrogen (TON) at Sampling Sites

5.8 Calcium

Streams draining Palaeozoic sediments such as in the Vartry catchment had median calcium concentrations greater than 1mg/L. Within each of the four catchments, streams draining afforested areas had lower calcium concentrations than comparable moorland streams due to ion exchange with hydrogen ions. ANOVA analysis indicated highly significant differences for calcium concentrations among the Vartry sites (Appendix B-1). T-test analysis pointed to significant differences between the afforested site upstream of V3 (u/s V3) and the afforested and clearfelled V3 site and also between the afforested V4 site and the partially afforested V6 site.

The lowest calcium values of the ten sampling dates were recorded on 21/03/04, the wettest period of the investigation. This phenomenon was less noticeable on the Vartry catchment, underlain by marine sediments, except for the heavily afforested V4 site (Fig. 5.15).

The afforested Lugduff River in the Glendalough catchment, draining Palaeozoic sediments, had the lowest median calcium concentration (0.60mg/L Ca) of any site in this study. It did not record a value greater than 0.72mg/L Ca during the investigation. This afforested river had considerably less calcium (Fig. 5.15) and non-marine calcium (Fig. 5.16) than the comparable moorland Glenealo River within the same catchment (t-test).

Other sites, both afforested and moorland, recorded values less than 1mg/L calcium on some sampling occasions, though these were draining granite (Fig. 5.15 & 5.16).

Calcium concentrations in the tributaries of the Cloghoge River (SHEEP, SG1 and SG2) displayed the greatest range of values. Non-Marine calcium (*i.e.* catchment-derived calcium) was highest on Palaeozoic sediments (Tables 5.20 to 5.23).

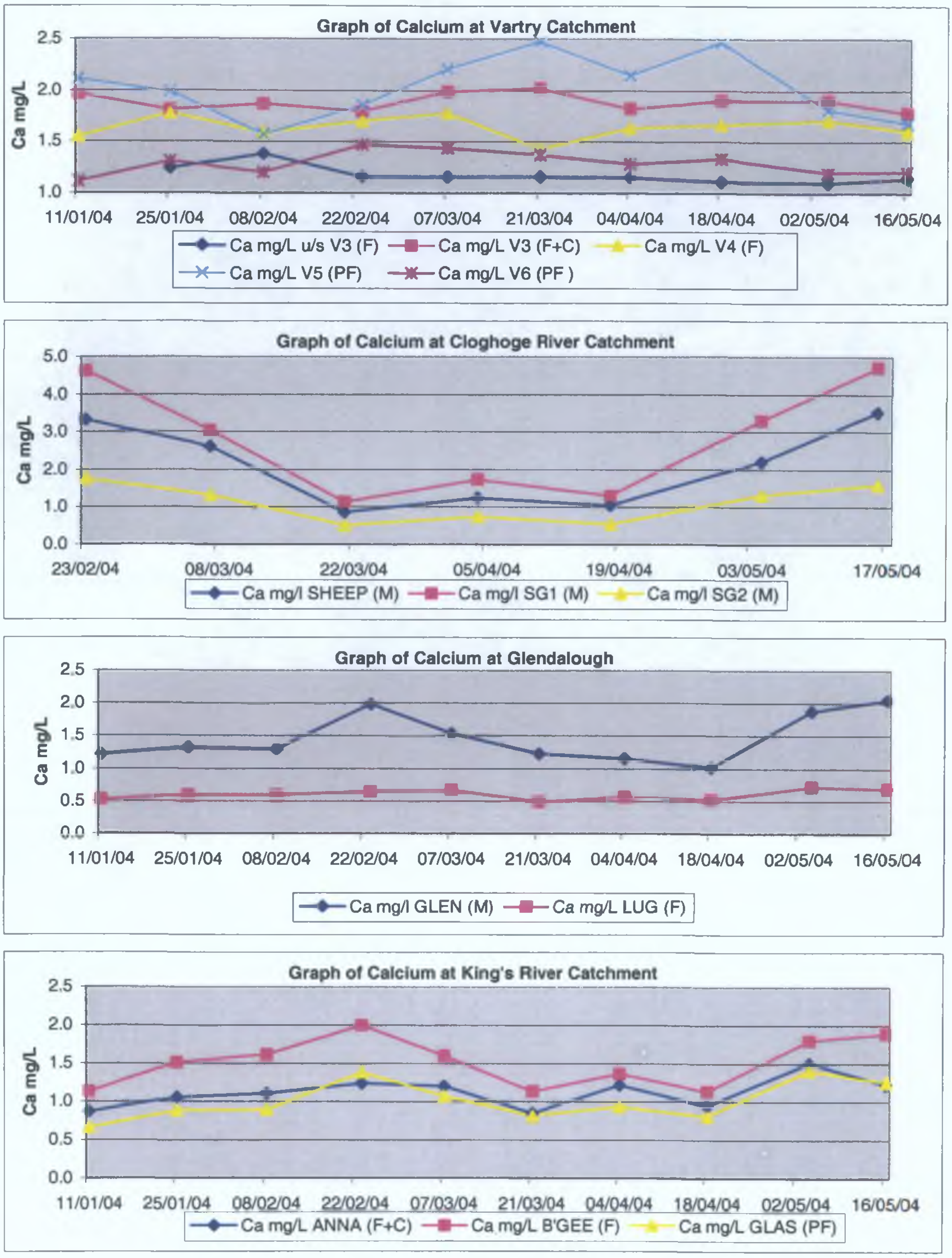


Fig. 5.15: Calcium at Sampling Sites

	NM Ca mg/L u/s V3 (F)	NM Ca mg/l V3 (F+CF)	NM Ca mg/L V4 (F)	NM Ca mg/L V5 (PF)	NM Ca mg/L V6 (PF)
11/01/04	NM	1.50	1.16	1.78	0.82
25/01/04	0.78	1.33	1.37	1.63	1.00
08/02/04	0.93	1.39	1.18	1.23	0.89
23/02/04	0.68	1.28	1.27	1.48	1.13
07/03/04	0.67	1.47	1.34	1.84	1.09
21/03/04	0.70	1.50	0.97	2.10	0.97
04/04/04	0.71	1.31	1.20	1.78	0.94
18/04/04	0.65	1.40	1.25	2.13	1.01
04/05/04	0.65	1.40	1.29	1.47	0.90
16/05/04	0.69	1.31	1.19	1.35	0.92

Table 5.20: Non-Marine Calcium at Vartry Catchment

	NM Ca SHEEP (M)	NM Ca SG1 (M)	NM Ca SG2 (M)
23/02/04	3.05	4.37	1.51
07/03/04	2.32	2.75	1.03
21/03/04	0.51	0.78	0.18
04/04/04	0.91	1.41	0.42
18/04/04	0.73	1.01	0.26
04/05/04	1.88	2.98	1.00
16/05/04	3.26	4.46	1.32

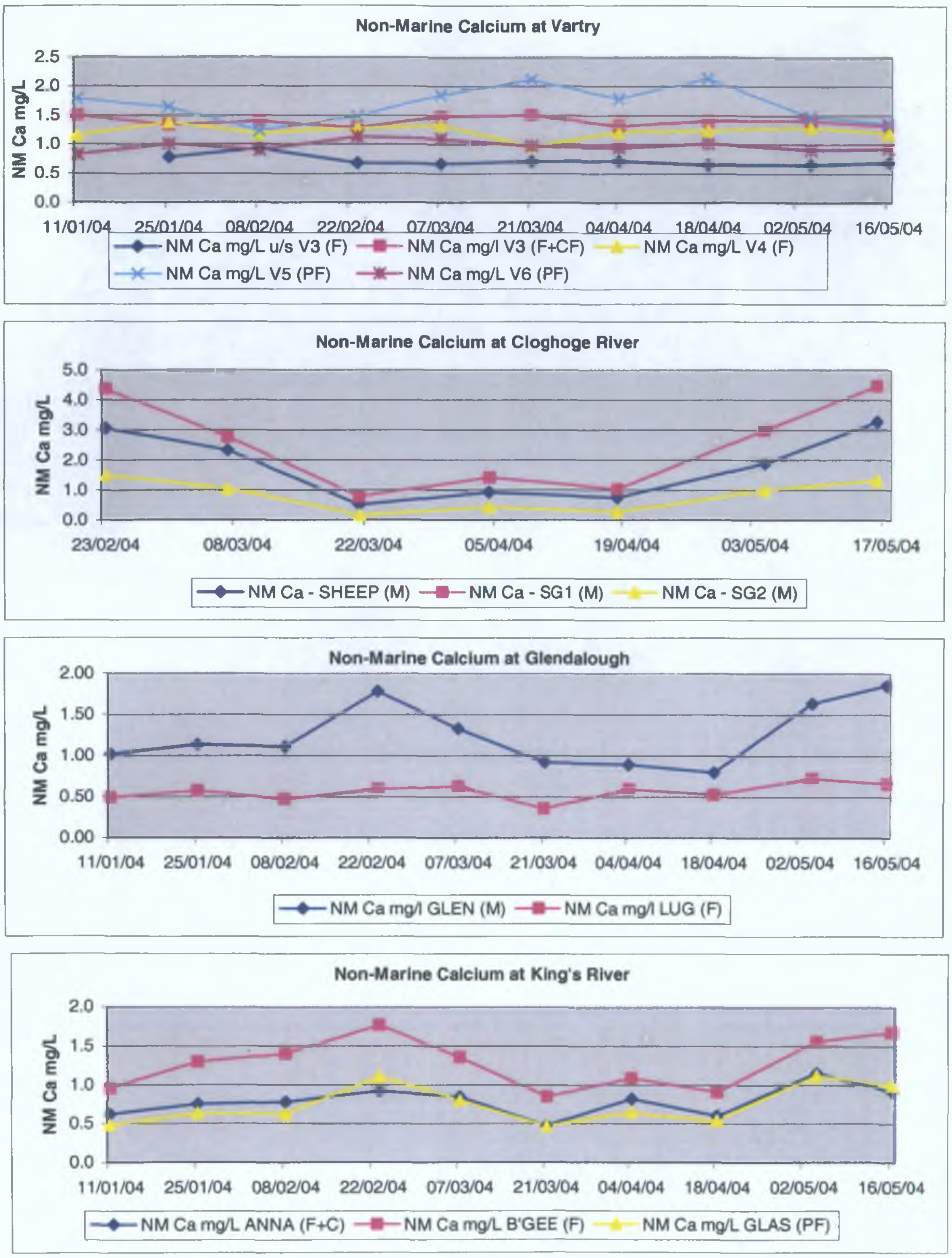
Table 5.21: Non-Marine Calcium at Cloghoge River Tributaries

	NM Ca mg/l GLEN (M)	NM Ca mg/l LUG (F)
11/01/04	1.02	0.48
25/01/04	1.13	0.57
08/02/04	1.11	0.47
23/02/04	1.78	0.59
07/03/04	1.32	0.62
21/03/04	0.91	0.35
04/04/04	0.89	0.59
18/04/04	0.79	0.52
04/05/04	1.63	0.72
16/05/04	1.85	0.65

Table 5.22: Non-Marine Calcium at Glendalough Catchment

	NM Ca ANNA (F+C)	NM Ca B'GEE (F)	NM Ca GLAS (PF)
11/01/04	0.62	0.95	0.48
25/01/04	0.75	1.29	0.63
08/02/04	0.77	1.39	0.62
23/02/04	0.91	1.76	1.11
07/03/04	0.84	1.35	0.80
21/03/04	0.47	0.84	0.47
04/04/04	0.82	1.08	0.64
18/04/04	0.60	0.90	0.54
04/05/04	1.14	1.55	1.12
16/05/04	0.91	1.67	0.98

Table 5.23: Non-Marine Calcium at King's River Tributaries


Non-Marine Calcium at Vartry

Non-Marine Calcium at Cloghoge River

Non-Marine Calcium at Glendalough

Non-Marine Calcium at King's River

Fig. 5.16: Non-Marine Calcium at Sampling Sites

5.9 Other Base cations

The highest magnesium, sodium and potassium concentrations were found in the streams draining Palaeozoic sediments such as in the Vartry catchment. In contrast, streams draining granite had values generally less than those draining marine sediments. Within each catchment, streams draining afforested areas had higher sodium concentrations due to scavenging of the forest canopy (Fig. 5.17). The afforested V3 site on the Vartry system had the highest sodium concentration at 7.5mg/L while the moorland Glenealo River in the Glendalough catchment recorded the lowest sodium concentration at 3.6mg/L.

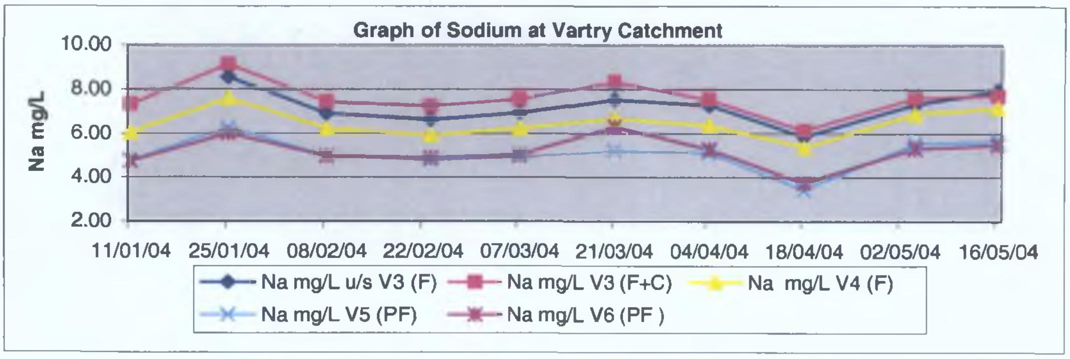


Fig. 5.17: Sodium at Vartry Catchment

While the Vartry system had the greatest median concentrations of magnesium, the next highest values were recorded on the moorland tributaries of the Cloghoge River. Afforested sites such as those in the King's River catchment and the Lugduff River all had median values less than 0.8mg/L. Magnesium can partly but not completely compensate for the lack of calcium.

Like the other cations, the highest potassium concentrations were found on the marine sediments of the Vartry system. The moorland tributaries of the Cloghoge River had similar values. The Lugduff River had the lowest median concentration of potassium at 0.14mg/L.

Some of the highest concentrations measured for these cations were recorded in the last two sampling periods, during drier conditions (Fig. 5.18).

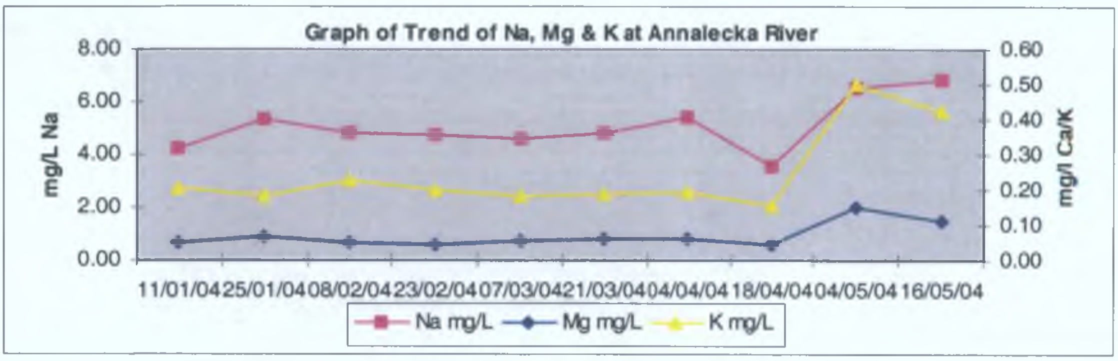


Fig. 5.18: Trends of base cations at Vartry Catchment

6. DISCUSSION

The objective of this investigation was to determine the extent of forestry-induced artificial acidification of acid-sensitive surface waters in the Wicklow Mountains. The impact on stream chemistry of geological substrate, soils, weather and extent of coniferous plantation was considered in this, one of the wettest areas of the country. Sites were selected on the headwaters of recognised salmonid and trout nursery streams and samples were taken for chemical analysis every fortnight from January to May inclusive. This is the time when young salmonid species are at their most sensitive to acidification and it is also during the wettest part of the year when wet acidic deposition could be at its greatest.

Thirteen streams and tributaries in four acid-sensitive catchments were selected for sampling. These surface waters drained catchments with varying amounts of afforestation, harvested blocks and moorland. Statistical analysis (ANOVA and t-test) of the chemical results demonstrated that streams containing afforested or harvested areas were subject to significantly greater acidification when compared to moorland or partially afforested sites within the same catchment.

6.1 Correlations between weather, flow & hydrochemical conditions

High rainfall was strongly negatively correlated with pH and alkalinity for the Ballinagee River and moderately so for the Annalecka (*i.e.* higher rainfall led to decreased pH and alkalinity values) (Appendix A). There was a moderate positive correlation between rainfall and flow at both rivers (*i.e.* higher rainfall led to greater flows) (Appendix A). A strong correlation was associated between flow and pH, alkalinity, aluminium, colour and calcium within the King's River catchment (Appendix A).

On one sampling occasion conductivities in all streams increased by several factors above the normal range, probably due to the exceptionally dry preceding two weeks. The dry spell afforded soil waters longer retention times, thus allowing for a greater accumulation of base cations (*e.g.* calcium and magnesium) in the soil from the normal weathering processes. These cations are important in imparting buffering capacity, and consequently the alkalinity increased during drier spells. Decreased runoff reduced the amount of humic and fulvic acids in the soil water and resulted in the lowest colour readings at most sites during the study. In contrast, the greater hydraulic loading during wetter months results in increased discharge and reduced residence time. Colour values increased during greater rainfall. The highest pH and alkalinity readings and lowest total aluminium values of the entire study period were recorded on these dates, as illustrated for the Ballinagee River (Fig. 6.1).

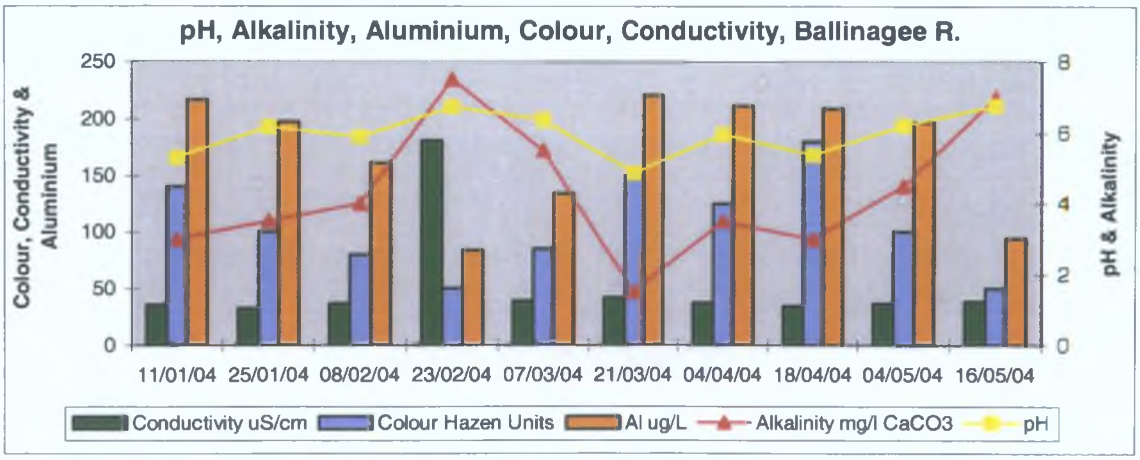


Fig. 6.1: pH, alkalinity, aluminium, conductivity & colour, Ballinagee R.

March had the highest number of hours of easterlies during the investigation (Fig. 3.6), the wettest fortnight (21/03/04) and the date of lowest pH and alkalinity values. Easterly airflow and rainfall decreased after this sampling date and pH and alkalinity gradually increased correspondingly. Rain after dry weather seemed to trigger organic acidity and an easterly airflow caused increases in non-marine sulphate. Met Éireann supplied wind data as monthly totals, therefore easterly wind correlations with rainfall and pH data (fortnightly results) could not be calculated.

Time constraints prevented the taking of biological kick-samples. Data on the populations and absence or presence of acid-sensitive species would have complemented the chemical data in ascertaining the full impact on aquatic life, the main tenet of the Water Framework Directive (2000/60/EC). Continuous pH and flow meters would have enabled the recording of specific acid episodes, yielding more information on the extent of 'acid-shocks'. Laboratory and time constraints prevented the analysis of labile monomeric aluminium, the form that is most toxic to fish.

6.2 Afforested Streams V Moorland Streams

With regard to the Forestry and Water Quality Guidelines of 2000, all sites tested during this project (both afforested and moorland) would be classified as being sensitive to acidification. All thirteen streams recorded values less than 10mg/L alkalinity or pH 5.5 at least once. The close relationship between pH, alkalinity and total aluminium was apparent at all sites.

Statistical analysis (ANOVA and t-test) demonstrated that afforested streams had lower pH and alkalinity values and higher total aluminium concentrations than comparable moorland or partially afforested sites within the same catchment. Sites with increasing proportions of afforested catchment experienced greater acidification. The effect of scavenging by the forest canopy was evident as significantly higher concentrations of chloride and non-marine sulphate were recorded at afforested sites. As it is the needles and branches that scavenge acidifying pollutants from the atmosphere, it follows that the effect will be greater with older or more mature forests.

The prevailing hydrochemical conditions at most of the afforested sites, particularly during wetter periods, could have had significant adverse implications for aquatic life. As described in Section 2.1.3, the effects on salmonids depend on the stage in the life cycle of the fish with salmonid eggs and juveniles being the most sensitive to low pH values. Concentrations of labile monomeric aluminium greater than 40μg/L are known to be toxic to salmonids. Acidification can cause stresses on aquatic carnivores and insect-eating fish by decreasing numbers of species like mayflies, craneflies and midges. The food supply for higher fauna can also be altered and decreased.

The heavily afforested Annalecka and Lugduff Rivers regularly recorded values less than pH 5 and on eight occasions the Lugduff River had pH values one unit less (*i.e.* ten times more acidic) than the comparable moorland Glenealo River. The Lugduff is strikingly clear, mainly because the humic and fulvic substances that normally colour the water precipitate out and fall to the bottom when the water becomes acidic (Elvingson &

Ågren, 2004). Decomposition slows down, which means that leaves and other organic matter often collect on the water body beds.

The inflows to the Vartry Reservoir (all afforested to some degree) were the only sites that recorded values greater than pH 5.5 (the minimum level desirable for salmonid waters) on all occasions, highlighting the buffering capacity afforded to the catchment by the underlying marine sediments.

The acidification status of the streams in the King's River, Glendalough and the Vartry Reservoir Inflows has changed little over the last five years when compared to data from the Eastern Regional Fisheries Board (ERFB) and Three Rivers Project (Appendix D).

The moorland tributaries of the Cloghoge River were the only streams where alkalinity values greater than 10mg/L as $CaCO_3$ were recorded, and these occurred during drier periods only. This is the alkalinity value below which sites are designated as acid-sensitive according to the Irish Forest Service and the EPA. Alkalinity values increased during low rainfall (and reduced runoff) conditions and decreased towards zero with increasing acidity during wetter periods. Organic acidity largely accounted for pH changes during high flows in the moorland tributaries of the Cloghoge River; these acid episodes were also associated with higher colour values.

The afforested tributaries of the King's River and the Lugduff River regularly exceeded the Mandatory Limit for Dinking Water for aluminium (200µg/L Al, 98/83/EC). Total aluminium at the Lugduff was nearly twice that of the moorland Glenealo River and it also recorded the highest value of the entire investigation at 345µg/L Al. The effect of high concentrations of total aluminum in the Lugduff may be exacerbated by the fact that the Lugduff River had the lowest median calcium concentration of the investigation at 0.6mg/L. The roots of conifer trees remove base cations such as calcium and magnesium from the soil solution and lower values of these ions in afforested streams was demonstrated by statistical analysis.

The importance of calcium in moderating the effects of high aluminium concentrations at low pH values has been shown (Muniz and Leivestad, 1980). The adverse physiological effects of acidification on fish are the result of a complex interaction of low pH levels, elevated metal concentrations (principally aluminium) and low calcium concentrations. The effect of hydrogen ion and aluminium toxicity are most pronounced when calcium concentrations are less than 1mg/L (Bowman, 1991). At concentrations greater than 1 mg/L of calcium the toxic effect is moderated. The Lugduff River, with very low pH and calcium levels and high aluminium concentrations, would pose a very serious threat to aquatic organisms and acid-sensitive species alike.

6.3 Harvested Streams V Afforested Streams

Due to the ability of vegetation, particularly trees, to utilise nutrients from the soil in the surrounding area, nutrient levels are generally low in streams draining mature forests. Following clearfelling and removal of vegetation however, nutrients such as nitrogen compounds are released and leached into streams *via* surface or subsurface flow. High concentrations of nitrate, which convert to nitrite, are undesirable for public health and can affect salmonid fish growth (nitrates) or be toxic (nitrites) (EPA, 2001).

A high correlation between flow and TON values was noted for the Annalecka River (partly clearfelled) than the Ballinagee (afforested). This is similar to the Vartry Reservoir inflow V3 where significant differences in pH and TON values were demonstrated (t-test) between an afforested site upstream (u/s V3) of a mixed harvested and afforested sampling site (V3).

The site downstream of the clearfelled area (V3) had consistently higher pH, alkalinity and colour values than the upstream site (u/s V3), indicating possible hydrogen ions being converted and bases generated in the presence of organic matter (Hildrew and Ormerod, 1995). There were significant differences (t-test) noted between the afforested site upstream of V3 (u/s V3) and V3 itself (afforested and clearfelled) for pH, chloride, aluminium and TON. It is possible that nitrogen is being leached from the soil of the harvested area and increasing concentrations of TON at the site downstream of the clearfelled area (V3).

The increase in pH downstream of the clearfelled area appears to be in agreement with international findings. In one study in North America, water quality became less acidic up to two years after clearfelling, after which pH returned to pre-felling levels (Pierce *et al*, 1993). Closer to home, results from a COFORD funded study carried out by the Forest Ecosystem Research Group (FERG), UCD, at Cloosh, Co. Galway, also has shown a consistent and immediate increase in pH of stream water after clearfelling, which was sustained for at least a year (T. Cummins, FERG, UCD, *pers. comm.*). There is some evidence that clearfelling indirectly affects pH through the introduction of large amounts of bark and other organic debris into the stream system. It can either lower pH by increasing the concentration of organic acids, as well as increasing carbon dioxide inputs due to respiration (Peters *et al*, 1976) or increase pH whereby hydrogen ions are converted and bases are generated in the presence of organic matter (Hildrew and Ormerod, 1995). In the case of Vartry Reservoir Inflow 3, a rise in pH downstream of the clearfelled area was observed on all occasions.

6.4 Moorland Streams V Harvested Streams

None of the four catchments contained streams draining both moorland and harvested sub-catchments. Moorland sites generally had higher alkalinity and pH values than catchments of mixed afforested and harvested areas.

Unlike the streams draining harvested areas (V3 and the Annalecka River), the non-forested catchment of the Cloghoge River tributaries recorded alkalinity values greater than 10mg/L during drier spells, though they were episodically acidic during wetter periods. These peat covered moorland sites (SG1, SG2 and SHEEP) were prone to natural organic acid episodes, indicating the sensitivity of such upland sites to afforestation.

A considerable amount of the calcium, sulphate and magnesium at the harvested Vartry site V3, on marine sediments, was catchment derived. Sulphate and nitrate concentrations were very low at the moorland sites, highlighting the absence of scavenging by conifers.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

This investigation examined the hydrochemical data of upland soft water streams in the Wicklow Mountains that are nurseries for brown trout (*Salmo trutta L.*). Consideration was also given to geographical and meteorological conditions. On inspection of the chemical data contained within this report, all thirteen sites examined would be designated as acid-sensitive according to the Forest Service's guidelines of 2000. These sites should not undergo further planting of conifer species. Extensively afforested sites experienced highly acidic episodes, usually during periods of easterly airflow and high rainfall.

Statistical analysis of chemical and meteorological data showed that afforested streams were artificially impacted by acidification during periods of high rainfall, greater flows and easterly airflows, concurring with domestic and international findings. This was underlined by the poor buffering capacity of these surface waters (all less than 10mg/L $CaCO_3$). Only the moorland Cloghoge River tributaries recorded values greater than 10mg/L $CaCO_3$ and only during drier periods. The most acidic value was recorded at the afforested Annalecka River, at pH 4.27, which also had the highest median total aluminum concentration at 254μg/L Al. The Lugduff River, also densely afforested, had a median pH of 5.16 and recorded the highest total aluminum concentration of the study at 345μg/L Al.

It could not be claimed that the same level of acidification due to afforestation would be experienced in all acid-sensitive areas of Ireland. The proportion of afforestation, underlying geology, soils, topography and weather are all critical to the overall effect. The rivers and streams sampled in this survey are located on poorly buffered soils high in the Wicklow Mountains, one of the wetter parts of the country. The east coast of Ireland would also be more likely to experience greater acidic loads when easterlies flow from the more industrialised continental Europe. Though afforested sites located on the west coast of Ireland would not experience the same loads of pollutants as the east coast, these conifer plantations would receive considerable amounts of marine sulphates (due to scavenging) from the 'sea-salt' effect.

The potential susceptibility of acid-sensitive surface waters to the effects of forest-mediated acidification in County Wicklow has been highlighted. This report contributes to a growing body of evidence that a similar effect would be experienced in other acid-sensitive areas of Ireland.

7.2 Recommendations

With the exception of reducing acidifying emissions at source, there are few tried and tested options available to remedy acidified surface waters. The application of liming materials to catchments and direct addition of lime to water bodies to mitigate acidification of freshwaters has been widely practiced worldwide for decades. Liming has also been shown to result in negative impact on both floral and faunal species (section 2.4.2).

These additions (liming) could therefore be classified as pollutants under the WFD. However, the application of liming materials to surface waters that have become acidified with the purpose of restoring them to 'good surface water chemical status' could be viewed as a mitigation measure under the WFD. As yet, no clear policy has emerged regarding the use of lime in catchments with reference to the WFD.

As conifer plantations sown in acid-sensitive areas from the mid 1980s onwards continue to mature, artificial acidification is sure to have a greater impact on aquatic life in nursery and angling streams in acid-sensitive locations in Ireland. A much greater emphasis by Coillte on adherence to the Forest Service's guidelines of achieving 20 percent broadleaf within plantations would have some welcome benefits, not just in terms of acidification, but also in relation to visual appearance and biodiversity.

Four afforested sites had median total aluminium concentrations greater than 200µg/L, advocating the consideration of labile monomeric aluminium (toxic level greater than 40µg/L) in association with pH and alkalinity in future designation of acid-sensitivy.

Very little research on remediation of acidified surface waters has been undertaken in Ireland. The most promising options for application in Ireland include stream dosers, spreading of lime on forest floors and riparian zones and direct addition of limestone to stream beds. The heavily afforested Lugduff River at Glendalough, which extensive monitoring and research has documented as being significantly acidified for nearly twenty years (Appendix D), might be a good place to start.

The data within this investigation coupled with previous data in Ireland should contribute to a review of the Forestry and Water Quality Guidelines, particularly in relation to the criteria used for the designation of acid-sensitivity, recommended forestry practices in these areas and remediation measures.

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APPENDIX A

CORRELATIONS

Annalecka River:

	Rainfall	Flow	pH	Alkalinity	Conductivity	Colour	TON	SO4	Al	Ca
Rainfall	1.000									
Flow	0.604	1.000								
pH	-0.675	-0.629	1.000							
Alkalinity	-0.575	-0.627	0.953	1.000						
Conductivity	-0.421	-0.157	0.674	0.581	1.000					
Colour	0.658	0.855	-0.846	-0.770	-0.425	1.000				
TON	-0.285	-0.798	0.536	0.654	0.016	-0.616	1.000			
SO4	-0.076	-0.336	0.508	0.661	0.470	-0.311	0.435	1.000		
Al	0.687	0.497	-0.932	-0.853	-0.748	0.789	-0.338	-0.523	1.000	
Ca	-0.735	-0.677	0.717	0.609	0.142	-0.771	0.395	-0.024	-0.577	1.000

Ballinagee River:

	Rainfall	Flow	pH	Alkalinity	Conductivity	Colour	TON	SO4	Al	Ca
Rainfall	1.000									
Flow	0.542	1.000								
pH	-0.716	-0.932	1.000							
Alkalinity	-0.705	-0.780	0.906	1.000						
Conductivity	-0.438	-0.306	0.529	0.759	1.000					
Colour	0.337	0.813	-0.853	-0.826	-0.580	1.000				
TON	-0.055	-0.538	0.583	0.665	0.742	-0.742	1.000			
SO4	-0.229	-0.720	0.614	0.667	0.404	-0.681	0.592	1.000		
Al	0.496	0.643	-0.775	-0.929	-0.792	0.831	-0.754	-0.689	1.000	
Ca	-0.580	-0.791	0.906	0.878	0.621	-0.917	0.620	0.450	-0.802	1.000

Table A of Correlation Coefficients between various parameters

The following general categories indicate a quick way of interpreting a calculated correlation coefficient:

0.0 to 0.2	Very weak to negligible correlation
0.2 to 0.4	Weak, low correlation
0.4 to 0.7	Moderate correlations
0.6 to 0.8	Strong, high correlation
0.9 to 1.0	Very strong correlation

APPENDIX B-1

STATISTICS FOR VARTRY RESERVOIR INFLOWS

Anova: Single Factor pH

SUMMARY

Groups	Count	Sum	Average	Variance
pH-u/s V3 (F)	9	52.9	5.878	0.0255
pH-V3 (F/CF)	10	63.54	6.354	0.0107
pH-V4 (F)	10	58.67	5.867	0.0246
pH-V5 (PF)	10	62.86	6.286	0.0319
pH-V6 (PF)	10	63.68	6.368	0.0212

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2.5424	4	0.6356	**27.9546**	1.39E-11	**2.5837**
Within Groups	1.0004	44	0.0227			
Total	3.5428	48				

ALKALINITY

SUMMARY

Groups	Count	Sum	Average	Variance
Alk-u/s V3 (F)	9	22	2.44	0.1528
Alk-V3 (F/CF)	10	48.5	4.85	0.3917
Alk-V4 (F)	10	27.5	2.75	0.4583
Alk-V5 (PF)	10	49	4.9	1.2111
Alk-V6 (PF)	10	43.5	4.35	0.3361

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	53.3354	4	13.3339	**25.7351**	4.94E-11	**2.5837**
Within Groups	22.7972	44	0.5182			
Total	76.1327	48				

TOTAL ALUMINIUM

SUMMARY

Groups	Count	Sum	Average	Variance
Al-u/s V3 (F)	9	654.5995	72.73328	249.4769
Al-V3 (F/CF)	10	935.1427	93.51427	708.6706
Al-V4 (F)	10	935.1127	93.51127	873.2088
Al-V5 (PF)	10	452.9251	45.29251	933.5034
Al-V6 (PF)	10	557.3045	55.73045	519.9123

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	19039.68	4	4759.921	**7.1447**	0.00016	**2.5837**
Within Groups	29313.47	44	666.2153			
Total	48353.16	48				

Table B-1.1: ANOVA analysis for pH, Alkalinity and Total Aluminium, Vartry

Anova: Single Factor **COLOUR**

SUMMARY

Groups	Count	Sum	Average	Variance
Colour-u/s V3 (F)	9	135	15	62.5
Colour-V3 (F/CF)	10	330	33	51.1111
Colour-V4 (F)	10	105	10.5	30.2778
Colour-V5 (PF)	10	150	15	66.6667
Colour-V6 (PF)	10	205	20.5	141.3889

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3008.265	4	752.0663	**10.6573**	3.98E-06	**2.5837**
Within Groups	3105	44	70.5682			
Total	6113.265	48				

CHLORIDE

SUMMARY

Groups	Count	Sum	Average	Variance
Cl-u/s V3 (F)	9	112.71	12.5233	0.1986
Cl-V3 (F/CF)	10	134.49	13.449	0.2952
Cl-V4 (F)	10	113.46	11.346	0.2169
Cl-V5 (PF)	10	92.86	9.286	0.2598
Cl-V6 (PF)	10	87.65	8.765	0.8550

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	161.2922	4	40.3230	**109.3074**	2.93E-22	**2.5837**
Within Groups	16.23142	44	0.3689			
Total	177.5236	48				

TON

SUMMARY

Groups	Count	Sum	Average	Variance
TON-V3 (F/CF)	10	11.808	1.1808	0.0369
TON-u/s V3 (F)	9	6.95	0.7722	0.0241
TON-V4 (F)	10	7.221	0.7221	0.0124
TON-V5 (PF)	10	7.666	0.7666	0.0211
TON-V6 (PF)	10	5.384	0.5384	0.0183

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2.2126	4	0.5532	**24.569**	9.92E-11	**2.5837**
Within Groups	0.9906	44	0.0225			
Total	3.2033	48				

Table B-1.2: ANOVA analysis for Colour, Chloride & TON, Vartry

Anova: Single Factor

SULPHATE

SUMMARY

Groups	Count	Sum	Average	Variance
SO4-V3 (F/CF)	10	37.74	3.774	0.2871
SO4-u/s V3 (F)	9	36.29	4.0322	3.3723
SO4-V4 (F)	10	48.07	4.807	0.6396
SO4-V5 (PF)	10	32.58	3.258	0.2616
SO4-V6 (PF)	10	29.41	2.941	0.2335

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	20.8582	4	5.2145	**5.7685**	0.000803	**2.5837**
Within Groups	39.7745	44	0.904			
Total	60.6326	48				

CALCIUM

SUMMARY

Groups	Count	Sum	Average	Variance
Ca-u/s V3 (F)	9	10.5805	1.1756	0.0073
Ca-V3 (F+CF)	10	18.8578	1.8858	0.0071
Ca-V4 (F)	10	16.3929	1.6393	0.0117
Ca-V5 (PF)	10	20.2241	2.0224	0.0946
Ca-V6 (PF)	10	12.9278	1.2928	0.013

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	5.1743	4	1.2936	**47.6134**	1.95E-15	**2.5837**
Within Groups	1.1954	44	0.0272			
Total	6.3697	48				

Table B-1.3: ANOVA analysis for Sulphate & Calcium, Vartry

	pH V6 (PF)	*pH V4 (F)*	*Alkalinity V5 (PF)*	*Alkalinity V4 (F)*	*Al V4 (F)*	*Al V5 (PF)*	*Colour V5 (PF)*	*Colour V4 (F)*
Mean	6.368	5.867	4.9	2.75	93.511	45.293	15	10.5
Variance	0.021	0.025	1.211	0.458333	873.209	933.503	66.667	30.278
Observations	10	10	10	10	10	10	10	10
Pearson Correlation	0.812		0.671		0.747		0.804	
Hypothesized Mean Difference	0		0		0		0	
df	9		9		9		9	
t Stat	**16.943**		**8.310**		**7.120**		**2.862**	
P (T<=t) one-tail	1.95E-08		8.16E-06		2.7722E-05		0.009	
t Critical one-tail	1.833		1.833		1.833		1.833	
P (T<=t) two-tail	3.9E-08		1.63E-05		5.5445E-05		0.019	
t Critical two-tail	**2.262**		**2.262**		**2.262**		**2.262**	

	Cl V4 (F)	*Cl V5 (PF)*	*TON V4 (F)*	*TON V6 (PF)*	*SO4 V4 (F)*	*SO4 V6 (PF)*	*Ca V4 (F)*	*Ca V6 (PF)*
Mean	11.346	9.286	0.722	0.538	4.807	2.941	1.639	1.293
Variance	0.217	0.26	0.012	0.018	0.64	0.2337	0.012	0.013
Observations	10	10	10	10	10	10	10	10
Pearson Correlation	0.806		0.963		0.059		0.319	
Hypothesized Mean Difference	0		0		0		0	
df	9		9		9		9	
t Stat	**21.227**		**14.219**		**6.488**		**8.453**	
P (T<=t) one-tail	2.683E-09		8.97E-08		5.65E-05		7.109E-06	
t Critical one-tail	1.833		1.833		1.833		1.833	
P (T<=t) two-tail	5.367E-09		1.79E-07		0.000113		1.422E-05	
t Critical two-tail	**2.262**		**2.263**		**2.262**		**2.262**	

Table B-1.4: T-test analysis of afforested (F) and partially afforested (PF) sites, Vartry

	pH V3 (F+C)	*pH u/s V3 (F)*	*Alkalinity-V3 (F+C)*	*Alkalinity-u/s V3 (F)*	*Al-V3 (F+C)*	*Al-u/s V3 (F)*	*Colour-V3 (F+C)*	*Colour-u/s V3 (F)*
Mean	6.358	5.878	4.833	2.444	92.247	72.733	32.222	15
Variance	0.012	0.025	0.438	0.153	779.201	249.477	50.694	62.5
Observations	9	9	9	9	9	9	9	9
Pearson Correlation	0.464		0.443		0.616		0.333	
Hypothesized Mean Difference	0		0		0		0	
df	8		8		8		8	
t Stat	**9.884**		**11.926**		**2.658**		**5.939**	
P (T<=t) one-tail	4.63E-06		1.12E-06		0.014		0.000173	
t Critical one-tail	1.86		1.86		1.86		1.859548	
P (T<=t) two-tail	9.26E-06		2.25E-06		0.029		0.000346	
t Critical two-tail	**2.306**		**2.306**		**2.306**		**2.306**	

	Cl-V3 (F+C)	*Cl-u/s V3 (F)*	TON V3 (F+C)	TON u/s V3 (F)	*SO4 -u/s V3 (F)*	*SO4 -V3 (F+C)*	Ca V3 (F+C)	Ca u/s V3 (F)
Mean	13.531	12.523	1.173	0.772	4.032	3.728	1.877	1.176
Variance	0.256	0.199	0.0409	0.0241	3.372	0.299	0.007	0.007
Observations	9	9	9	9	9	9	9.000	9.000
Pearson Correlation	0.691		0.45		0.366		-0.147	
Hypothesized Mean Difference	0		0		0		0.000	
df	8		8		8		8.000	
t Stat	**7.992**		**6.28**		**0.533**		**16.408**	
P (T<=t) one-tail	2.2E-05		119E-06		0.304		9.59E-08	
t Critical one-tail	1.86		1.86		1.86		1.860	
P (T<=t) two-tail	4.4E-05		238E-06		0.609		1.92E-07	
t Critical two-tail	**2.306**		**2.306**		**2.306**		**2.306**	

Table B-1.5: T-test analysis of afforested (F) and afforested/clearfelled (F+C) sites, Vartry

APPENDIX B-2

STATISTICS FOR CLOGHOGE RIVER TRIBUTARIES

Anova: Single Factor **pH**

SUMMARY						
Groups	Count	Sum	Average	Variance		
pH-SG1 (M)	7	43.52	6.2171	1.1934		
pH-SG2 (M)	7	43.62	6.2314	1.1434		
pH-SHEEP (M)	7	39.88	5.6971	1.5087		
ANOVA Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.2975	2	0.6487	**0.5061**	0.6112	**3.5546**
Within Groups	23.073	18	1.2818			
Total	24.3705	20				

ALKALINITY

SUMMARY						
Groups	Count	Sum	Average	Variance		
Alk-SG1 (M)	7	63.5	9.0714	55.3691		
Alk-SG2 (M)	7	54.5	7.7857	43.9048		
Alk-SHEEP (M)	7	27.5	3.9286	15.5357		
ANOVA Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	100.2857	2	50.1429	**1.3102**	0.2943	**3.5546**
Within Groups	688.8571	18	38.2698			
Total	789.1429	20				

ALUMINIUM

SUMMARY						
Groups	Count	Sum	Average	Variance		
Al-SG1 (M)	7	841.3674	120.1953	1400.229		
Al-SG2 (M)	7	899.4599	128.4943	1798.2		
Al-SHEEP (M)	7	864.6674	123.5239	714.8297		
ANOVA Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	244.1975	2	122.0987	**0.0936**	0.9111	**3.5546**
Within Groups	23479.56	18	1304.42			
Total	23723.75	20				

Table B-2.1: ANOVA analysis for pH, Alkalinity & Total Aluminium, Cloghoge R.

Anova: Single Factor	**COLOUR**					
SUMMARY						
Groups	Count	Sum	Average	Variance		
Colour-SG1 (M)	7	1035	147.8571	2665.476		
Colour-SG2 (M)	7	1100	157.1429	3823.81		
Colour-SHEEP (M)	7	1165	166.4286	1855.952		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1207.143	2	603.5714	**0.217**	0.8070	**3.5546**
Within Groups	50071.43	18	2781.746			
Total	24.3705	20				
	CHLORIDE					
SUMMARY						
Groups	Count	Sum	Average	Variance		
Cl-SG1 (M)	7	56.54	8.0771	0.9098		
Cl-SG2 (M)	7	54.65	7.8071	0.6119		
Cl-SHEEP (M)	7	56.53	8.0757	0.6299		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.3384	2	0.1692	**0.2359**	0.7922	**3.5546**
Within Groups	12.9097	18	0.7172			
Total	13.2481	20				
	SULPHATE					
SUMMARY						
Groups	Count	Sum	Average	Variance		
SO4-SG1 (M)	7	1.07	0.1529	0.0444		
SO4-SG2 (M)	7	1.47	0.21	0.0423		
SO4-SHEEP (M)	7	1.45	0.2071	0.0621		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.0145	2	0.0073	**0.1464**	0.8649	**3.5546**
Within Groups	0.8925	18	0.0496			
Total	0.907	20				

Table B-2.1: ANOVA analysis for Colour, Chloride & Sulphate, Cloghoge R.

	pH-Sheep (PZ)	*pH-SG1 (PT)*	*pH-SG2 (PT)*	*pH-SHEEP (PZ)*	*pH SG1 (PT)*	*pH SG2 (PT)*
Mean	6.2314	6.2171	6.2314	5.6971	6.2171	5.6971
Variance	1.1434	1.1934	1.1434	1.5087	1.19339	1.5087
Observations	7	7	7	7	7	7
Pearson Correlation	0.9676		0.8538		0.9549	
Hypothesized Mean Difference	0		0		0	
df	6		6		6	
t Stat	**0.137**		**2.2093**		**3.684**	
P (T<=t) one-tail	0.4478		0.0346		0.0051	
t Critical one-tail	1.9432		1.9432		1.9432	
P (T<=t) two-tail	0.8955		0.0692		0.0103	
t Critical two-tail	**2.4469**		**2.4469**		**2.4469**	

	Alkalinity-SG1 (PT)	*Alkalinity-SG2 (PT)*	*Alkalinity-SHEEP (PZ)*	*Alkalinity-SG1 (PT)*	*Alkalinity-SG2 (PT)*	*Alkalinity-SHEEP (PZ)*
Mean	9.0714	7.785714	3.9286	9.0714	7.7857	3.9286
Variance	55.369	43.90476	15.5357	55.369	43.9048	15.5357
Observations	7	7	7	7	7	7
Pearson Correlation	0.9798		0.989		0.9709	
Hypothesized Mean Difference	0		0		0	
df	6		6		6	
t Stat	**2.0878**		**3.7895**		**3.4546**	
P (T<=t) one-tail	0.0409		0.0045		0.0068	
t Critical one-tail	1.9432		1.9432		1.9432	
P (T<=t) two-tail	0.0819		0.0091		0.0136	
t Critical two-tail	**2.4469**		**2.44691**		**2.4469**	

	Al-SG2 (PT)	*Al-SG1 (PT)*	*Al-SHEEP (PZ)*	*Al-SG1 (PT)*	*Al-SG2 (PT)*	*Al-SHEEP (PZ)*
Mean	128.4943	120.1953	123.5239	120.1953	128.4943	123.5239
Variance	1798.2	1400.229	714.8297	1400.229	1798.2	714.8297
Observations	7	7	7	7	7	7
Pearson Correlation	0.9282		0.341		0.3739	
Hypothesized Mean Difference	0		0		0	
df	6		6		6	
t Stat	**1.3809**		**0.2327**		**0.3223**	
P (T<=t) one-tail	0.1083		0.4119		0.3791	
t Critical one-tail	1.9432		1.9432		1.9432	
P (T<=t) two-tail	0.2165		0.8238		0.7582	
t Critical two-tail	**2.4469**		**2.4469**		**2.4469**	

Table B-2.2: T-test analysis of SG1, SG2 (PT; Peat, peaty podsols) & SHEEP (PZ; Brown Podsolic)

	Cl-SG1 (M) (PT)	*Cl-SG2 (M) (PT)*	*Cl-SG1 (M) (PT)*	*Cl-SHEEP (M) (PZ)*	*Cl-SHEEP (PZ)*	*Cl-SG2 (PT)*
Mean	8.0771	7.8071	8.0771	8.0757	8.0757	7.8071
Variance	0.9098	0.6119	0.9098	0.6299	0.6299	0.6119
Observations	7	7	7	7	7	7
Pearson Correlation	0.9518		0.9945		0.9467	
Hypothesized Mean Difference	0		0		0	
df	6		6		6	
t Stat	**2.2444**		**0.0205**		**2.7586**	
P (T<=t) one-tail	0.033		0.4922		0.0165	
t Critical one-tail	1.9432		1.9432		1.9432	
P (T<=t) two-tail	0.0659		0.9843		0.0329	
t Critical two-tail	**2.4469**		**2.4469**		**2.4469**	

	Colour-SG2 (PT)	*Colour-SG1 (PT)*	*Colour-SHEEP (PZ)*	*Colour-SG1 (PZ)*	*Colour-SG2 (PT)*	*Colour-SHEEP (PZ)*
Mean	166.4286	147.8571	157.1429	147.8571	166.4286	157.1429
Variance	1855.952	2665.476	3823.81	2665.476	1855.952	3823.81
Observations	7	7	7	7	7	7
Pearson Correlation	0.9233		0.8252		0.9434	
Hypothesized Mean Difference	0		0		0	
df	6		6		6	
t Stat	**2.414**		**0.7033**		**0.961**	
P (T<=t) one-tail	0.0261		0.2541		0.1868	
t Critical one-tail	1.9432		1.9432		1.9432	
P (T<=t) two-tail	0.0523		0.5082		0.3737	
t Critical two-tail	**2.4469**		**2.4469**		**2.4469**	

Table B-2.4: T-test analysis of SG1, SG2 (PT; Peat, peaty podsols) & SHEEP (PZ; Brown Podsolic)

APPENDIX B-3

STATISTICS FOR GLENDALOUGH LAKE UPPER CATCHMENT

	pH GLEN (M)	*pH LUGf (F)*	*Alkalinity-GLEN (M)*	*Alkalinity-LUG (F)*	*Al -LUG (F)*	*Al-GLEN (M)*	*Colour-GLEN (M)*	*Colour-LUG (F)*
Mean	6.276	5.245	4.6	1.75	204.9077	100.493	53	10.5
Variance	0.158	0.067	4.4333	0.3472	5792.63	1511.82	262.22	46.94
Observations	10	10	10	10	10	10	10	10
Pearson Correlation	0.743		0.2463		0.7554		0.0851	
Hypothesized Mean Difference	0		0		0		0	
df	9		9		9		9	
t Stat	**12.1402**		**4.4137**		**6.203**		**7.8883**	
P (T<=t) one-tail	3.49E-07		0.0008		7.91E-05		1.24E-05	
t Critical one-tail	1.8331		1.8331		1.8331		1.8331	
P (T<=t) two-tail	6.97E-07		0.0017		0.000158		2.48E-05	
t Critical two-tail	**2.26212**		**2.2622**		**2.2622**		**2.2622**	

	TON-LUG (F)	*TON-GLEN (M)*	*Cl-LUG (F)*	*Cl-GLEN (M)*	*SO4-LUG (F)*	*SO4-GLEN (M)*	*Ca-GLEN (M)*	*Ca-LUG (F)*
Mean	0.1533	0.097	8.191	5.799	3.12	2.08	1.4599	0.6031
Variance	0.0029	0.0029	0.1911	1.1295	0.048	2.1583	0.1394	0.0058
Observations	10	10	10	10	10	10	10	10
Pearson Correlation	0.8703		0.5312		-0.04		0.8497	
Hypothesized Mean Difference	0		0		0		0	
df	9		9		9		9	
t Stat	**6.4533**		**8.318**		**2.2013**		**8.7089**	
P (T<=t) one-tail	5.88E-05		8.09E-06		0.0276		5.58E-06	
t Critical one-tail	1.8331		1.8331		1.8331		1.8331	
P (T<=t) two-tail	0.000118		1.62E-05		0.05522		1.12E-05	
t Critical two-tail	**2.2622**		**2.2622**		**2.2622**		**2.2622**	

Table B-3.1: T-test analysis of Lugduff River (F) and Glenealo River (M) sites, Glendalough

APPENDIX B-4

STATISTICS FOR KING'S RIVER TRIBUTARIES

Anova: Single Factor **pH**

SUMMARY

Groups	Count	Sum	Average	Variance
pH-ANNA (F/CF)	10	50.79	5.079	0.5521
pH-B'GEE (PF)	10	59.61	5.961	0.3877
pH-GLAS (F)	10	55.79	5.579	0.5755

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.912827	2	1.956413	**3.8732**	0.0332	**3.3541**
Within Groups	13.63827	27	0.505121			
Total	17.5511	29				

ALKALINITY

SUMMARY

Groups	Count	Sum	Average	Variance
Alk-ANNA (F/CF)	10	15.5	1.55	1.6917
Alk-B'GEE (PF)	10	43	4.3	3.5111
Alk-GLAS (F)	10	29	2.9	4.1556

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	37.8167	2	18.9083	**6.0614**	0.0067	**3.3541**
Within Groups	84.225	27	3.1194			
Total	122.0417	29				

ALUMINIUM

SUMMARY

Groups	Count	Sum	Average	Variance
Al-ANNA (F/CF)	10	2370.714	237.0714	2308.853
Al-B'GEE (PF)	10	1723.017	172.3017	2658.89
Al-GLAS (F)	10	1962.201	196.2201	2499.079

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	21453.4	2	10726.7	**4.3097**	0.0237	**3.3541**
Within Groups	67201.4	27				
Total	88654.8	29				

Table B-4.1: ANOVA analysis for pH, Alkalinity and Total Aluminium, King's River

Anova: Single Factor **COLOUR**

SUMMARY						
Groups	Count	Sum	Average	Variance		
Colour-ANNA (F/CF)	10	1525	152.5	3773.611		
Colour-B'GEE (PF)	10	1060	106	1821.111		
Colour-GLAS (F)	10	1370	137	2084.444		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	11211.67	2	5605.833	**2.19**	0.1314	**3.3541**
Within Groups	69112.5	27	2559.722			
Total	80324.17	29				

CHLORIDE

SUMMARY						
Groups	Count	Sum	Average	Variance		
Cl-GLAS (F)	10	73.14	7.314	1.0647		
Cl-ANNA (F/CF)	10	89.99	8.999	1.3556		
Cl-B'GEE (PF)	10	65.34	6.534	0.8166		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	31.7462	2	15.8731	**14.7114**	4.77E-05	**3.3541**
Within Groups	29.132	27	1.079			
Total	60.87814	29				

SULPHATE

SUMMARY						
Groups	Count	Sum	Average	Variance		
SO4-ANNA (F)	10	10.6	1.06	0.773689		
SO4-GLAS (F)	10	6.05	0.605	0.133161		
SO4 B'Gee (PF)	10	14.4	1.44	0.844733		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.4955	2	1.74775	**2.993435**	0.066959	**3.3541**
Within Groups	67201.4	27	2488.941			
Total	19.25975	29	2488.941			

Table B-4.2: ANOVA analysis for Colour, Chloride & Sulphate, King's River

	pH-B'GEE (PF)	***pH-ANNA (F/CF)***	***pH-GLAS (F)***	***pH-ANNA (F/CF)***	***pH-B'GEE (PF)***	***pH-GLAS (F)***
Mean	5.961	5.079	5.579	5.079	5.961	5.579
Variance	0.3877	0.5521	0.5755	0.5521	0.3877	0.5755
Observations	10	10	10	10	10	10
Pearson Correlation	0.9057		0.8778		0.9369	
Hypothesized Mean Difference	0		0		0	
df	9		9		9	
t Stat	**8.7438**		**4.2563**		**4.3223**	
P (T<=t) one-tail	5.4E-06		0.0011		0.001	
t Critical one-tail	1.8331		1.8331		1.8331	
P (T<=t) two-tail	1.08E-05		0.0021		0.0019	
t Critical two-tail	**2.2622**		**2.2622**		**2.2622**	

	Alkalinity-B'GEE (PF)	***Alkalinity-GLAS (F)***	***Alkalinity-B'GEE (PF)***	***Alkalinity-ANNA (F/CF)***	***Alkalinity-GLAS (F)***	***Alkalinity-ANNA (F/CF)***
Mean	4.3	2.9	4.3	1.55	2.9	1.55
Variance	3.5111	4.1556	3.5111	1.691667	4.1556	1.6917
Observations	10	10	10	10	10	10
Pearson Correlation	0.9905		0.9506		0.9555	
Hypothesized Mean Difference	0		0		0	
df	9		9		9	
t Stat	**14**		**11.5241**		**4.8321**	
P (T<=t) one-tail	1.03E-07		5.43E-07		0.0005	
t Critical one-tail	1.8331		1.8331		1.8331	
P (T<=t) two-tail	2.05E-07		1.09E-06		0.000931	
t Critical two-tail	**2.2622**		**2.2622**		**2.2622**	

	Al-GLAS (F)	***Al-B'GEE (PF)***	***Al-ANNA (F/CF)***	***Al-B'GEE (PF)***	***Al-ANNA (F/CF)***	***Al-GLAS (F)***
Mean	196.2201	172.3017	237.0714	172.3017	237.0714	196.2201
Variance	2499.079	2658.89	2308.853	2658.89	2308.853	2499.079
Observations	10	10	10	10	10	10
Pearson Correlation	0.8202		0.9486		0.8679	
Hypothesized Mean Difference	0		0		0	
df	9		9		9	
t Stat	**2.4812**		**12.5333**		**5.1121**	
P (T<=t) one-tail	0.0175		2.66E-07		0.0003	
t Critical one-tail	1.8331		1.8331		1.8331	
P (T<=t) two-tail	0.0349		5.31E-07		0.0006	
t Critical two-tail	**2.2622**		**2.2622**		**2.2622**	

Table B-4.3: T-test analysis of pH, alkalinity and Total aluminium, King's River

	Cl-ANNA (F/CF)	*Cl-GLAS (F)*	*Cl-GLAS (F)*	*Cl-B'GEE (PF)*	*Cl-ANNA (F/CF)*	*Cl-B'GEE (PF)*
Mean	8.999	7.314	7.314	6.534	8.999	6.534
Variance	1.3556	1.0647	1.0647	0.8166	1.3556	0.8166
Observations	10	10	10	10	10	10
Pearson Correlation	0.8511		0.9299		0.931	
Hypothesized Mean Difference	0		0		0	
df	9		9		9	
t Stat	**8.6992**		**6.428**		**16.887**	
P (T<=t) one-tail	5.63E-06		6.06E-05		2.01E-08	
t Critical one-tail	1.8331		1.8331		1.8331	
P (T<=t) two-tail	1.13E-05		0.000121		4.01E-08	
t Critical two-tail	**2.2622**		**2.2622**		**2.2622**	

	Colour-ANNA (F/CF)	*Colour-B'GEE (PF)*	*Colour-B'GEE (PF)*	*Colour-GLAS (F)*	*Colour-ANNA (F/CF)*	*Colour-GLAS (F)*
Mean	152.5	106	106	137	152.5	137
Variance	3773.611	1821.111	1821.111	2084.444	3773.611	2084.444
Observations	10	10	10	10	10	10
Pearson Correlation	0.8901		0.91132		0.950813	
Hypothesized Mean Difference	0		0		0	
df	9		9		9	
t Stat	**4.8269**		**5.207**		**2.1398**	
P (T<=t) one-tail	0.0005		0.0003		0.0305	
t Critical one-tail	1.8331		1.8331		1.8331	
P (T<=t) two-tail	0.0009		0.0006		0.061	
t Critical two-tail	**2.2622**		**2.2622**		**2.2622**	

	SO4-B'GEE (PF)	*SO4-GLAS (F)*	*SO4-B'GEE (PF)*	*SO4-ANNA (F/CF)*	*SO4-ANNA (F/CF)*	*SO4-GLAS (F)*
Mean	1.44	0.605	1.44	1.06	1.06	0.605
Variance	0.8447	0.1332	0.84473	0.7737	0.7737	0.1332
Observations	10	10	10	10	10	10
Pearson Correlation	0.3266		0.7287		0.8132	
Hypothesized Mean Difference	0		0		0	
df	9		9		9	
t Stat	**3.0312**		**1.8112**		**2.3194**	
P (T<=t) one-tail	0.0071		0.0518		0.0228	
t Critical one-tail	1.8331		1.8331		1.8331	
P (T<=t) two-tail	0.0142		0.1035		0.0455	
t Critical two-tail	**2.2622**		**2.2622**		**2.2622**	

Table B-4.4: T-test analysis of Chloride, Colour & Sulphate, King's River

APPENDIX C

NON-MARINE CALCULATIONS

The following equations were used for the calculations of non-marine ions:

Non-marine $Ca^{2+} = Ca^{2+} - 0.037 * Cl^{-}$

Non-marine $SO_4^{2-} = SO_4^{2-} - 0.1025 * Cl^{-}$

Ref: Aquafor Report

APPENDIX D

PREVIOUS DATA

	ANNA		B'GEE	
	pH	Alkalinity	pH	Alkalinity
28/02/96	4.73	0.2	5.99	1.9
02/04/96	5.24	0.2	6.29	2.9
13/01/97	-	-	4.67	0

Table D.1: pH & Alkalinity at Annalecka & Ballinagee Rivers, 1996-1999 (ERFB)

	pH 1987-89	pH 2004	Alk. 1987-89	Alk. 2004
Glenealo R. (M)	5.29-7.09	5.47-6.73	3-14	2.5-8.5
	(6.13)	(6.21)	(9)	(3.8)
Lugduff R. (F)	4.21-5.7	4.95-5.62	2-9	1.0-3.0
	(4.94)	(5.16)	(5)	(1.8)

Table D.2: pH & Alkalinity at Glendalough Lake, 1989 & 2004 (EPA)

	ANNA					B'GEE					GLAS				
	2000	2001	2002	2003	2004	2000	2001	2002	2003	2004	2000	2001	2002	2003	2004
11/01	4.26	5.03	5.25	5.32	4.43	5.34	6.4	6.49	6.45	5.3	6.39	6.29	6.21	6.09	4.75
25/01	5.56	4.24	4.09	3.9	4.85	6.34	5.14	4.99	5.05	6.17	4.37	4.96	4.39	4.22	5.31
08/02	4.65	4.4	4.37	4.44	4.86	5.78	5.82	5.18	5.86	5.89	6.53	5.05	4.5	4.95	5.47
23/02	4.63	4.56	4.49	-	6.29	6.04	5.57	5.85	-	6.73	5.78	6	5.26	-	6.67
07/03	4.18	-	4.64	4.59	5.35	4.83	6.32	6.14	5.86	6.37	5.68	4.52	5.27	4.88	6.17
21/03	5.73	-	4.63	6.3	4.27	6.47	-	6.26	6.83	4.86	4.72	-	5.37	6.54	4.48
04/04	5.19	4.77	4.63	6.69	4.60	6.3	-	6.2	6.77	5.95	6.37	-	5.39	6.72	5.95
18/04	4.25	5.03	5.26	6.17	4.39	5.13	6.11	6.45	6.89	5.38	6.2	6.21	5.97	7.03	4.89
04/05	5.17	5.96	4.38	5.09	5.5	6.27	6.51	5.46	6.28	6.2	6.53	4.39	4.89	5.91	5.5
16/05	6.42	4.42	5.21	5.59	6.25	6.73	5.52	6.29	6.59	6.76	6.64	4.5	6.49	6.32	6.6

NB: 2004 pH results in grey are those contained within this investigation

Table D.3: pH at King's River Tributaries, 2000-2004