Evaluation of the use of the Sodium Dominance Index as a potential measure of acid sensitivity

WATERAC

FINAL REPORT

(2000-LS-3.2.1a-M2)

Prepared for the Environmental Protection Agency and Council for Forest Research and Development

by

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March 6th 2006

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ACKNOWLEDGEMENTS

This report has been prepared as part of the Environmental Research Technological Development and Innovation Programme under the Productive Sector Operational Programme 2000-2006. The programme is financed by the Irish Government under the National Development Plan 2000-2006. It is administered on behalf of the Department of the Environment and Local Government by the Environmental Protection Agency which has the statutory function of co-ordinating and promoting environmental research. The joint funding by the Council for Forest Research and Development is gratefully acknowledged. The comments and reviews of the external review panel members Professor Steve Ormerod, Prof Cardiff School of Biosciences, Wales, Dr Tom Nisbet (Forest Research, Forestry Commission), Dr David Tervet (Bell College) and Ms. Helen Walsh, Dr. Connor Clenegahan, Dr Deirdre Tierney, Dr Jim Bowman, Dr Eugene Hendrick and Mr Joe O'Carroll are gratefully acknowledged.

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Executive Summary

In view of the ecological importance of soft-waters for salmonid production, it is critical that measures are taken to avoid increased rates of acidification, particularly those relating to changes in land use. This necessitates the identification of acid-sensitive waters. The most commonly adopted indicators are pH (state) and alkalinity (sensitivity). Low pH (<5.5) and low alkalinity (<10 mg L^{-1} $CaCO_3$) are clearly indicative of low buffering capacity, but they are extremely variable within any one catchment, depending on flow conditions and geology. The contribution of sodium (Na^{+}) to the sum of the major cations (Sodium Dominance Index, SDI, or Weathering Index) in river waters has been proposed as an indicator of the acid sensitivity of rivers of upland Scotland, particularly where sea salt inputs dominate the base cation composition. The extent of Sodium Dominance provides a quantitative indication of catchment weathering rate, incorporating the effects of diverse geological composition. This project set out to test the following two hypotheses: that SDI is more stable across the range of stream flows than the two most commonly used indicators and is thus a better indicator of stream sensitivity to acidification than pH and that there is a graded response by the stream macroinvertebrates to values of the index, and hence some ecological underpinning of the chemical relationship

These hypotheses were tested by examining the water chemistry of 257 sites across Ireland, encompassing a range of underlying geologies, during base flow. A further sub-set of 55 sites were sampled at both base and elevated flow and a number of more detailed hydrological events were monitored at a smaller number of sites. pH, conductivity, hardness, alkalinity and SDI were determined for each site, together with a range of environmental variables, including geology type, presence or absence of forest, distance from the south-west of Ireland and distance from the sea. The values of pH recorded for the sites sampled ranged from pH 4.9 to 8.8. Most values were in the circum-neutral range (pH 6.5-7.5). SDI values for all sites sampled ranged from 10.1 to 81.9: the highest values of SDI were recorded in upland sites in Wicklow, Donegal, Galway and Kerry. Within any geologically classified group of sites, no significant difference in SDI was detected between the non-forested and forested sites. Some forested sites become substantially more acidic than similar non-forested sites, and yet

the two had similar SDI values, thus the index is not an impact, but an indication of susceptibility of sites to impact. A negative linear relationship between pH and the SDI was found, for both non-forested and forested sites, individually and combined. Of particular interest was the relationship between potentially acid-sensitive sites and the SDI. Although SDI showed some variation, this variation seemed to decline after about 5-6 hours of elevated flow, when it again showed less variation than pH or alkalinity. It appears that a thresh hold level of SDI of 50-60 is indicative of sensitivity to acidification as measured by ANC and alkalinity. A highly significant linear relationship between SDI and conductivity was found for two groupings of sites (sites with conductivities > 250µS/cm and 150µS/cm excluded), although there was considerable scatter in the data. The data suggested that an SDI value of between 40-60 identified sites which are at potential risk of acidification, while sites with values of greater than 60 are at risk of acidity. Acid-Neutralising Capacity (ANC) was calculated for 117 sites from the present extensive study. The ANC value fell to zero with an approximate SDI value of 60. In the same way, when SDI was plotted against alkalinity, it appeared that an SDI 50-60 represents a critical value in rivers.

SDI values increased with flow at all sites except ten. Generally there was less than a 15 unit SDI difference between low and elevated water levels. Most of the sites that did show a substantial increase in the Index at elevated flow were located in catchments with mixed geology. Overall, the variation in the SDI was substantially less than that for alkalinity. No significant differences were found in SDI between base flow and elevated flow at un-forested or forested sites when examined separately within each geological type (One-Way ANOVA, $P > 0.05$) except for forested sites ($F_{,4}=10.75$, $P = 0.031$) on schist and felsite. Likewise, there was no significant effect of forest cover on SDI ($P>0.05$, Mann-Whitney) on the elevated and base flow values.

At base flow, SDI was closely correlated with alkalinity, hardness, conductivity and pH. At higher flows, the correlation coefficients declined (although remaining highly significant). No significant differences were found in SDI between base flow and elevated flow at the un-forested or forested sites when examined separately within each geological type. When SDI data were ranked by % forestry cover, there was no significant effect of forest noted on the elevated and base flow values. A similar result was noted when related to the percentage conifer cover. There was no significant trend in SDI with distance from the sea. The sampling locations in relation to the prevailing winds (SW) did not appear to have a significant effect on SDI during changing flow conditions. The absence of clear relationships may be in part due to the fact that the majority of sites exhibited only small changes in SDI. For those sites showing stability of the index it is probable that rainfall simply dilutes the base cations, but maintains the relative proportions of each. In general the pattern of change in both alkalinity and SDI were fairly similar when individual hydrological events were examined. However, the coefficient of variation was highest for alkalinity (3.44- 836.41%) followed by pH (0.74-18.87 %) and least for the Sodium Dominance Index (2.21-20.5%).

A total of 237 taxa were recorded over the two seasons representing 75 families. The number of taxa recorded per site ranged from 33 to 78. A total of 33 taxa were present in over 50% of the 65 sites sampled. Trichoptera was the most diverse group (48 species) followed by the Coleoptera (41 species). Ephemeroptera were represented by nineteen species while eighteen plecopteran species were recorded. There were seventeen genera/subfamilies of Diptera, two crustacean orders, namely Malacostraca and Entomostraca, with four and two representative species recorded respectively, while the Annelida were represented by six Hirundinae species. Fourteen gastropod species and two lamellibranch species were also recorded.

The Ephemeroptera constituted an increasing proportion of the community with progression from sites with SDI>80 to those in the 30-40 SDI band (Figure 10). In contrast, Plecoptera increased in proportion with increasing acid sensitivity (particularly at highly forested sites). While crustacean and molluscan numbers decreased predictably with increasing acid sensitivity, the representation of dipteran larvae generally increased. The pattern was similar for both seasons.

TWINSPAN of the spring faunal dataset (non-forested sites only) resulted in seven validated groups (Groups 1-7). Group 7 consisted mostly of acid tolerant sites with mean SDI of 21.6 (SDI range 7.6 to 59.7). Groups1 to 6 tended to have higher mean SDI (50.1 to 74.9), largely acid sensitive conditions. Analysis of the autumn faunal data (non-forested sites) yielded relatively similar results with again seven groups. The mean SDI values in Group 7 were 23.8 (range from 12.7 to 35.5). Groups 1-6 consisted of moderately to highly sensitive sites. Mean SDI values for Groups 1-6 ranged from 38.8 to 60.3. A significant correlation between the physico-chemical parameters and the spring faunal dataset for the non-forested sites was demonstrated by Canonical Correspondence Analysis. The autumn data also showed low eigenvalues with the total cumulative data variation explained at 23.7%. SDI, slope, elevation and total aluminium were indicated as being important variables in the autumn analysis.

The total taxon richness significantly negatively correlated with SDI for all sites combined and for forested sites alone, for spring but not for the autumn data. The correlations with ephemeropteran and trichopteran richness (decrease) were only significant for the spring period (non-forested site data). Plecopteran taxon richness increased with increasing SDI and this relationship was the only significant one in autumn.

Analysis of variance (two-way) on the spring data showed differences in total taxon richness between SDI bands Plecopteran species richness demonstrated significant differences between SDI bands in both seasons, generally species richness increased with increasing SDI. Trichopteran richness differed between bands in the spring ($F_{6,50}$=3.749, P=0.004,) but not in the autumn. There was no significant interaction between forestry and SDI bands for these taxonomic groups.

A significant differences in total taxon abundance between SDI bands was found in spring and autumn (Two-way ANOVA, $F_{6,50}$=2.721, P=0.023,) and autumn ($F_{6,52}$=3.354, P=0.007), Neither forestry nor the forestry SDI band interaction were significant. A similar finding applied to the Ephemeroptera in both seasons (spring - $F_{6,50}$=2.355, P=0.044; autumn - $F_{6,52}$=3.233, P=0.009.). Plecopteran and trichopteran abundances showed no significant effect of forestry or SDI bands in the spring. However, significant differences in plecopteran ($F_{6,52}$=3.903, P=0.003,) abundance between SDI bands were detected in the autumn dataset.

In general, most of the significant differences in both taxon richness and abundances could be attributed to differences between the lowest SDI band (<20) and the two highest, 60-70 and >70.

Mean EPT (the sum of ephemeropteran, plecopteran and trichopteran abundance) and mean E/P (ephemeropteran divided by plectopteran abundance) were both correlated to mean SDI within each band of SDI. An additional metric, crustacaean/dipteran (C/D), was also tested. While the study found a significant negative relationship between EPT and SDI for all sites and non-forested sites considered separately, it did not hold for forested sites in spring. For the autumn data the relationship was significant for all sites combined. The negative relationship between SDI and C/D was significant for all sites combined and the non-forested sites in both seasons. There were no significant correlations between E/P and SDI in this study.

Some evidence of a response in biology across the SDI bands was detected. TWINSPAN on the non forested sites distinguished between those sites with SDI values > 50 and those < 20, between these two extremes, the site grouping were characterised by a mix of SDI values. This pattern was largely maintained when the forested sites were included in the TWINSPAN. Further work is required to validate these data within each catchment in the context of risk assessment under the Water Framework Directive.The links with the fauna will require further analysis and more detailed consideration. In particular the contribution of river typology (RIVTYPE after Kelly-Quinn *et al.*, 2004) may well help to elucidate more fully the relationship between SDI and fauna and this may lead to both the identification of indicator species, ideally with a graded response to the SDI index. Given the errors associated with the measurement of pH, compared to base cations, SDI could perhaps a more reliable measure of acid sensitivity.

1 Introduction and current state of knowledge

1.1 Introduction

Ireland is part of the temperate deciduous forest biome. Forests were gradually cleared for agriculture and urbanisation, such that by about 1900, less than 1.5% of the Irish landscape was forested. The process of reafforestation began early in the 20th century and has been based almost entirely on exotic coniferous species such as Sitka Spruce (*Picea sitchensis* (BONG.) Carr.) and Lodgepole Pine (*Pinus contorta* Dougl.). These species grow well in the mild maritime climate and coniferous plantation forests are an increasingly important land-use in Ireland. Plantation forests cover 10% of the landscape at present, with the planted area projected to reach 17% by 2010. This has raised concerns as to the possible effects such new plantations and associated forestry practices may have on aquatic resources in the country (O'Halloran & Giller, 1993). These concerns arise because of the direct links between catchment land use and aquatic ecosystems (Hynes, 1975; Giller & Malmqvist, 1998) and the fact that many Irish river systems rise in or pass through forested catchments.

In the U.K., coniferous forestry exacerbates the acidification of soft-waters draining geologically sensitive areas which receive atmospheric pollutants (Hynes, 1975; Giller & Malmqvist, 1998). The causes of acidification have been extensively reviewed and it is now clear that anthropogenically-mediated acidification occurs where atmospheric deposition of strong acid anions (SO_4^{2-} and NO_3^-), accompanied by H^+ and NH_4^+, exceed the buffering capacity of the soil resulting in the leaching of Ca^{2+}, Mg^{2+} and Al^{3+}. The ecological consequences of acidification have been summarised by many workers (e.g. Edwards *et al.*, 1990; Hildrew & Ormerod, 1995) and impact across a number of scales from sub-physiological to global (Table 1.1).

While the deposition of acidifying ions has shown a decline by 40% in European Environment Agency (EEA) membership countries (EEA, 2000), there is still considerable concern about the impacts of acidifying ions on surface water quality and its associated ecology. The contribution of forest developments to this problem requires further investigation.

Table 1. 1. Potential responses to freshwater acidification at different scales (after Hildrew and Ormerod, 1995).

Scale of effect	Type of effect
Sub-physiological	Tissue metal concentrations in fish
Physiological	Physiological dysfunction and reproductive effects in aquatic vertebrates
Behavioural	Foraging times in birds and avoidance behaviour in fish.
Individual	Change in body condition, growth and energetics in birds and fish.
Species Populations	Presence/absence.
Community	Altered community structure in invertebrates and aquatic plants. Altered predator prey relationships.
Ecosystem	Altered quality of production and reduced decomposition.
Landscape/Biome	Cumulative responses across ecosystems (e.g. lakes and rivers).
Global	Cumulative responses across biomes and continents.

1.2 Water quality issues and forestry in Ireland

Up to the early 1970s, water quality issues were of little interest in Ireland as there was low level extensive farming and a small industry base, which was based around major coastal centres. Greater awareness of pollution arose with increased industrialization and intensification of agriculture in the mid 1970s and early 1980s, and, coupled with this, came the realization that forestry might also have an impact on water quality. This recognition was largely based on lessons from abroad (e.g. Harriman & Morrison, 1982; Stoner *et al.*, 1984; O'Halloran & Giller, 1993), and largely focused on the potential exacerbating effects that plantation forestry might have on stream acidity. Indeed, Allot *et al.* (1990) suggested that there was a correlation between percentage forest cover and acidity, aluminium and dissolved organic carbon concentrations in stream waters in Connemara and south Mayo. Based on these earlier studies, together with a study by Bowman (1986) on the impact of acid precipitation on selected lakes of low buffering capacity, the Irish Forest Service introduced 'Forestry Fishery

Guidelines', focusing on the interactions between forests, forest operations and water quality (Anon, 1995). Plantation forests and their management can influence water quality in a number of ways (e.g. nutrients or energy) and at different stages of the forest cycle. The present study focuses on an evaluation of the Sodium Dominance Index (SDI) as a measure of stream sensitivity to acidification and hence the identification of potential sites for forest development (or not).

As in most western European countries, forest development has largely taken place in the marginal upland areas and in areas of less intensive agriculture (Giller & O'Halloran, 1993). The Irish Forest Service introduced regulations that all applications for grant-aid in areas designated as being acid sensitive required an assessment. These regulations were largely targeted at the protection of salmonid waters. The designation of sensitivity was (and is) based on alkalinity determined on a minimum of four sampling occasions at intervals not greater than 4 weeks between February and May. Where the minimum alkalinity of the runoff water is < 8 mg $CaCO_3$ l^{-1} no afforestation is permitted. In areas where concentrations exceed 15 mg $CaCO_3$ l^{-1}, afforestation is permitted, and if the values fall in between, full, partial, or no afforestation may be allowed. To help refine these regulations and study the interactions between forestry and aquatic ecology, a national study (AQUAFOR,) was established in two areas recognised as poorly buffered, west Galway-Mayo and part of Wicklow Mountains, along with the larger, but geologically less sensitive area of Munster. Acidity in these areas was essentially episodic in character. In Wicklow and Galway-Mayo, atmospheric acid deposition resulted primarily from industrial emissions (Farrell *et al.*, 1997b; Farrell *et al.*, 1997a). Other sources of stream acidity, such as marine salts and high background levels of organic acids, were of lesser importance (Allott *et al.*, 1997). Acid episodes at a number of Wicklow and Galway-Mayo sites in poorly buffered streams, chiefly on granite and schist, had minimum pH values below those recommended for salmonid waters (Kelly-Quinn *et al.*, 1997a; Kelly-Quinn *et al.*, 1997b). These acid episodes were also most severe and longer lasting in certain afforested catchments, and tended to occur in winter and spring, when salmonids are at particularly vulnerable stage of their life cycle. In Wicklow, high concentrations of labile monomeric aluminium were recorded in certain forested catchments/sub-catchments, which were naturally predisposed to acid episodes (values > 40 µg l^{-1}) (Kelly-Quinn *et al.*, 1997a;

Kelly-Quinn *et al.*, 1997b). A lower diversity of stream macroinvertebrates was also found at these sites (see below). In the Munster region (set largely on Old Red sandstone) to the south, there were no obvious relationships between forest cover and stream acidity and the influence of plantation forests on water chemistry appeared to be far less important than in other parts of the country (Giller *et al.*, 1997a).

Whilst forestry-related hydrochemical changes were evident in the east and west of the country, it is considered that plantation forests do not lead to acidification and the related problems in the south of Ireland (Giller & O'Halloran, 2004). Even where alkalinity levels in forested catchments were within the sensitive range, as defined by the forestry-fishery guidelines, ecological effects were not discerned in most cases. In fact, detailed studies at the catchment level revealed that pH levels can increase as the stream flows from moorland into a plantation forested area (Cleneghan *et al.*, 1998), while the precise reasons for this increase were not clear, it is likely that local geological changes and perhaps limestone chippings on the road, may have given rise to this increase in pH. In one tributary, pH rose by 1.7 units over a distance of 1.2 km as the stream entered the forest. Temporal fluctuations in most hydrochemical variables were minor and no acid pulses were noted during spates (Cleneghan *et al.*, 1998). It should be noted however, that the number of sites in this case was restricted to one catchment and limited in number. Where catchment specific effects of plantation forests have been identified they have been related more to habitat effects than chemical ones in Munster (Giller & O'Halloran, 2004). Whilst extensive surveys across sites, seasons and flow conditions can indicate general patterns, the key to understanding the factors underlying such patterns lies in process studies at the individual catchment scale, in harmony with the EU Water Framework Directive (EC Directive 2000/60/EC).

The current methods used for designating acid sensitive sites appear to be rather coarse: alkalinity varies across flow conditions and there is a poor relationship between peak acidity and lowest alkalinity values (e.g. in Wicklow, Kelly-Quinn *et al.*, 1997a; Kelly-Quinn *et al.*, 1997b). Once-off sampling is inappropriate, because on the one hand, it may fail to identify sensitive sites, and on the other, may identify acidity levels, which are not serious in the long-term. Thus many sites might be designated as sensitive based on alkalinity, yet ecological data do not support the designation (e.g. Munster area, Giller *et al.*, 1997b; Giller & O'Halloran, 2004).

In view of the ecological importance of soft-waters for salmonid production, it is important that measures are taken to avoid increased rates of acidification, particularly those relating to changes in land use. This necessitates the identification of acid-sensitive waters. As previously mentioned, the most commonly adopted indicators are pH and alkalinity. Low pH (<5.0) and low alkalinity (<10 mg L^{-1} $CaCO_3$) are clearly indicative of low buffering capacity but they are extremely variable within any one catchment, depending on flow conditions and geology. Clearly, what is needed is a parameter that is both relatively stable and independent of season and flow. The contribution of sodium (Na^+) to the sum of the major cations (Sodium Dominance Index or Weathering Index) in river waters has been proposed by White *et al.* (1998, 1999) as an indicator of the acid sensitivity of rivers of upland Scotland, particularly where sea salt inputs dominate the base cation composition. The extent of Sodium Dominance provides a quantitative indication of catchment weathering rate, incorporating the effects of diverse geological composition. The potential application of this index to classify/identify acid-sensitive Irish rivers was reviewed by this project team (Kelly-Quinn *et al.*, 1999) and was investigated in detail in this project. The SDI is calculated as the relative contribution of sodium to the major cations as follows:

$$SDI = \frac{[Na^+]}{[Na^+] + [Ca^{2+}] + [Mg^{2+}]} * 100$$

Base cations (particularly Ca^{2+}) may be derived from weathering of geologies (e.g. limestone). Increases in their concentrations relative to sodium infer an increased acid neutralising capacity to the catchment, and conversely, high sodium dominance infers reduced neutralising capacity. As weathering rates ($mmol_C$ ha^{-1} yr^{-1}) increase, the SDI-value declines in response. As such the SDI provides a quantitative value of the weathering upstream of the sampling point.

The ultimate goals of this present study were

1. to evaluate the efficacy of the SDI approach to site designation under Irish conditions and
2. to provide objective scientific information to help to set out some possible approaches to understand more fully the relationship between surface water quality and forestry in Ireland.

1.3 Scale of Approach

There are three spatial scales, which are considered to be critically important in examining the acidification issue in terms of identifying sensitive catchments and in developing tools for amelioration of problems in this context.

1.3.1 Supra Catchment or Regional Scale

At the supra-catchment or regional scale, the objective is to identify potentially sensitive areas to help plan forest development with minimum impact on water quality and ecology (e.g. fisheries). Because of Ireland's geographical position and prevailing weather systems, the deposition of acidifying compounds is low although local scale ammonium deposition may be very important in the future (EPA, 2000). In this context, national-scale evaluation of SDI has been undertaken in the present project.

1.3.2 Catchment and sub-catchment scale

At smaller scales, the research efforts have been largely focussed on preventing or mitigating against acidification and ensuring that acidification is not exacerbated locally (Hildrew & Ormerod, 1995). This can lead, for example, to planting regimes being controlled in sensitive catchments. At the subcatchment-scale, liming has been the most widely used approach. Direct application of lime (as ground limestone or dolomite) to the hydrological source areas of catchments has been effective in increasing pH and calcium concentrations and reducing aluminium in a number of countries including Sweden, Norway, Scotland and Wales (e.g. Kramer and Kraft 1995).

In lakes, liming treatments bring about a very rapid improvement in water quality (Svenson *et al.* 1995) but only remain effective for a period equivalent to between two and four residence times. Liming of rivers is often carried out by automatic continuous dosing, particularly in Sweden (Svenson *et al.* 1995) and Norway (Larson and Hestigan

1995). The more sophisticated dosing machines are capable of automatically altering the dose rate depending on water level and pH. This approach can be effective in increasing pH and alkalinity while reducing the concentration of Fe, Mn and labile monomeric Al. However, this requires expensive infrastructure, regular maintenance and the installations can be unsightly intrusions into areas of attractive, semi-natural scenery. For these reasons, automatic dosing is unlikely to be acceptable in Ireland except in limited circumstances.

Alternatively, rivers can be treated by direct addition to the river bed of granular limestone (Downey *et al.* 1994) or crushed shells (Larson and Hestigan 1995 missing) which are distributed downstream by the flowing water. Liming to ameliorate surface water acidification has been reviewed by Jennings *et al.* (2001) and submitted to the Environmental Protection Agency (EPA) and Council for Forest Research and Development (COFORD) as a separate stand alone report. In this project a number of catchments were investigated at low and high flow in attempt to evaluate the temporal responses of the SDI and to look at a range of important variables which might influence the SDI value, and hence its use as a tool in designating sites.

1.3.3 The riparian or reach scale

There have been a small number of recent attempts to devise and implement methods of riparian management to ameliorate the effects of forestry on acidification (e.g. Ormerod *et al.*, 1993; Mitsch and Mander, 1997). These measures include various kinds of buffer strips, either of moorland vegetation or native broadleaf trees. Ormerod *et al.* (1993) assessed these approaches using water chemistry and stream macroinvertebrates. The results indicated that buffer strips had little effect on aluminium concentrations. However, catchments with pure conifers and no buffer strips had the lowest mean species richness. The main conclusions from this limited range of studies were that these management methods provided modest benefits, and that the approach did little to reduce acidification on their own, at least in highly acidified streams.

At the reach scale it is also possible to investigate the stability of the SDI over a range of stream conditions. In this study the stability of the SDI at a number of hydrological events was examined across a number of sites.

In summary the SDI provides a potential quantitative value of the weathering upstream of a sampling point. According to White *et al.* (1999) the index is preferable to base flow measurements of pH for a number of reasons. Firstly, pH is notoriously difficult to measure accurately (this has implications for alkalinity tests). On the other hand base cations are relatively straightforward to measure and more variable between catchments. Finally the expression of the results as an index based on ratios 'smooths' out small variations. The values of the SDI indicative of acid-sensitive conditions remain to be defined. The limited data analysed by Kelly-Quinn *et al.* (1999) suggested that sites with low pH and alkalinity would have SDI values greater than 40%.

2 Objectives of this study

The overall objective of this project was to test if the SDI is a better approach at designating sites than the current methods employed, and secondly whether there is any relationship between the SDI values and biological character of streams. This was approached by undertaking studies at a national scale at base flow level, a subset of sites were selected for study at base and elevated flow and a series of studies were conducted during the course of several hydrological events at as smaller number of sites.

A number of hypotheses were tested as follows:

- That SDI is more stable than pH or alkalinity across the range of stream flows and is thus a better indicator of stream sensitivity to forest mediated acidity;
- That there is a graded response by the stream macro-invertebrates to values of the index;
- That buffer strips provide a method to ameliorate acidification in forested catchments on sensitive geologies.

These hypotheses were tested through the following work packages:

2.1 Work Package 1 (Literature review of the efficacy of buffer strips)

Although this work package was associated with the project, the output was submitted as a stand alone element (see Jennings *et al.* (2001)for detailed consideration).

2.2 Work Package 2 (Sodium Dominance Index)

This work package set out to test the hypothesis that SDI is more stable across the range of stream flows and is thus a better indicator of stream sensitivity to forest mediated acidity.

There were two sub-tasks (2.2.1 and 2.2.2 below) in this work package

Work Package 2.1: Extensive sampling of 256 sites across the country during base flow-national scale supra catchment scale

Work Package 2.2: Elevated and base flow sampling was undertaken at 55 sites

This study involved repeated sampling of a subset of sites under both base and elevated flow conditions.

2.2.1 Work Package 2.1. Hydrological events

This sampling involved sampling during several hydrological events at the reach scale.

2.2.2 Work Package 2.2

This work package set out to test the hypothesis that there is a graded response by the stream macro invertebrates in non-forested and forested sites to values of the index;

2.3 Work Package 3. Efficacy of buffer strips in mitigating acidification

Progress on this work package (3.1.1) was deferred pending discussions with COFORD/EPA on the outcome on the literature review in Work Package 1 and eventually it was agreed not to undertake this work package.

2.4 Work Package 4

The sites selected by the Evaluation of Continuous Cover Forestry (ECCF) project lacked any freshwater water systems making them unsuitable for investigation within this work package. EPA/COFORD were advised of the situation and the matter was reported in a number technical reports and it was agreed with the funding agencies that no further progress work package was possible during the project.

Two teams of researchers undertook the research: one from University College Dublin (UCD) and another team from University College Cork (UCC)

3 Description of study sites

3.1 Extensive Survey (Work Package 2.1.)

3.1.1 Site selection and sampling

Site selection for the extensive sampling was undertaken in consultation with EPA/COFORD to ensure collection of data for areas where a paucity of data exists. This included site visits and detailed examination of forest management plans, and the determination of Q-value data availability. All information was collated in an ArcView GIS database which was completed in June 2002. A total of 257 potential sites were identified across Ireland (192 non-forested and 65 forested) potential sites were of good water quality with a minimum EPA rating of Q4 and above, which meant there was no evidence of organic pollution or eutrophication based on macro-invertebrate fauna (EPA, 2000). For practical purposes, the country was divided into two areas, (Northern Ireland was not surveyed i.e. North-East Corner) each research group being responsible for one of these areas (Figure 3.1). Final site sampling distribution was weighted, based on the base cation weathering index map obtained from Aherne and Farrell (2000) (Figure 3.2).

This weighted sampling ensured the required geographical spread of sites was achieved along with sufficient replication across the SDI scale. In addition to the resulting 257 sites, 65 forested sites were selected (across a range of base cation weathering concentrations) in order to determine the influence if any of plantation forestry on the SDI index, on the basis that the majority of these sites were likely to be located in the lower base cation weathering bands. The finalised site selection criteria are summarised in Table 3.1.

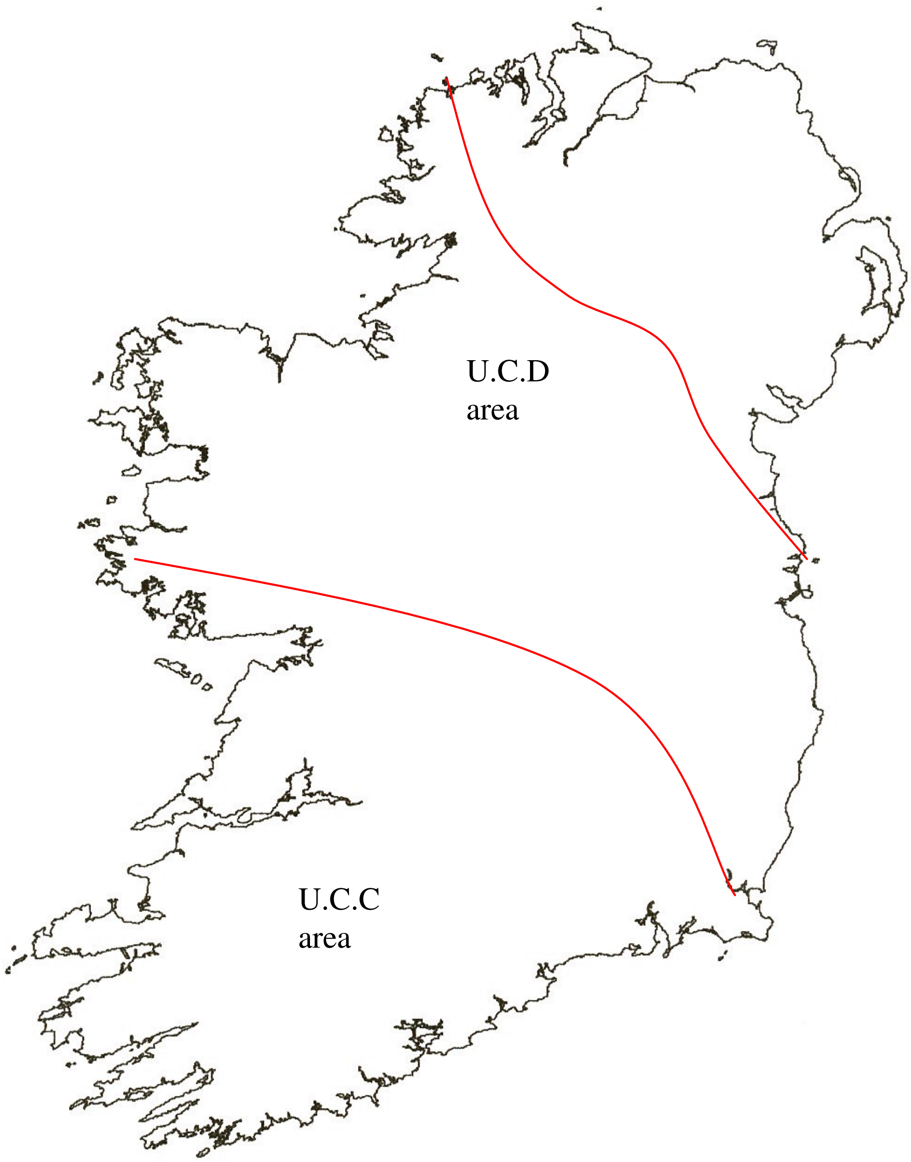


Figure 3. 1. The division of sampling areas for UCC and UCD (Northern Ireland was not sampled).

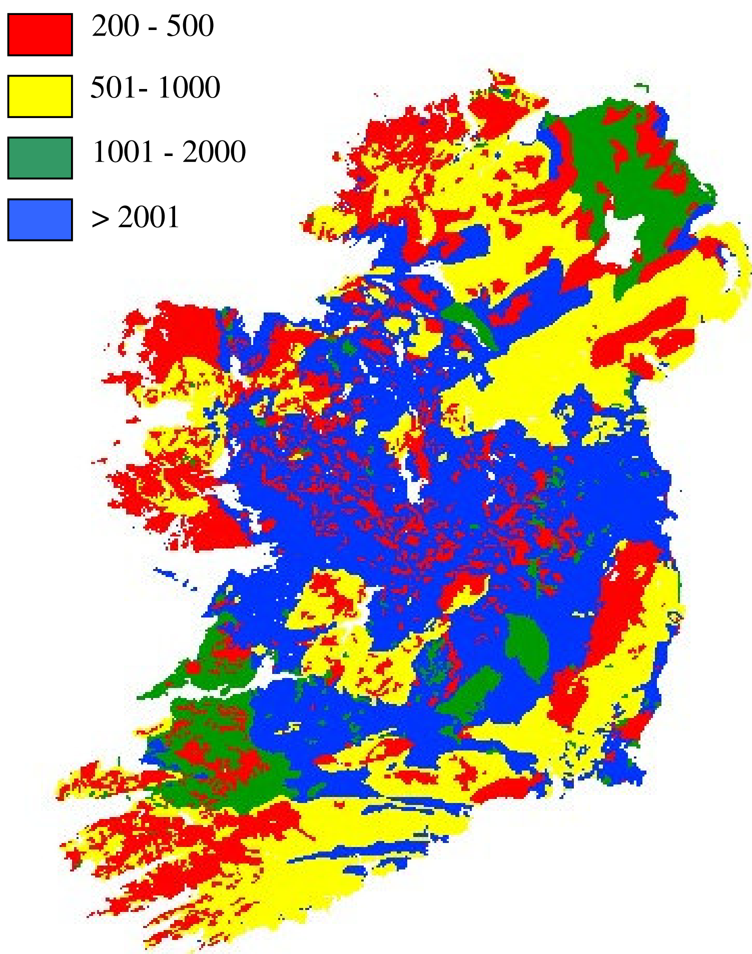


Figure 3.1. The base cation weathering index map (mol_c ha^{-1} $year^{-1}$) after Aherne and Farrell (2000).

Table 3. 1 Summary of site selection criteria

General criteria	
Aim	Collect data from areas where a paucity of suitable data exists
Total number of sites	**200** non-forested and **50** forested
Site geographical distribution	Base cation weathering index (Aherne and Farrell 2000)
University sampling areas	Division of the country in two areas
Site sampling areas	No sites to be sampled in Northern Ireland
Access to forested sites	COFORD/Coillte access enabled
Site details	
Site altitude	>50 m and <300 m
Site length	50 m
Site quality	Q-value greater than or equal to Q4
Stream order	Sites located on 2^{nd} to 4^{th} order streams (avoiding 1^{st} and > 4^{th} order)
Definition of 'forested' sites	Presence of closed canopy forestry in catchment (>20% if possible)
Riparian zone	Intact
Water sample collection	Non-turbulent areas (glides)
Biological sample collection	Multi-habitat using kick samples

3.1.2 Site location and characteristics

The locations of all sites sampled, as well as whether they were forested or not (non-forested: 0 - 20% forest cover; forested: >20% forest cover based on maps), base geology and soil types are indicated in Figure 3.3 - 3.5.The electronic database may be consulted for a detailed identification of sites county by county.

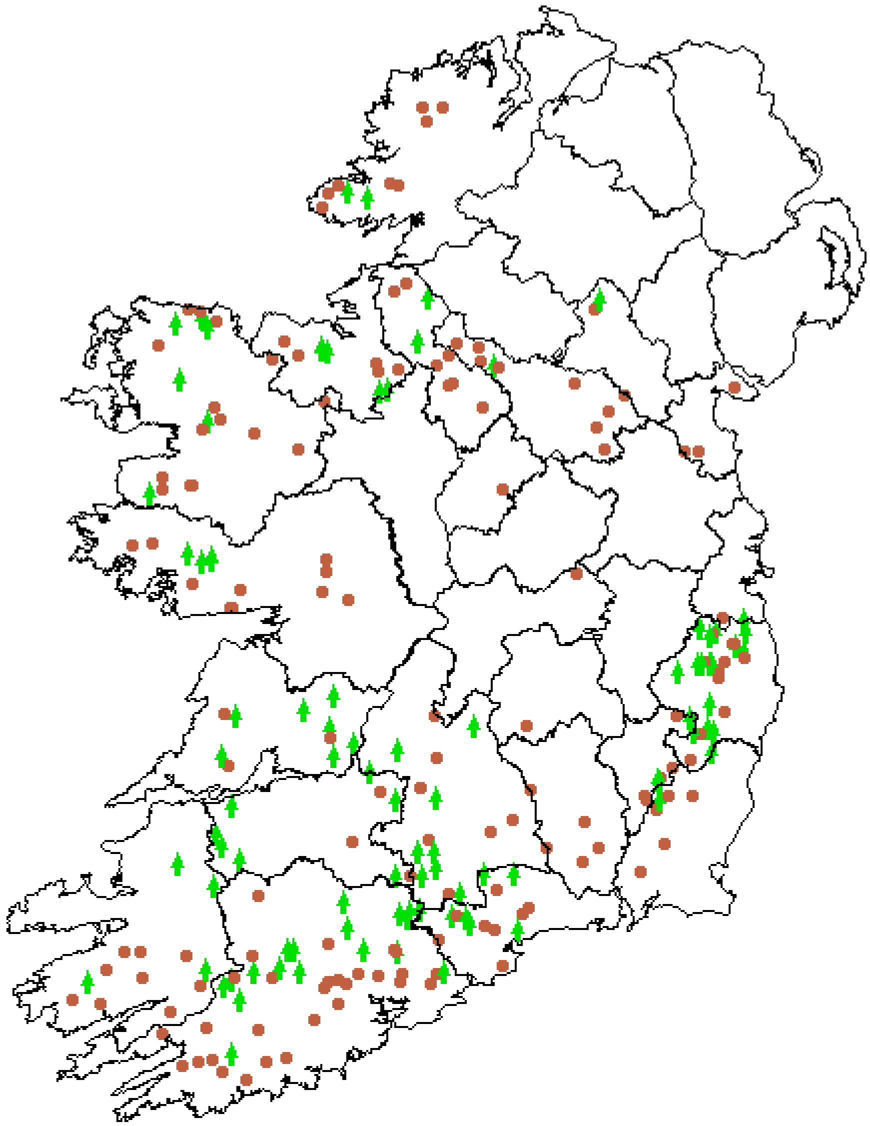


Figure 3. 2. Location of all sampled sites : forested sites; : non-forested sites

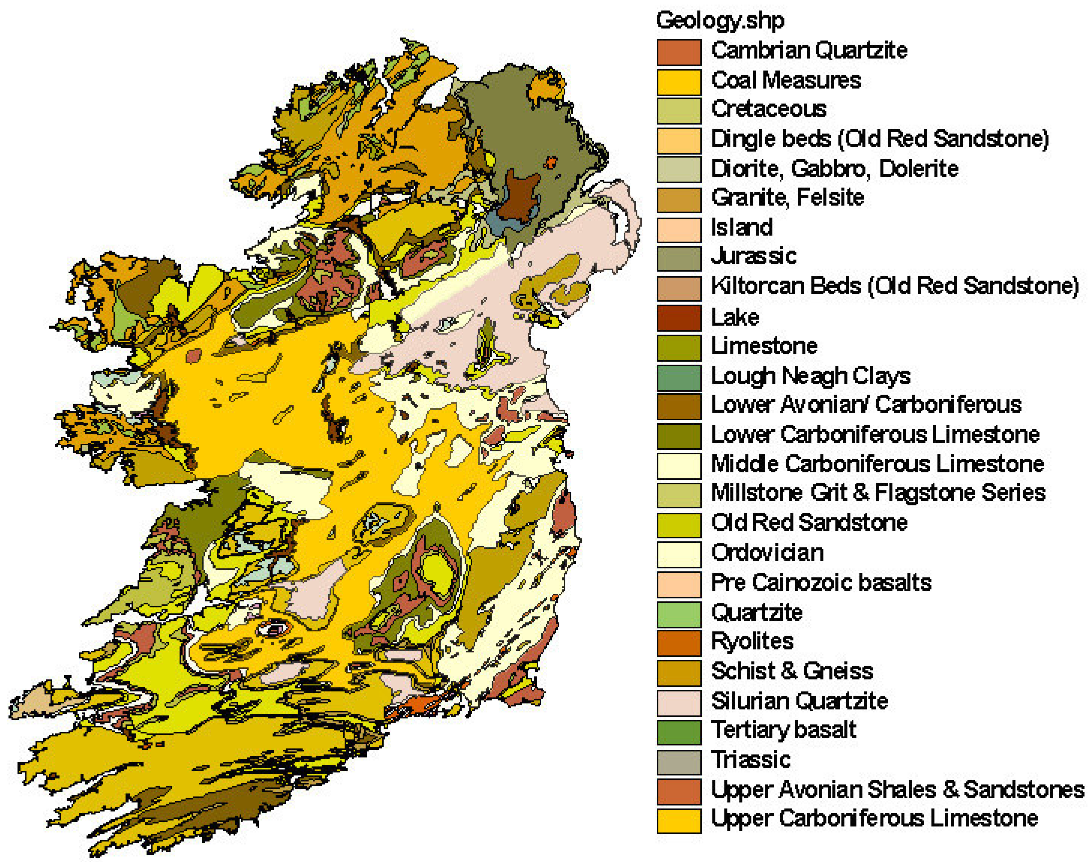


Figure 3. 3. Geological map of Ireland

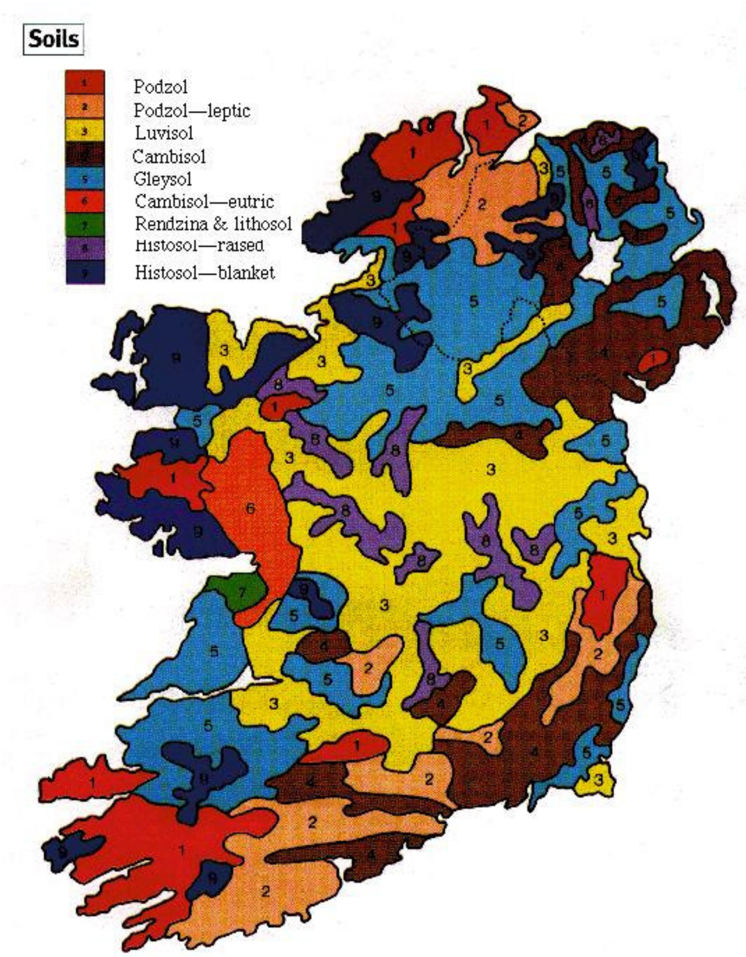


Figure 3. 4. Dominant soil types

3.2 Paired sites of base and elevated flow sampling

3.2.1 Site selection

Following the completion of the extensive sampling phase a sub-set of sites was identified, based on a range of SDI values from the extensive sampling, and sampled at base and elevated flow conditions. This sampling regime was designed to examine the temporal stability in the Sodium Dominance Index and in order to establish whether a single sample is adequate to characterise acid sensitivity of the site. The 65 sites sampled were spread across each research region and sampled between 12 February, 2003 and June 19th 2005, during base and elevated- flow conditions.

3.2.2 Site description

A list of all intensive sites sampled together with river name and reference code, exact sampling location altitude, as well as, where available, photographs of the sampling site during base and high flow conditions are listed in electronic database.

3.3 Hydrological event sampling study sites (work package 2.1)

The sampling during several separate hydrological events at the reach scale was undertaken at the sites listed in Table 3.3. The results were used to examine in greater detail the influence of hydrological state on the SDI at the reach level, in order to provide data on small-scale temporal fluctuations. The landuse in the catchments selected consisted of either moorland, plantation forest or agriculature (or a mixture). See Table 3.3 for details of forest cover.

Table 3. 2. Sites and dates of sampling for the reach scale study (grid references are provided in electronic database) need to fix formatting of this table

Site	Dates sampled	Forest cover	Site	Date	Forest cover
Dripsey	22.01-24.01.04	23%			
		23%		25.04.2005	0%
	30.01-03.02.04		Glencullen	28.04.2005	
		41%		22.06. 2004	0%
				14.03.2005	
Douglas River	13.04-14.04.03		Glendassan		
		43%		20.04.2004	30%
Douglas River (left)	13.04-14.04.03		Annalecka	22.06.2004	
Agalode Bridge	10.02-11.02.05	50%			
Aughboy Bridge	09.02-11.02.05	16%			

4 Methods

4.1 Water Sampling

Few of the sampling sites had gauges to accurately assign flow. However, both research teams have significant experience of their respective catchments and this experience together with rainfall data were used to assess the extent of base or elevated flow. For 'base flow' data collection, sampling was undertaken after 7 days of little or no rainfall (<0.22mm), elevated flow samples were collected following continuous or heavy rainfall. It should be noted that in 2004, both November and December were among the driest on record with less than 40% of the average monthly rainfall recorded for each month (compared with a 30 year mean, Met Eireann web data).

Elevated flow samples were collected from 65 sites, in a similar manner, between February, 2003 and June, 2005, following periods of heavy rain (see 4.2). The reach sampling was undertaken using Sigma samplers (Plate 4.1) that were programmed to collect samples after flow actuation. In most cases the pre-event level was 0.09m and the enabling level was 0.14m: a stream rise of 5cm. For Aghalode the pre-event level was 0.10m and the enabling level was 0.14m, a stream rise of 4cm.

Plate 4. 1. Sigma Auto-sampler deployed to collect Reach Scale samples at river Douglas, Cork

4.2 Protocol for the Measurement of Depth at Flooded Sites

In order to address the problem of measuring the degree of depth change occurring during an 'elevated flow' event in rivers and streams in this study, and thus quantitatively defining an elevated flow level site, the following protocol was used (see Fig. 4.1). For safety reasons, where possible, measurements were obtained from a bridge. In the absence of a bridge, it was deemed acceptable to move downstream of the original sampling point to the closest available bridge (usually a very short distance away). Measurements were carried out using either a long calibrated measuring stick or a weighted line, in order to determine (a) water depth and (b) the height of the bridge above the water surface. Base flow water levels were determined after a period of dry weather and confirmed by a second measurement following a period of rainfall. For low flow data collection, sampling was undertaken after 7 days of little or no rainfall (0.22mm), elevated flow data were collected following continuous or heavy rainfall.

Total drop (from the bridge) $z_{ii} = x_{ii} + y_{ii}$

Using the following equation, the degree of high flow was calculated without the hazards associated with entering the water during fast flow conditions.

Degree of flood (d) = $(x_{ii} - x_i) * 100 / (z_{ii} - w)$

$(z_{ii} - w)$ = maximum possible flood value i.e. the bank height.

An elevated flow event was categorised as the % increase from base flow (Water depth during low flow = x_i; Water depth during a flood event = x_{ii}; Water level during a flood event = $y_{ii;}$ Height of the bridge to the top of the bank =w)

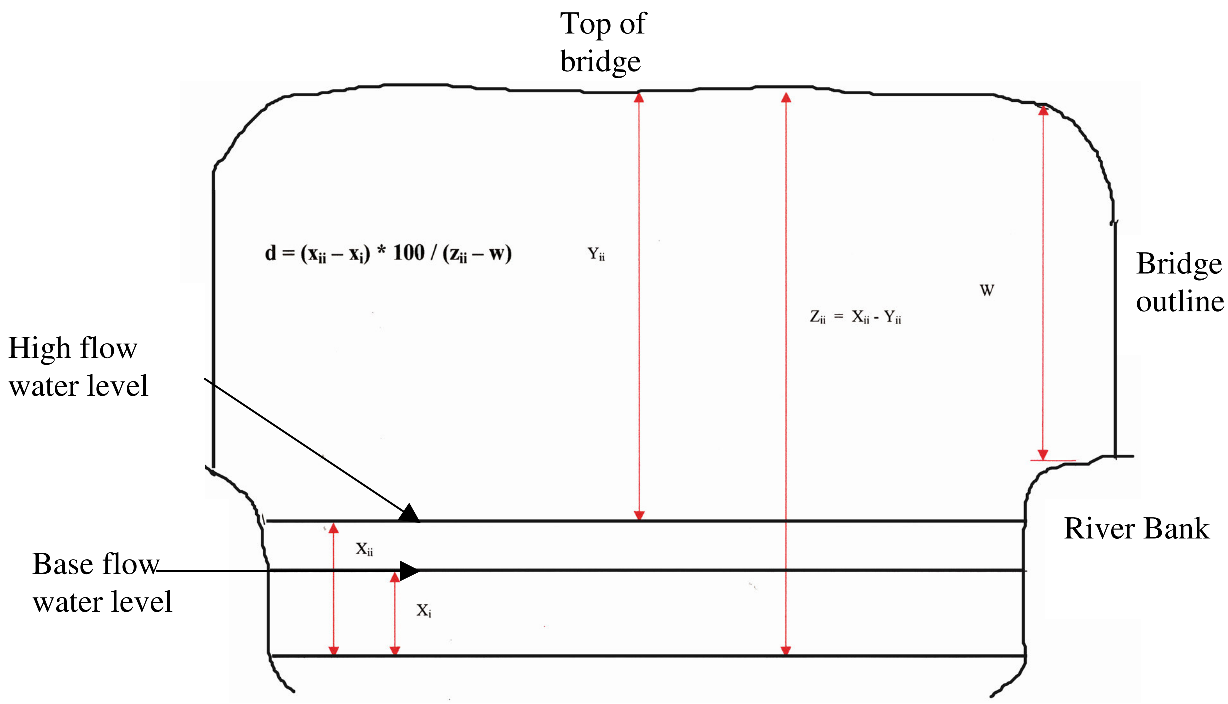


Figure 4. 1. Diagrammatic representation of the measurements made to determine water level during elevated flow.

4.3 Chemical analysis of water samples

pH and conductivity readings were made in the field using meters, all other parameters were determined in the laboratory usually within 12 hours following collection (no later than 24 hours after the event). The detailed methods for each of the hydrochemical parameters are set out below.

Table 4. 1. Summary of the analytical methods used

Parameter	Method	Unit
pH	pH meter	units pH
Conductivity	Conductivity meter	$\mu S\ cm^{-1}$ @25^0C
Alkalinity	Depended on pH: Gran titration or standard titration	mg l^{-1} $CaCO_3$
Calcium	Ion Chromatography	mg l^{-1} Ca^{2+}
Magnesium	Ion Chromatography	mg l^{-1} Mg^{2+}
Sodium	Ion Chromatography	mg l^{-1} Na^+
Potassium	Ion Chromatography	mg l^{-1} K^+
Chloride	Ion chromatography	mg l^{-1} Cl^-
Colour	Colorimetry	mg l^{-1} Pt^+/Co
Organic carbon	Colorimetry/conversion equation	mg l^{-1} DTOC
Aluminium	Colorimetry	mg l^{-1} Al^{3+}

4.3.1 Na^+, K^+, Mg^{2+}, Ca^{2+}

The major cations were analysed by Ion Chromatography using Dionex (UCD) or the Lachat IC system (UCC).

4.3.2 Conductivity

Conductivity was determined using a LF 330 conductivity meter (WTW, Weilheim.Germany). Regular laboratory calibrations were made.

4.3.3 pH

pH was determined using a 330i pH meter (WTW Weilheim. Germany) and calibrated using buffers at pH 4 and 7.

4.3.4 Alkalinity

The method used to determine alkalinity depended on the conductivity of the sample as follows:-

4.3.5 Alkalinity when conductivity was greater than 200µS cm^{-1}

Alkalinity was determined by titration of 100ml of sample against 0.01N HCl, using BDH 4.5 indicator to determine the end-point.

4.3.6 Alkalinity when conductivity was <200µS cm^{-1}

A -Gran Titration was used. pH values were measured at several points within the range of 4.4 to 3.7. and the following function was calculated:-

$F_2 = |\text{antilog (a-pH)}|\ (V_0+v)$

Where a = any convenient number such as 5

V_0 = initial sample volume,

V = titrant volume

4.3.7 Colour

Samples were filtered through GF/C filter papers and the optical density was measured at 455nm using a 4cm cuvette. The calculations were as follows:

$f = H_a \div A_a$

$H_s = f \times A_s$

Where f = f factor

H_a = Hazen units of colour standard

A_a = Absorbance of colour standard

H_s = Hazen units of sample

A_s = Absorbance of sample

4.3.8 Dissolved Total Organic Carbon (DTOC)

Samples were filtered through GF/C filter papers and the colour of the sample read on UV/VIS Light Spectrometer @ 340nm

Resulting absorbance values plugged into following equation

[DOC] = 50.143 (Abs. @ 340nm) + 2.72

(*from*, AQUAFOR, Kelly-Quinn *et al.*, 1997a).

4.3.9 Aluminium

Total aluminium was determined according to the Pyrocatechol Violet Method using an FIAstar 5010 Analyser (Tecator, Höganäs, Sweden).

4.3.10 Inorganic Aluminium Speciation Method

This method is an adaptation of a method using a glass column mixing. Polyethylene snap cap vials were used instead of a glass column to speed up the process while retaining the accuracy of the results (adaptation *from* Allot *et al*. (1990)).

Resin Preparation and Activation:

Sodium (Na+) and hydrogen (H+) form Amberlite resins were used in the speciation procedure. The resins were activated using sodium chloride and hydrochloric acid solutions respectively. Fifteen millilitres of sample river water was added to the appropriate activaited resin. The amount of either type of resin used for each water sample is dependent on original pH of the sample. Mixing approximately 95% Na+ resin and 5% H+ resin will keep the pH constant at ~4 during the exchange. If the sample is above pH 4.80 use the Na+ form only, while if pH is below 3.5 use the H+ form only. Mixing approximately 95% Na+ form and 5% H+ form will keep the pH of the sample constant at ~4 during the exchange. The water sample (and resin) were mixed for 10 minutes to absorb the inorganic form of aluminium into the resin. Following a colourimetric test, the resulting organic aluminium concentration was subtracted from the total aluminium to gain the inorganic concentration.

4.3.11 Chloride

Chloride was determined according to the Mercury Thiocyanate Method using a FIAstar 5010 Analyser (Tecator, Höganäs, Sweden).

4.3.12 Acid neutralising capacity (ANC)

Acid neutralising capacity (ANC) was calculated as follows:-

ANC = Gran Alkalinity + 54 ([DOC]/12) – ([Total Aluminium]/9)

Where, alkalinity units are meq/l

DOC units are mg/l

and Aluminium units are mg/l

(*from* Foster *et al.* (2001))

4.3.13 Total Hardness

Total hardness of water samples was calculated as follows:-

Total Hardness = ($[Ca^{2+}]$*2.497) + ($[Mg^{2+}]$*4.118)

Where, calcium and magnesium are in mg l^{-1}.

4.3.14 Non-marine Ion Equations

Non-marine ion concentrations were calculated as follows:

NM Ca^{2+} = Ca^{2+} - 0.037 * Cl^-

NM Mg^{2+} = Mg^{2+} - 0.193 * Cl^-

NM Na^+ = Na^+ - 0.851 * Cl^-

NM SO_4^{2-} = SO_4^{2-} - 0.1025 * Cl^-

(*from* Kelly-Quinn *et al*. (1997).

4.3.15 Inter-calibration of water chemistry

Inter-calibration exercises were conducted to ensure the quality and standardisation of the water chemistry analyses in the laboratories at UCD and UCC. Three hard water and three soft water samples collected by each laboratory were analysed. The source of the initial variation in inter-calibration results between laboratories was identified to equipment problems, the subsequent results of a suite of analyses showed close agreement (Table 4.2). The differences in the two results had a minor influence on the values of Sodium Dominance Index. To further confirm laboratory performance a set of water samples with prepared concentrations of the major cations was acquired and analysed by both laboratories and also by an independent accredited laboratory. The UCD and UCC results were largely within the 95% confidence limits (Table 4.3).

When batches of project samples were being analysed it was routine practice to retest standards at several points during the analysis run. The dataset was also scanned for possible errors by testing ions balance where full suite of ions were analysed. Data, considered to be out of line, were tested, by plotting alkalinity against pH or the various cations against conductivity and alkalinity. Some data were rejected on this basis.

Table 4. 2 Results of the December 2003 intercalibration exercise for the major cations

	Sodium (mgl^{-1})		Calcium (mgl^{-1})		Magnesium (mgl^{-1})		SDI	
Sample	UCD	UCC	UCD	UCC	UCD	UCC	UCD	UCC
Soft 1	4.64	5.06	0.71	0.68	0.69	0.79	62.55	77.47
Soft 2	3.42	3.65	1.25	1.49	0.61	0.70	72.85	63.98
Soft 3	4.40	4.48	2.70	3.48	0.63	0.78	52.20	51.51
Hard 1	11.46	11.66	29.54	35.21	6.95	6.99	23.69	22.27
Hard 2	10.59	10.72	22.77	24.50	5.62	5.67	26.55	26.34
Hard 3	9.82	9.89	18.64	19.91	5.13	5.18	28.73	27.89

Table 4. 3 Results of the inter-calibration exercise for the major cations based on prepared samples

	Sample no.	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Sodium							
	Prepared concentration (mgl^{-1})	7.5	10	10.5	6	6	8
	UCC	8.00	10.29	11.13	6.29	5.96	7.89
	UCD	7.86	10.32	10.86	5.97	5.97	7.95
	Independent lab	7.80	12.00	10.00	6.80	7.00	9.00
	Mean	7.79	10.65	10.62	6.27	6.23	8.21
	Standard Deviation.	0.21	0.91	0.49	0.38	0.51	0.53
	(+) 95% Confidence Limits	8.03	11.68	11.18	6.70	6.81	8.81
	(-) 95% Confidence Limits	7.55	9.62	10.07	5.83	5.65	7.61

Magnesium							
	Prepared concentration (mgl^{-1})	3.75	3.5	5.25	1	1.5	3.2
	UCC	2.60	2.66	3.78	0.93	1.41	3.15
	UCD	3.80	3.54	5.31	1.36	1.36	3.10
	Independent lab.	3.23	3.14	4.55	0.96	1.45	3.09
	Mean	3.34	3.21	4.72	1.06	1.43	3.13
	Standard Deviation.	0.56	0.41	0.72	0.20	0.06	0.05

(+) 95% Confidence Limits	3.98	3.67	5.53	1.29	1.50	3.19
(-) 95% Confidence Limits	2.71	2.75	3.91	0.84	1.36	3.08

Calcium							
	Prepared concentration (mgl^{-1})	50.00	30.00	70.00	2.00	4.00	11.00
	UCC	51.21	29.50	66.80	2.98	4.49	11.99
	UCD	52.48	32.67	72.03	1.53	4.44	11.93
	Independent lab.	46.06	29.52	64.03	2.76	4.72	11.79
	Mean	49.94	30.42	68.21	2.32	4.41	11.68
	Standard Deviation	2.77	1.52	3.52	0.67	0.30	0.46
	(+) 95% Confidence Limits	53.08	32.14	72.20	3.08	4.75	12.20
	(-) 95% Confidence Limits	46.80	28.71	64.23	1.56	4.07	11.16

4.4 Biological sampling

4.4.1 Site selection

The database generated by the extensive water-sampling programme provided the information used in the site selection for biological assessment. A sub-set of 65 sites was selected for macroinvertebrate sampling from the 257 sites previously sampled in the extensive sampling stage. These sites covered the following SDI bands: 0-10, 20-30, 40-50, 60-70 and >70. The number of sites sampled in each SDI band was not the same but most bands had six forested and six non-forested sites. A complete list of sites where macroinvertebrates were sampled is given in the electronic database.

4.4.2 Macroinvertebrate Sampling

Samples were collected in both spring and autumn 2003 from 65 sites to determine biological indicators for sensitivity grades within the sodium dominance index. Macroinvertebrates were collected using three-minute multi-habitat kick sampling together with a one-minute hand search/stone wash. This approach attempted to ensure that the maximum biodiversity was sampled at each site. A 50m reach was surveyed for different habitat types – riffles, glides, pools, backwaters, vegetated areas and margins. The time allotted to sampling each habitat type was weighted according to the percentage representation of each in the 50m reach. Three replicate samples were taken at each site together with descriptions of the respective habitats.

4.4.3 Sorting and identification of macroinvertebrates

All taxa were removed except those which were highly abundant and required sub-sampling. Sub-sampling was carried out using the following protocol:

1. Having identified the taxa to be sub-sampled (i.e. with large numbers of very small individuals that were extremely difficult to separate taxonomically) the sample was well mixed, and the sorting tray was divided into 12 grids of equal size and 3 grids were randomly selected, within which the numbers of the taxa in question were counted. The specimens counted were not collected. However, if rare species of the taxa were encountered they were collected.
2. The total number of the given taxa in the sample was then estimated by multiplication (x4).
3. A minimum of 100 specimens per taxa were collected at random from the tray. Identifiable specimens were removed (minimum 100) and the relative proportion of each was calculated.
4. The total number of each taxa in the sample was calculated by multiplying the total number of the taxa by the relative proportion of each taxa. The number of specimens within each taxon was calculated according to the total number counted at family/genus level in the whole sample and the relative abundance of the taxon within the 100 collected specimens.

4.4.4 Taxonomic levels

The levels of taxonomic resolution adopted are shown in Table 4.4.

Table 4. 4 Summary of the identification level used for the steam macroinvertebrates sampled

Taxonomic group	**Identification level**
Turbellaria	Species
Hirudinea	Species
Crustacea	Species
Plecoptera	Species
Ephemeroptera	Species
Trichoptera	Species
Coleoptera	Species
Heteroptera	Species
Odonata	Species
Mollusca	Species/genus
Diptera	Genus/family
Other taxa	Family/order

4.5 Statistical Analyses

4.5.1 Overall analysis

TWINSPAN was used to classify the 65 sites - spring and autumn faunal datasets (initially using non- forested sites and then a further TWINSPAN included both the forested and non-forested sites) separately- based on macroinvertebrate species assemblages (Hill, 1979). TWINDEND analysis was applied to indicate the degree of heterogeneity, reported as a percentage value, in the site groups derived from the TWINSPAN. As low levels of heterogeneity within groups are desirable, values of ~60% or below were accepted. Resulting TWINSPAN Groups were validated using MRPP (PC-ORD). The indicator species, were confirmed by IndVal (PC-ORD). Detrended Correspondence Analysis (DCA) was initially used to determine which multivariate techniques were most appropriate for the datasets (Ter Brakk, 1991; Birks, 2000). Canonical Correspondence Analysis (CCA with forward selection) was used to examine the relationships between the faunal dataset and the physico-chemical parameters (Ter Braak, 1991). Canonical Correspondence Analysis was run using Ecological Community Analysis 2.0 (ECOM™ 2.0) A total of 31 physical and chemical variables were entered into the analysis including catchment area, alkalinity, catchment perimeter (km^2), pH (units), slope (%), conductivity ($\mu S\ cm^{-1}$), elevation (m), distance from source (km), % forestry, % riffle, % Glide, % Pool, magnesium ($mg\ l^{-1}$), calcium ($mg\ l^{-1}$), sodium ($mg\ l^{-1}$), chloride ($mg\ l^{-1}$),, non-marine sodium ($mg\ l^{-1}$), non-marine calcium ($mg\ l^{-1}$), non-marine magnesium (mg l-1), marine sodium ($mg\ l^{-1}$), marine calcium ($mg\ l^{-1}$), marine magnesium ($mg\ l^{-1}$), total aluminium ($\mu g\ l^{-1}$), % bedrock, % boulder, % cobble, % gravel, % sand, and % mud. Summary statistics were calculated and standard tests (including ANOVA and correlation analysis) were conducted to compare hydrochemical values between site types (e.g. forested and non-forested; geological classes and SDI classes) and to examine for relationships between parameters.

Hydrological event calculations:

The factors contributing to loss of buffering during a selection of the events were examined using the methodology outlined in Kahl *et al.* (1992). The loss of alkalinity due to dilution was estimated from the following equation

$$[\{((\sum BC_b - \sum BC_m)/ \sum BC_b)*Alk_b)\} /(Alk_b - Alk_m]*100$$

b=base flow, m=point of minimum alkalinity

BC= Base Cations

Values of 100% indicate that only dilution is affecting buffering. Lower values indicate titration by an acid anion. Loss of alkalinity due to titration is further evidenced by changes in the ratio of alkalinity/$\sum$BC. The contribution of the sulphate, nitrate and organic anions to the titration process were calculated from anion/$\sum$anions

All base cation and anion calculations were based on non-marine fractions.

5 Results

5.1 Extensive water chemistry survey

Results of the hydrochemical examination of extensive sites are presented below. Summary statistics for these sites grouped according to dominant watershed geology are given in Table 5.1.

5.1.1 pH

The values of pH recorded for the sites sampled ranged from pH 4.9 to 8.8 (Table 5.1). Most (84%) values were in the circum-neutral range (pH 6.5-7.5). The majority of sites with pH values <7 were located in the west (north west and south west) and some in the east (Figure 5.1).

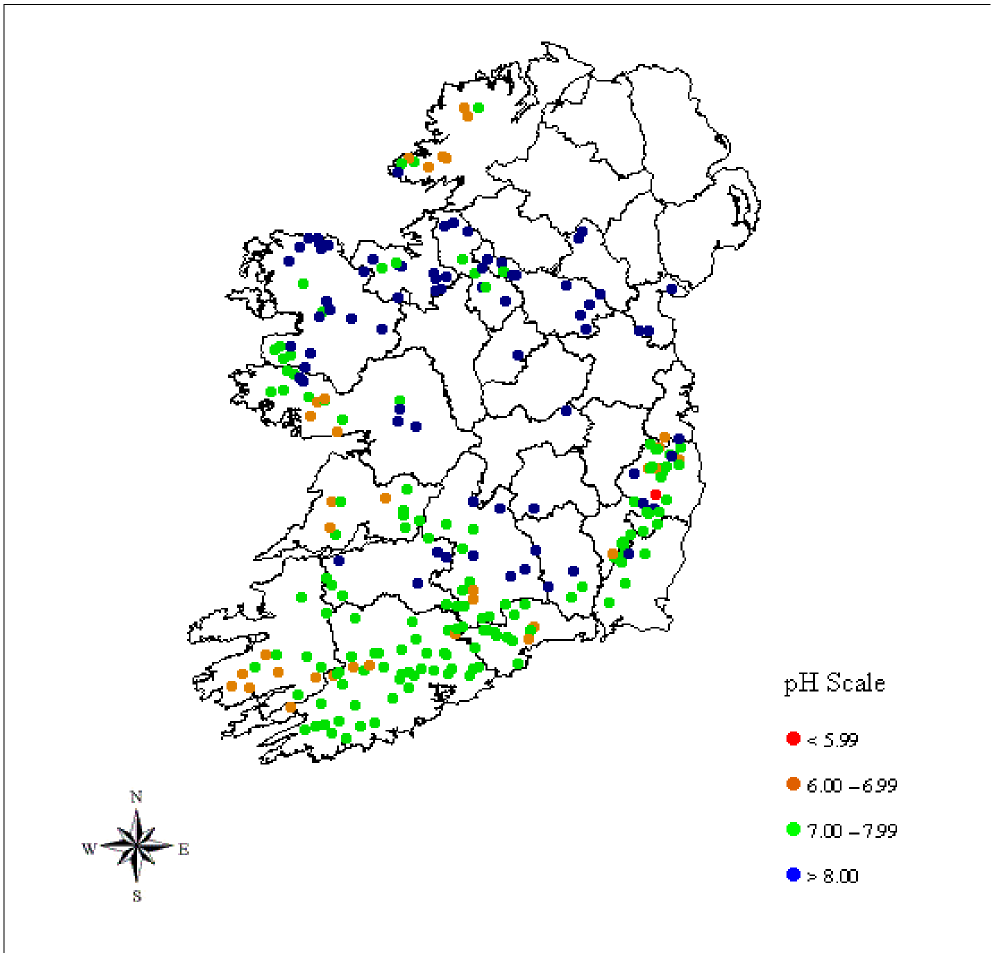


Figure 5. 1. pH values across the range of extensive sites.

5.1.2 Conductivity

Figure 5.2 shows the conductivity data for all sites sampled. Low conductivity values (red and blue) were associated with poorly buffered areas (e.g. granite) whilst higher values (yellow and white) were linked with well-buffered areas (e.g. limestone). Conductivity values (over geological types) ranged from 43 to 628.6 µS cm^{-1}.

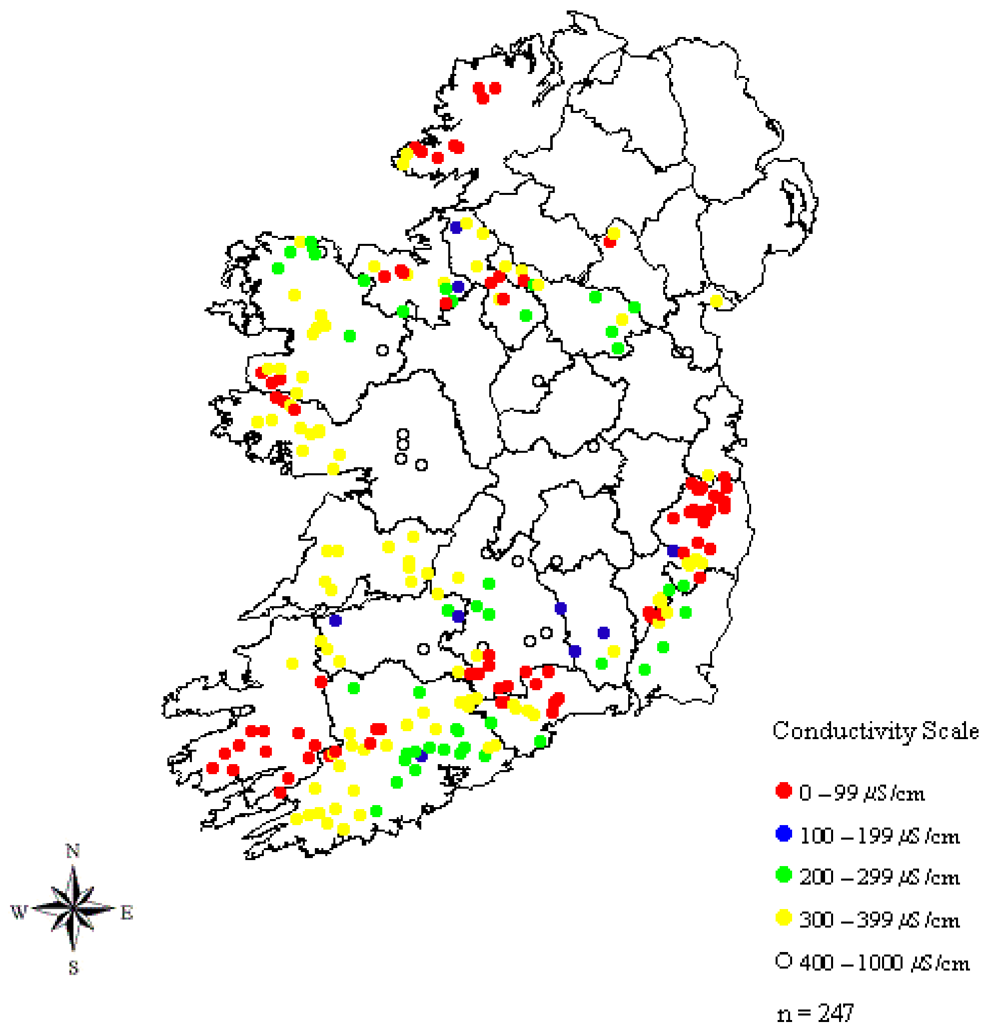


Figure 5. 2. Spatial distribution of conductivity results for the extensive sites. Low conductivity values (white and blue) are associated with poorly buffered areas (e.g. granite) whilst higher values (orange and red) are linked with well-buffered areas (e.g. limestone).

Table 5. 1 Summary statistics for selected chemical parameters measured at the extensive sites (grouped according to dominant watershed geology)

Dominant Watershed Geology	pH	Conductivity $\mu S\ cm^{-1}$	Alkalinity $mg\ l^{-1}$ $CaCO_3$	Sodium $mg\ l^{-1}$	Potassium $mg\ l^{-1}$	Magnesium $mg\ l^{-1}$	Calcium $mg\ l^{-1}$	SDI	Chloride $mg\ l^{-1}$	Total Aluminium $\mu g\ l^{-1}$	DOC $mg\ l^{-1}$
Limestone											
Mean	8.2	473.8	212.7	9.2	2.3	6.0	59.6	21.4	18.1	62.1	8.4
Median	8.2	525.0	257.3	8.8	2.1	5.3	49.6	20.6	18.3	50.2	7.1
Max.	8.8	628.5	306.0	11.7	3.3	10.0	130.0	32.8	33.7	157.0	12.7
Min.	7.7	153.0	44.4	5.9	1.1	1.7	17.6	10.1	10.8	31.6	3.2
Quartzite and Sandstone Mix											
Mean	7.8	193.8	64.4	7.0	1.0	3.8	14.6	39.6	14.1	103.8	9.3
Median	7.7	179.1	61.1	7.3	0.9	3.8	14.8	35.1	14.3	129.5	9.3
Max.	8.3	332.5	135.5	8.3	1.8	5.6	23.5	56.3	16.9	137.0	15.8
Min.	7.3	90.2	13.2	5.8	0.3	1.9	5.0	28.9	11.6	37.0	4.5
Upper Avonian Shales and Sandstones											
Mean	7.8	133.4	35.3	8.7	1.2	2.9	17.4	43.8	17.0	60.7	8.1
Median	7.7	110.0	24.8	8.3	1.0	2.8	16.5	42.6	15.6	64.6	5.5
Max.	8.7	269.0	112.5	11.2	2.1	4.2	34.9	79.7	35.2	96.6	15.9
Min.	6.9	76.0	0.9	6.1	n/d	1.8	1.8	24.8	10.1	32.0	3.6
Lower Avonian Shales and Limestone											
Mean	7.5	216.6	75.5	12.3	1.2	3.9	21.1	47.4	24.7	74.1	8.3
Median	7.8	213.0	50.0	13.2	1.0	3.4	18.2	51.3	26.0	60.8	7.1

Table 5.1. cont.

Dominant Watershed Geology	pH	Conductivity $\mu S\ cm^{-1}$	Alkalinity $mg\ l^{-1}\ CaCO_3$	Sodium $mg\ l^{-1}$	Potassium $mg\ l^{-1}$	Magnesium $mg\ l^{-1}$	Calcium $mg\ l^{-1}$	SDI	Chloride $mg\ l^{-1}$	Total Aluminium $\mu g\ l^{-1}$	DOC $mg\ l^{-1}$
Max.	8.0	538.0	322.5	16.6	2.6	6.9	68.3	59.5	34.8	135.0	18.1
Min.	6.5	58.0	3.3	5.8	0.1	1.8	6.6	24.3	10.2	42.1	3.7
Old Red Sandstone											
Mean	7.3	139.5	26.3	8.4	1.2	2.8	10.7	53.6	16.0	93.1	9.3
Median	7.2	118.3	18.6	8.2	0.7	2.2	8.2	53.1	15.4	68.0	8.8
Max.	8.1	308.5	112.5	13.8	4.0	6.7	34.9	80.1	31.3	1039.7	19.6
Min.	6.2	46.8	1.2	4.4	n/d	0.8	1.5	30.4	4.6	24.0	3.3
Quartzite											
Mean	7.6	178.3	54.0	9.1	1.3	4.1	12.7	49.3	18.5	58.2	6.5
Median	7.7	164.5	44.9	8.6	0.9	3.8	13.7	41.9	15.7	48.4	5.1
Max.	8.6	469.6	207.5	15.8	3.9	8.7	28.4	78.0	44.0	117.0	15.6
Min.	6.3	56.0	1.3	5.1	0.4	1.0	2.0	26.7	8.2	32.4	1.9
Ordovician											
Mean	7.3	136.2	22.6	9.7	1.1	4.4	9.8	52.0	19.3	57.0	4.2
Median	7.3	111.5	20.8	10.1	0.8	3.9	10.1	48.0	18.5	41.6	3.2
Max.	7.8	250.6	55.0	12.0	2.3	8.2	21.6	73.6	39.7	180.0	16.1
Min.	6.1	66.0	1.4	6.0	0.3	1.3	1.6	31.7	10.5	33.1	1.3

Table 5.1. cont.

Dominant Watershed Geology	pH	Conductivity $\mu S\ cm^{-1}$	Alkalinity $mg\ l^{-1}\ CaCO_3$	Sodium $mg\ l^{-1}$	Potassium $mg\ l^{-1}$	Magnesium $mg\ l^{-1}$	Calcium $mg\ l^{-1}$	SDI	Chloride $mg\ l^{-1}$	Total Aluminium $\mu g\ l^{-1}$	DOC $mg\ l^{-1}$
Old Red Sandstone Mix											
Mean	7.5	181.0	44.5	9.8	1.9	3.2	14.9	47.5	19.3	85.9	9.1
Median	7.4	163.9	28.5	10.0	1.8	2.7	12.3	53.1	17.2	82.0	8.9
Max.	8.1	348.3	131.5	12.2	5.4	8.9	37.4	60.2	28.3	140.0	13.0
Min.	7.1	90.0	14.2	7.0	0.8	1.7	6.8	31.3	12.9	39.5	5.9
Millstone Grit & Flag Series											
Mean	7.4	237.3	60.8	13.6	1.7	3.7	13.5	57.7	25.3	96.6	21.9
Median	7.1	177.0	21.1	14.5	1.8	3.0	10.1	63.8	27.6	111.0	21.9
Max.	8.3	356.5	150.0	16.9	2.0	5.9	30.9	79.0	31.6	137.0	35.4
Min.	6.5	137.7	0.7	7.0	0.9	2.3	2.9	30.5	13.4	53.0	8.4
Granite and Felsite Mix											
Mean	7.1	83.7	10.1	7.8	0.6	2.3	5.8	59.8	17.1	73.5	5.1
Median	7.2	72.0	6.2	7.3	0.7	1.8	5.7	54.1	17.8	71.7	4.9
Max.	7.5	139.0	20.9	12.4	1.3	5.1	10.1	77.5	24.7	123.0	7.9
Min.	6.4	43.0	1.9	5.6	0.2	0.8	1.7	44.2	10.5	31.9	1.1
Granite and Felsite											
Mean	6.9	82.5	9.4	8.2	0.7	2.0	7.0	61.6	14.0	76.3	6.8
Median	7.1	65.0	4.8	7.2	0.6	2.0	4.6	64.4	11.8	69.1	5.6
Max.	8.2	195.6	45.1	15.8	2.6	5.8	27.4	81.9	30.7	156.5	21.5
Min.	4.9	29.0	-0.2	4.3	n/d	0.6	1.5	29.4	5.2	33.9	1.9

Table 5.1. cont.

Dominant Watershed Geology	pH	Conductivity $\mu S\ cm^{-1}$	Alkalinity $mg\ l^{-1}\ CaCO_3$	Sodium $mg\ l^{-1}$	Potassium $mg\ l^{-1}$	Magnesium $mg\ l^{-1}$	Calcium $mg\ l^{-1}$	SDI	Chloride $mg\ l^{-1}$	Total Aluminium $\mu g\ l^{-1}$	DOC $mg\ l^{-1}$
Schist and Gneiss											
Mean	7.5	124.5	32.1	11.2	0.5	2.7	11.3	57.4	26.0	47.9	5.8
Median	7.6	107.0	17.1	10.6	0.7	2.6	8.1	57.8	25.1	35.4	4.4
Max.	8.7	270.0	137.5	15.1	0.9	4.8	34.8	77.1	46.5	103.0	18.6
Min.	6.5	63.0	2.2	6.1	n/d	1.5	3.4	30.6	11.0	33.3	3.4
Coal Measures											
Mean	7.5	146.2	16.1	13.3	1.4	3.2	7.1	66.1	23.8	69.0	16.0
Median	7.5	146.2	15.6	13.3	1.4	3.3	6.4	66.1	23.8	69.0	15.8
Max.	7.7	184.2	26.1	15.7	2.6	3.7	12.9	74.0	31.6	124.0	20.8
Min	7.2	94.0	9.7	10.0	0.6	2.5	2.0	59.2	16.7	34.0	9.6

5.1.3 Cation composition

Data for the cation composition of the extensive sites are illustrated in Figure 5.3. Calcium dominated the sites located in well-buffered limestone areas whereas, sodium dominated those sites located in poorly buffered areas. Most (90-100%) of the calcium was from non-marine sources in over 98% of the sites. In contrast, 50% of the magnesium recorded at 86 of the sites was of marine origin. At the remaining sites, marine derived magnesium accounted for 10% (34 sites) to 40% (37 sites) of the total concentration. Potassium contributed less than 3% of the major cation concentration at the majority (80%) of sites.

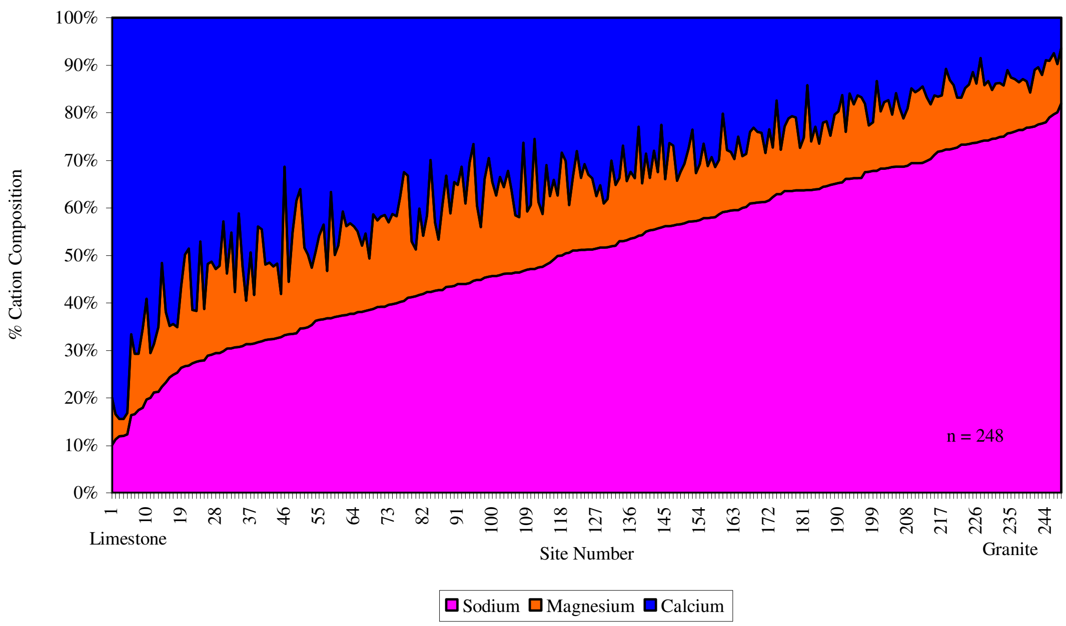


Figure 5. 3. Percentage cation composition (calculated in terms of mmol l^{-1}) at extensive sites

5.1.4 The spatial variability of the Sodium Dominance Index

Figure 5.4 shows the spatial distribution of sites within SDI bands. Values ranged from 10.1 (Yellow River, Co. Meath) to 81.9 (Cashla River, Co. Galway). The highest values of the index were recorded in upland sites in Wicklow, Donegal, Galway/Mayo and Kerry

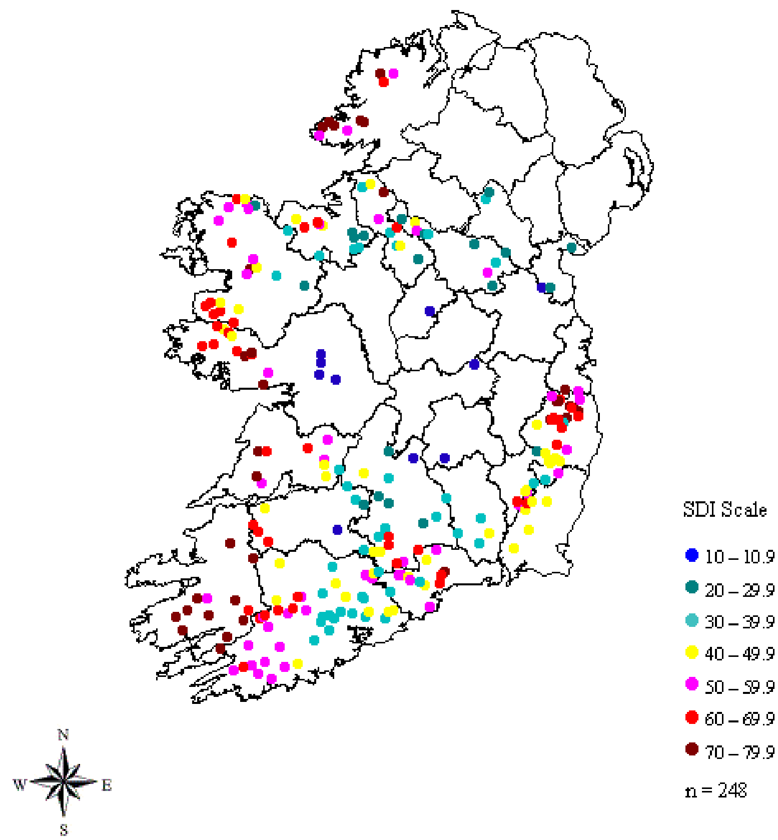


Figure 5. 4. Spatial distribution of SDI results for the extensive sites see text for details

The sites were assigned to one of thirteen groups based on dominant watershed geology. These groupings did not always take into account site geology, which can have a substantial influence on water chemistry. For example two sites (Owemore, Co. Mayo – Schist & Gneiss and Big River, Co. Louth – Granite & Felsite) were placed into hard geology groups had high calcium and Sodium Dominance values compared to all other sites in the group (see maximum values on Table 5.1).

A strong relationship between SDI and geology is clear from Figure 5.5. The lowest values were recorded on limestone with values steadily increasing as one moves on to the more weather resistant rocks such as granite. Significant differences were detected (ANOVA $F_{12,182}$ =9.323, P<0.001) across the geological groups for the non-forested sites but not among the forested sites (ANOVA $F_{8,35}$ =1.124, P =0.371). The post hoc tests on the non-forested sites revealed significant differences (Table 5.2) between limestone and all other geologies except Silurian quartzite and sandstone mixes. Within any geological group no significant difference in SDI was detected between the non-forested and forested sites.

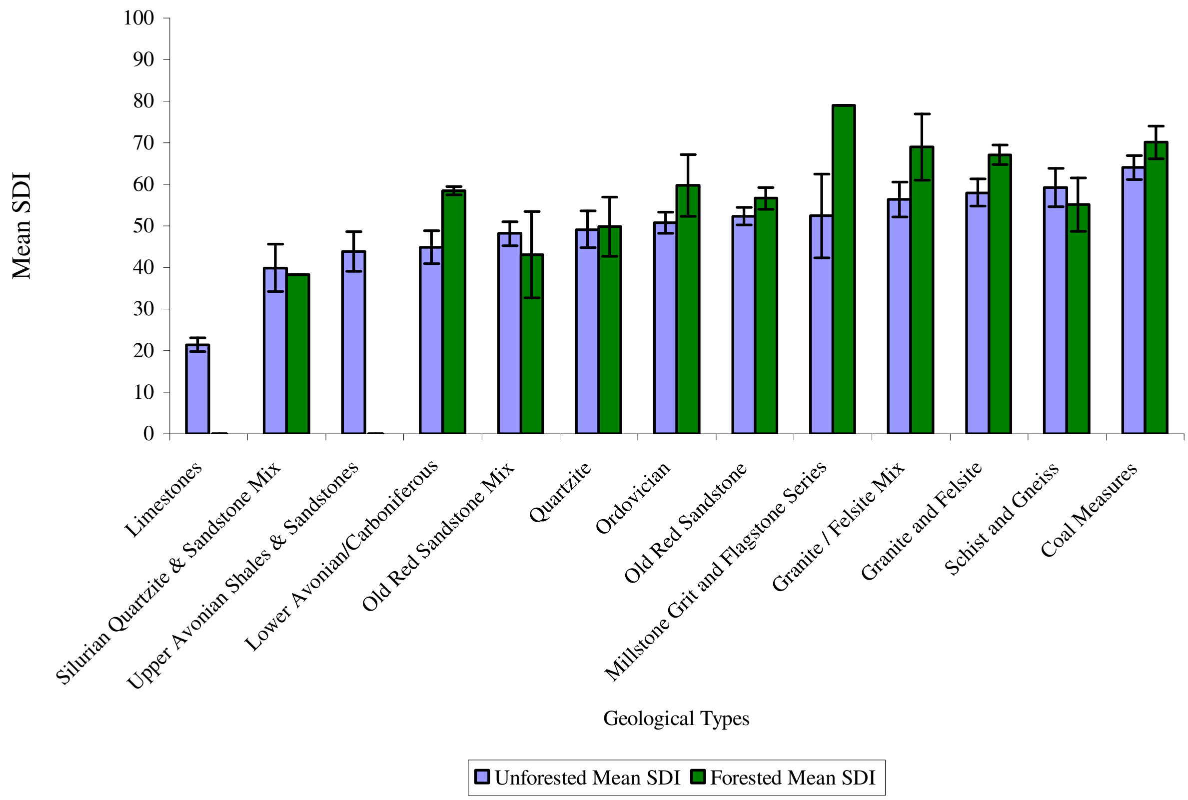


Figure 5. 5. Mean SDI (± S. E.) results for sites grouped according to dominant watershed geology (no forested sites on limestone sampled).

Table 5. 2. Post hoc test for non-forested sites grouped according to dominant watershed geology (next page)

Table 5.2 (legend previous page)	Limestones	Silurian Quartzite / Sandstone Mix	Upper Avonian Shales / Sandstones	Lower Avonian / Carboniferous	Old Red Sandstone Mix	Quartzite	Ordovician	Old Red Sandstone	Millstone Grit & Flagstone Series	Granite / Felsite Mix	Granite and Felsite	Schist and Gneiss	Coal Measures
Limestones	-												
Silurian Quartzite & Sandstone Mix	0.288												
Upper Avonian Shales & Sandstones	**0.02 ***	1.000	-										
Lower Avonian/Carboniferous	**0.03 ***	1.000	1.000										
Old Red Sandstone Mix	**0.00 ***	0.996	1.000	1.000	-								
Quartzite	**0.00 ***	0.984	0.999	1.000	1.000	-							
Ordovician	**0.00 ***	0.945	0.985	0.998	1.000	1.000	-						
Old Red Sandstone	**0.00 ***	0.804	0.846	0.964	0.999	1.000	1.000	-					
Millstone Grit and Flagstone Series	**0.05 ***	0.983	0.998	1.00	1.000	1.000	1.000	1.000	-				
Granite / Felsite Mix	**0.00 ***	0.697	0.786	0.902	0.984	0.991	0.999	1.000	1.000	-			
Granite and Felsite	**0.00 ***	0.310	0.232	0.464	0.680	0.685	0.905	0.926	1.000	1.000	-		
Schist and Gneiss	**0.00 ***	0.486	0.547	0.717	0.891	0.918	0.979	0.992	1.000	1.000	1.000		
Coal Measures	**0.00 ***	0.344	0.409	0.546	0.737	0.775	0.886	0.928	0.994	1.000	1.000	1.000	-

* Significant difference at the 0.05 level

5.1.5 The relationship between the SDI and pH, conductivity and alkalinity

A significant negative linear relationship between pH and the SDI was found (Fig. 5.6) for all sites combined (r=–0.729 P <0.01, R^2=0.532, n=248, non-forested sites; r=-0.708, P<0.01, R^2=0.502, n=195; forested sites; r=-0.758, P<0.01, R^2=0.574, n=53). There was no clear separation of forested and non-forested sites in the overall pattern. In fact when two separate lines were fitted to the plot (one for forested, one for non-forested) no significant difference was found in the slopes of lines for all sites combined, or indeed when an analysis was undertaken of slopes on SDI on pH for sites with low (<150 µS/cm) and medium (<250µS/cm) conductivity (ANCOVA, P>0.05).

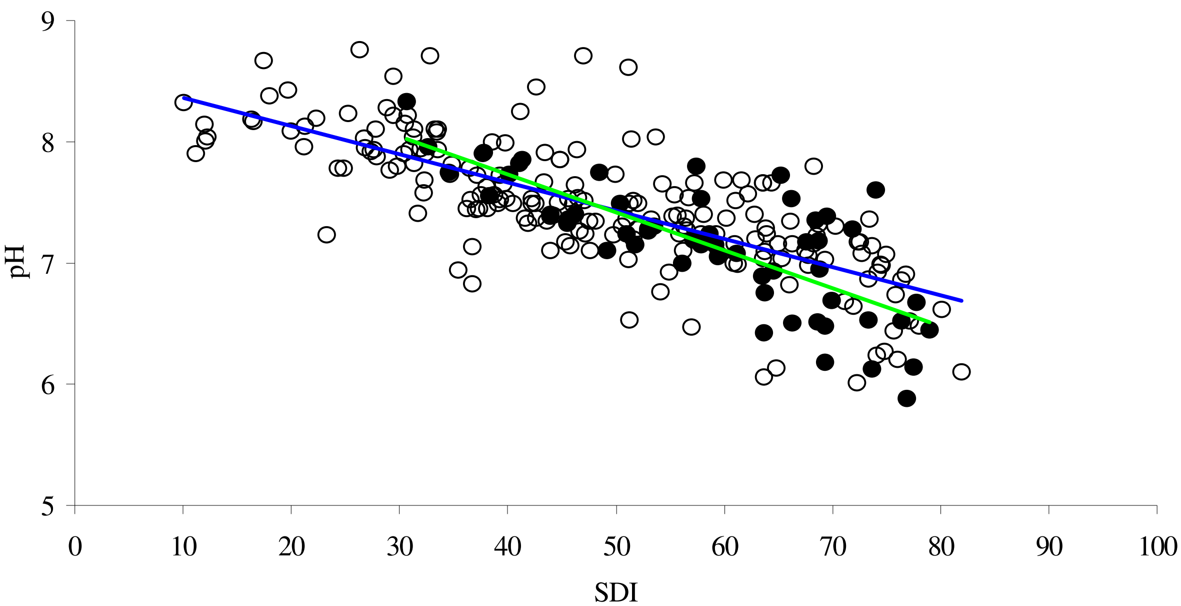


Figure 5. 6. Relationship between pH and the SDI for non-forested (open circles, blue line) and forested sites (filled circles, green line) at base flow, n=248 sites. The two lines represent the relationship between pH and SDI for forested and non-forested sites.

Figure 5.7 displays the relationship between conductivity and SDI. Low SDI sites (i.e. well buffered) were generally associated with high conductivity values and *vice versa.* With one exception, the conductivity of forested sites were below 300 µS cm^{-1}, although there was no clear separation of forested and non-forested sites in the overall pattern. The correlation coefficient of –0.754 was highly significant for all sites (P<0.01, R^2=0.678, n=247), (non-forested sites, r=-0.761, R^2=0.678, P<0.01, n=194; forested sites, r=-0.586, P<0.01, R^2=389, n=53). Analysis of covariance showed no significant difference between the slopes of the trend lines for non-forested and forested sites (ANCOVA, P>0.05).

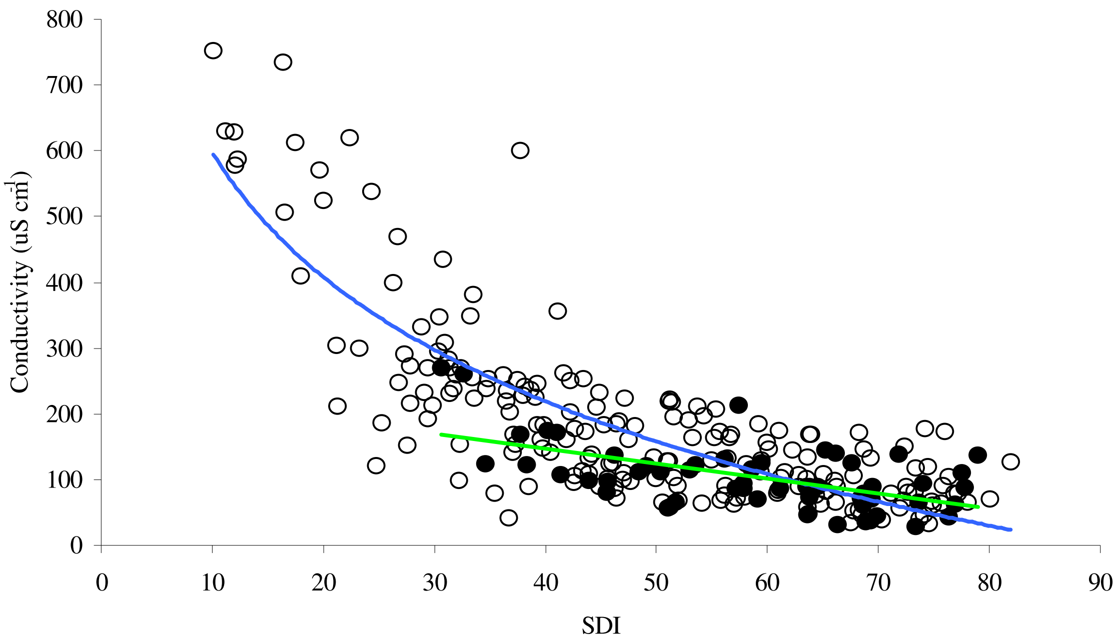


Figure 5. 7. Relationship between conductivity and the SDI for non-forested (open circles and blue line) and forested sites (filled circles and green line), n=247 sites.

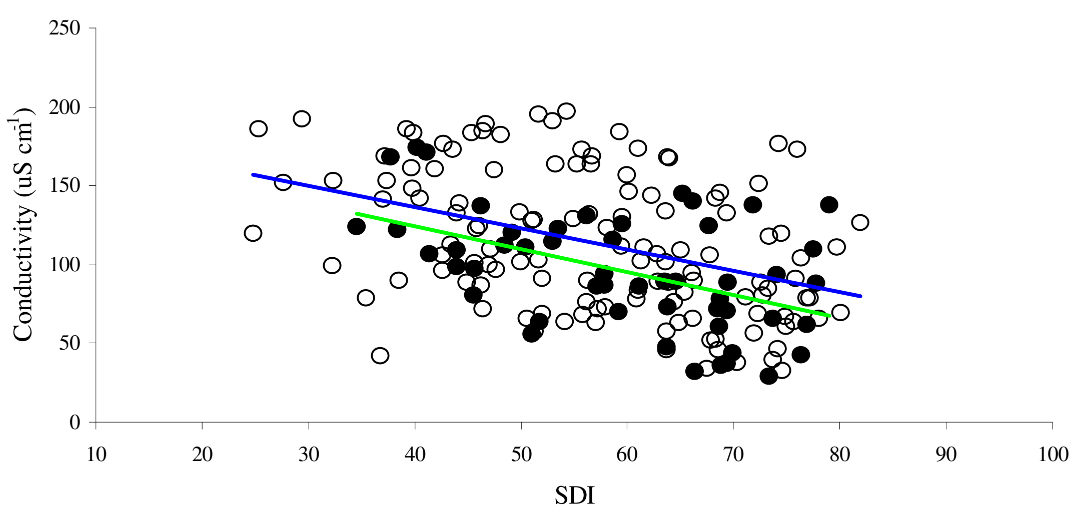


Figure 5. 8. The relationship between conductivity less than 250 μS cm^{-1} and the SDI for non-forested (open circles and blue line) and forested sites (closed circles and green), n=180. The two lines represent the relationship between conductivity and SDI for forested and non-forested sites.

A significant negative relationship was also found between alkalinity for all sites ($r=-0.826$, $P<0.01$, $R^2=0.668$, $n=248$), (non-forested sites, $r=-0.819$, $P<0.01$, $R^2=0.671$, $n=195$; forested sites, $r=-0.781$, $P<0.01$, $R^2=0.603$, $n=53$). Again there was no clear separation of forested and non-forested sites in the overall pattern. With the exception of two points, all forested sites recorded alkalinity values below 50 mg $CaCO_3$ l^{-1}. This may be due to the simple fact that most forest sites are in such locations. The slopes of trend lines for non-forested and forested sites showed no significant difference (ANCOVA, $P>0.05$).

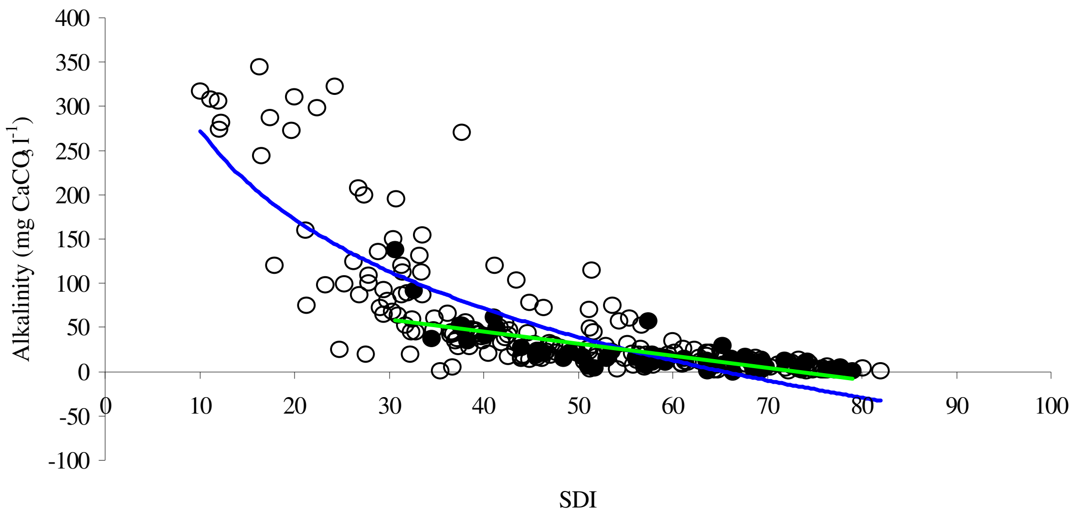


Figure 5. 9. The relationship between alkalinity and the SDI for non-forested (open circles, blue line) and forested sites (filled circles, green line), n=248 sites.

The relationship between alkalinity of potentially acid-sensitive sites and SDI values was also examined and highly a significant relationship was found ($r=-0.721$, $P<0.01$, $R^2=0.520$, $n=187$) although again considerable scatter was evident (non-forested sites, $r=-0.697$, $P<0.01$, $R^2=0.486$, $n=137$; forested sites, $r=-0.776$, $P<0.01$, $R^2=0.641$, $n=50$).

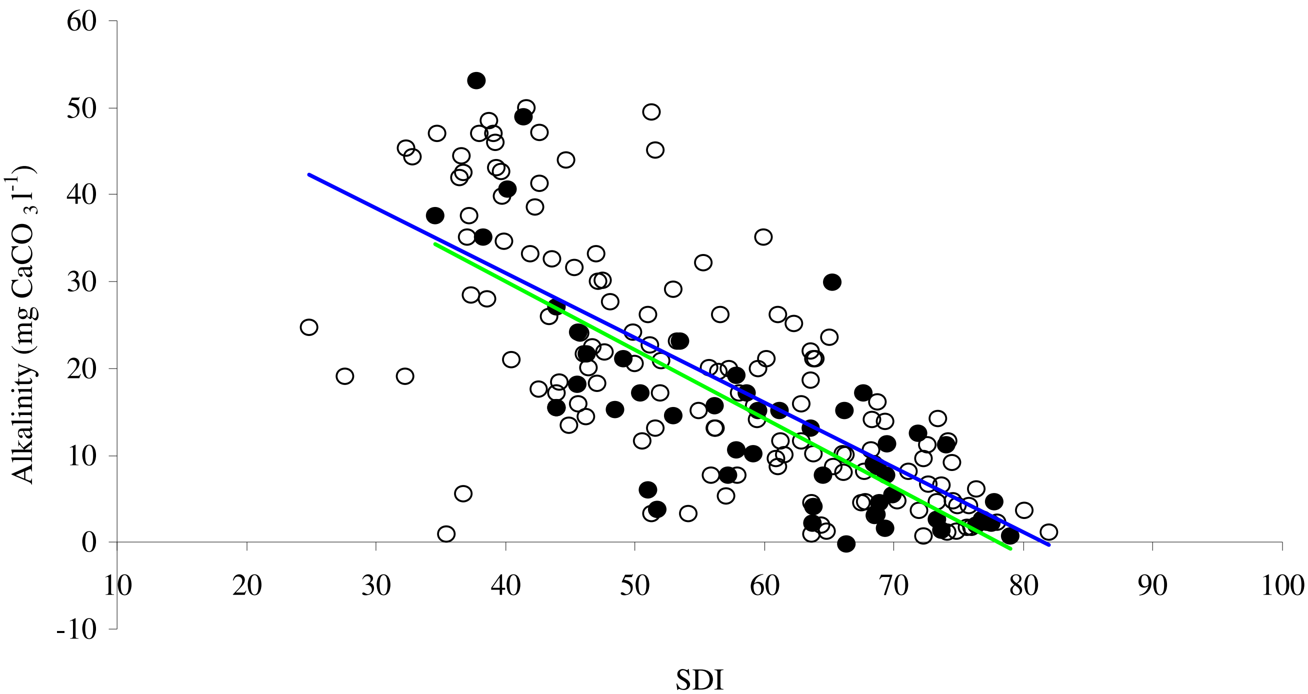


Figure 5. 10. Relationship between alkalinity <50 mg $CaCO_3$ l^{-1} and SDI for non-forested (open circles, blue line) and forested sites (filled circles, green line), n=186. The two lines represent the relationship between alkalinity and SDI for forested and non-forested sites.

Given that SDI is considered to reflect catchment weathering the relationship between the index values and calcium was examined. The correlation was highly significant (all sites, r=-0.746, R^2=0.854, P <0.01; non-forested sites, r=-0.744, P<0.01, R^2=0.861,195; forested sites, r=-0.818, R^2=0.824, n=53) with relatively low scatter in the data. The relationship did not improve when only non-marine calcium data were used, presumably because, as previously stated, most of the calcium detected was of non-marine origin. When magnesium was included to derive hardness values the correlation became stronger (all sites; r=-0.925, R^2=0.856, P=<0.01; non-forested sites, r=-0.932, P<0.01, R^2=0.868, n=195; forested sites, r=-0.819, P<0.01, R^2=0.712, n=53). The relationship between SDI and other chemical parameters revealed no further significant relationships (total aluminium - r=-0.098 P =0.124; chloride – r=0.027 P =0.668; DTOC – r=0.075 P =0.275).

5.1.6 The relationship between the SDI, Critical Loads and ANC

Previous work has characterised the acid sensitivity of Irish lakes with the use of Critical Loads for Acidity (Aherne and Farrell, 2000). Using the cation concentration data for the155 lakes in that study, SDI was calculated and correlated with the Critical Loads (CL) values. The results indicated a strong relationship between the two parameters ($r = -0.755$, $R^2=0.814$, $P<0.01$, $n=155$, Figure. 5.11). Figure 5.12 shows the relationships of SDI to pH and alkalinity for the 155 lakes. Significant relationships were found between SDI and pH (pH: $r = -0.773$, $R^2=0.6901$, $P<0.01$) and SDI and alkalinity (alkalinity: $r = -0.821$, $R^2=0.8207$, $P<0.01$).

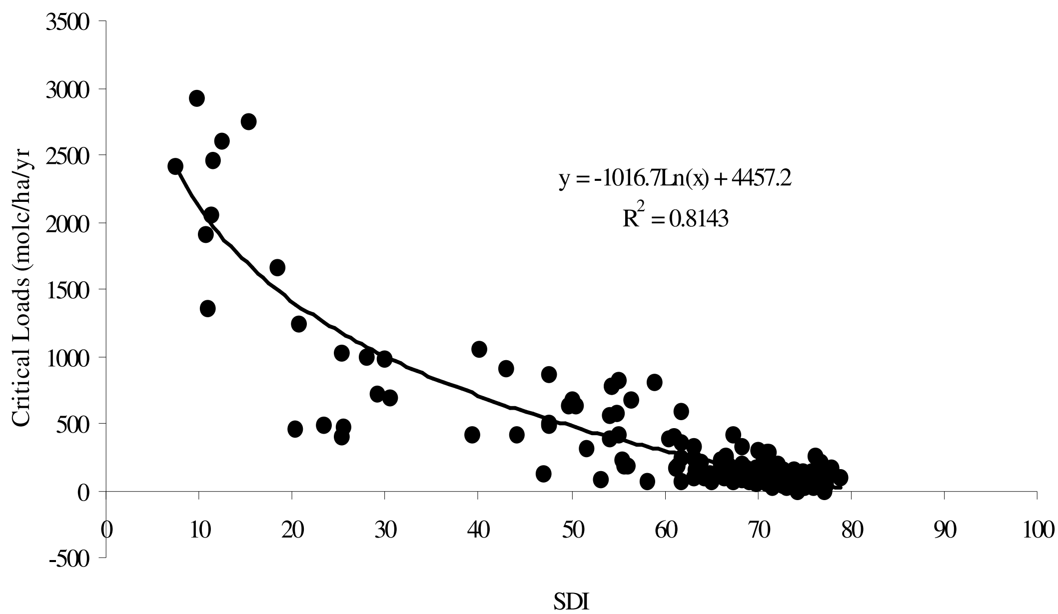


Figure 5. 11. Relationship between Critical Loads and SDI for 155 lakes.

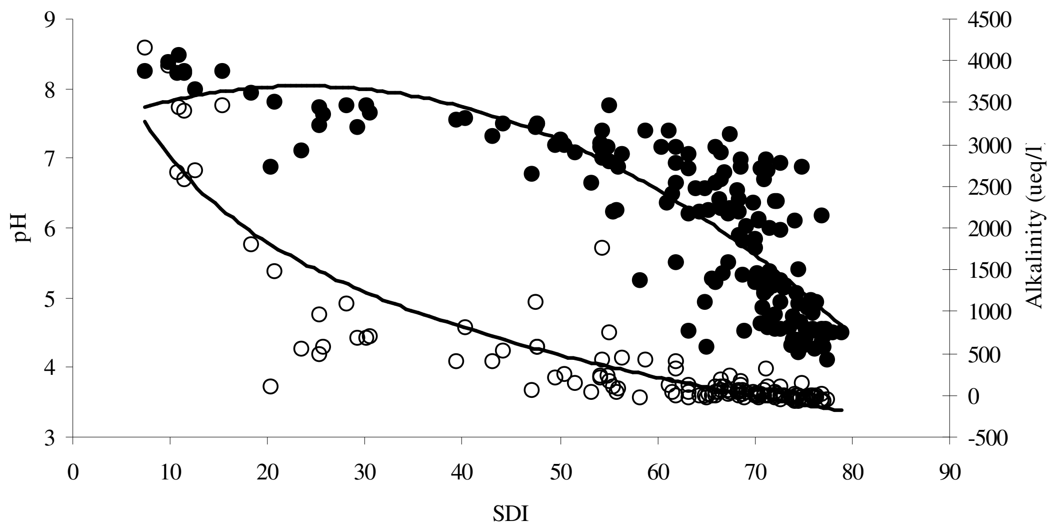


Figure 5. 12. Relationship of SDI with pH (open circles) and alkalinity (filled circles) for 155 lakes.

Acid-Neutralising Capacity (ANC) was calculated for 117 sites from the present extensive study, using data from Gran titration alkalinity, total aluminium and DTOC concentrations according to the methodology outlined by Foster *et al*. (2001). A significant relationship was evident between Acid Neutralising Capacity (ANC) and SDI (r= –0.671, R^2=0.594, P<0.01, n=117, Figure 5.13).

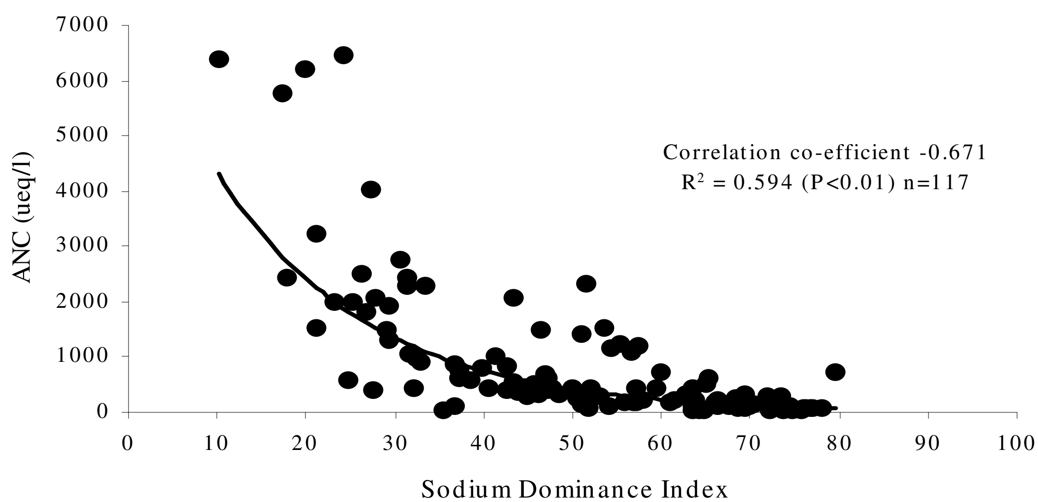


Figure 5. 13. Relationship between ANC and SDI for 117 WaterAc extensive study sites

5.2 Base and elevated flow sampling Sodium Dominance Index results

5.2.1 Comparison of SDI between base and elevated flow conditions

The mean values of the SDI at base and elevated flow are illustrated in Figure 5.14. Sites are ranked in terms of base flow SDI. With the exception of ten sites the SDI increased with flow. The lowest variation over the period of the sampling occurred at sites with SDI less than 20, these were located largely on limestone. Generally there was less than a 15 unit differences between the low and elevated water levels as evidenced by the coefficient of variation values given in Table 5.3. Some sites did show a substantial increase in the Index at elevated flow, many of these were located in catchments with mixed geology. For example, one site sampled on the Owenmore in Co. Mayo is situated on limestone, but the upstream geology is predominately granite/felsite. This site had an index value less than 30 at low flow but during one flood event the Sodium Dominance Index increased to 61.2. This could be largely attributed to dilution by flood waters from the granitic catchment with low base cation concentrations. Overall, the variation in the Sodium Dominance Index was substantially less than that for alkalinity (Table 5.3).

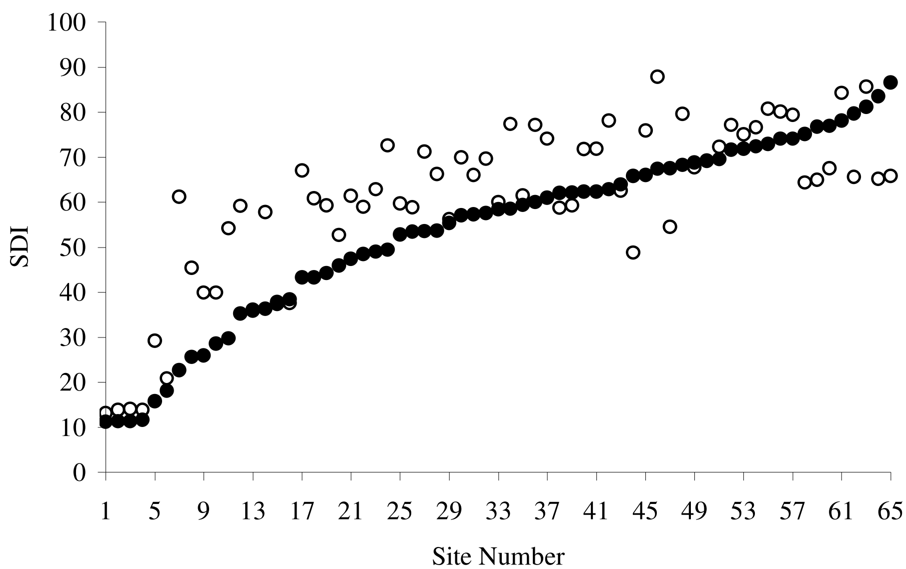


Figure 5. 14. Mean base flow (filled circles) and elevated water (open circles) SDI values at 65 sites.

At base flow, SDI was closely correlated with alkalinity, hardness, conductivity and pH. At higher flows, the correlation coefficients declined (although remaining highly significant) for these parameters (Table 5.4). The correlation with chloride became significant at elevated flow.

Table 5. 3. Co-efficient of variation results for alkalinity and SDI at Intensive sites (n = 65).

Site Number *	River name	Alkalinity CV	SDI CV
UCC002	River Martin	11.01	3.56
UCC003	River Shournagh	10.08	3.13
UCC006	River Douglas	60.23	16.25
UCC007	Glenfinnish Stream	17.79	10.26
UCC018	Derrylaura River	50.24	3.93
UCC019	Cashla River	25.71	4.39
UCC023	Abbert River	14.20	18.03
UCC024	Kilalogher River	11.33	20.89
UCC025	Cloonkeen River	14.59	21.33
UCC026	Raford River	23.10	20.40
UCC028	Greygrove River	63.25	5.24
UCC030	Inagh River	43.72	7.19
UCC037	Leamlara River	6.11	4.17
UCC042	Glenshelane River	51.68	23.07
UCC069	Owengarve River	45.07	13.72
UCC070	Boohill River	31.83	17.29
UCC071	Roughty River	62.81	12.02
UCC085	River Inny	59.73	6.25
UCC089	River Sheen	57.20	6.11
UCC097	Smearleagh River	65.80	4.78
UCC105	Glenary River	48.48	9.27
UCC107	Glasha River	32.18	10.06
UCC109	Dripsey River	29.76	10.07
UCC111	Owenagluggin River	69.03	21.32
UCC112	River Laney	46.68	13.72
UCC121	Munster River	44.77	38.07
UCC126	Thonoge River	124.37	20.11
UCC127	Geeragh River	58.00	30.27
UCC128	Atherlow Trib 1	57.62	36.17
UCC129	Atherlow Trib 2	159.99	13.42
UCC130	Glengalla River	67.96	21.96
UCC131	River Duag Trib	110.90	9.11
UCD 132	Glenlack	24.95	18.8
UCD 136	Cornaniv Burn	141.77	8.61
UCD 138	Owentonisky	78.10	14.68
UCD 139	Glen	64.80	5.25
UCD 140	Roechrow	110.40	16.18
UCD 142	Cornnavanoge	57.69	31.97
UCD 146	Bonet	57.02	35.89
UCD 148	Owenbeg 1	60.68	27.19
UCD 149	Owenbeg 2a	31.06	18.33
UCD 153	Owengarve	59.76	27.71
UCD 155	Owenmore (Mayo)	84.24	62.85
UCD 158	Little	42.24	20.46
UCD 159	Addergoole	47.88	11.94
UCD 160	Glenamoy	45.36	24.65
UCD 169	Carrownisky	100.11	8.94
UCD 176	Athdown	35.84	14.40
UCD 180	Boleyhorrigan	82.05	9.97
UCD 181	Vartry V4	59.01	1.11
UCD 182	Vartry V1	15.20	1.03
UCD 183	Ballylow	485.28	22.79
UCD 184	Ballydonnell	104.33	19.66
UCD 186	Glenmacnass	-293.59	16.77
UCD 187	Glendassan	49.14	18.43
UCD 189	Annalecka	-370.06	19.03
UCD 191	Knockalt	108.39	11.45
UCD 192	Garryknock	37.54	1.28
UCD 197	Yellow (Cavan)	91.08	15.66
UCD 198	Owenmore (Cavan)	92.62	21.08
UCD 208	Lugduff	196.84	14.41
UCD 211	Glencullen	51.69	13.03
UCD 212	Glenealo	19.87	15.32
UCD 244	White Mountain	16.96	8.41
UCD 255	Ballycreen	18.90	17.85

Table 5. 4. Summary of relationships between SDI and selected environmental variables under base and elevated flow conditions (n = 65).

SDI vs	Base flow r	R^2	P	Elevated flow r	R^2	P
pH (units)	-0.803	0.640	<0.001 *	-0.535	0.240	<0.001 *
Alkalinity (mg $CaCO_3$ l^{-1})	-0.826	0.880	<0.001 *	-0.563	0.360	<0.001 *
Conductivity (µS cm^{-1})	-0.839	0.870	<0.001 *	-0.503	0.190	<0.001 *
Total Hardness (mg l^{-1})	-0.819	0.670	<0.001 *	-0.580	0.260	<0.001 *
Chloride (mg l^{-1})	-0.164	0.040	0.199	0.302	0.120	0.01 *
Total Aluminium (µg l^{-1})	0.110	0.000	0.392	n/a	0.050	0.154
DTOC (mg l^{-1})	-0.097	0.010	0.453	-0.139	0.010	0.417
Forest cover (%)	0.250	0.060	0.048	0.229	0.000	0.633
Conifer cover (%)	0.289	0.080	0.022	0.212	0.010	0.463
Distance from source (km)	-0.330	0.110	0.008 *	-0.422	0.140	0.001 *
Distance from coast (SW) (km)	0.167	0.030	0.19	0.164	0.010	0.376
Distance from nearest coast (km)	-0.241	0.060	0.06	-0.102	0.000	0.573

* significant to 0.05 level

SDI values were pooled for base flow or elevated flow and initially compared for variation regardless of forest cover, underlying geology, soil type or distance from the sea**.** No significant differences were noted in SDI under flow conditions (P>0.05, two-way ANOVA and confirmed by a Paired t-Test).

Sites were then grouped according to dominant watershed geology and presence/absence of forestry to further test for differences in base and elevated flow values of the index. No significant differences were found in SDI between base flow and elevated flow at the non-forested or forested sites when examined separately within each geological type (One-Way ANOVA, P >0.05) except for forested sites ($F_{1,4}$=10.75, P =0.031) on schist and felsite. Low numbers of forested sites did not permit statistical comparisons between forested and non-forested sites within most individual geological bands. However, the analysis was run for granite and felsite sites and schist and gneiss sites separately but revealed no significant differences between SDI at non-forested and forested sites.

When SDI data were ranked by % forestry cover, there was no significant effect of forest was noted (P>0.05, Mann-Whitney) on the elevated and base flow values. A similar result was noted when specifically examining the percentage conifer cover as opposed to total forestry cover (Figure. 5.15).

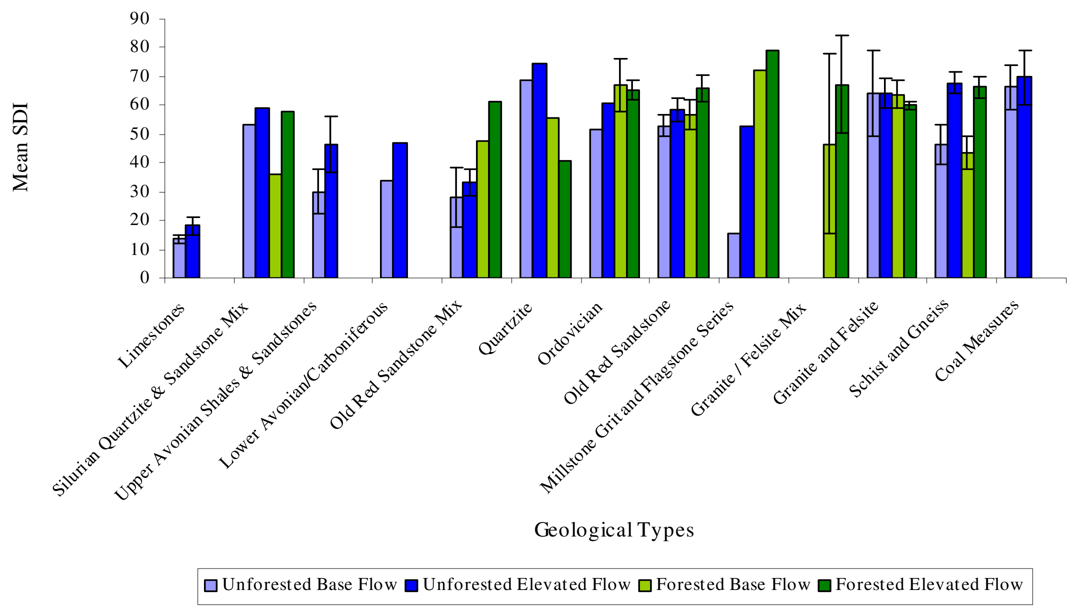


Figure 5. 15. Variation in base and elevated flow SDI at sites grouped according to dominant watershed geology and forest cover**.** (note no forested sites were sampled in areas of limestone bedrock).

There were insufficient forested sites to permit an analysis of the effect of degree of forest cover on SDI within any one geological band. Instead the data were explored for relationships between the change in SDI between base and elevated flow and degree of forest cover (deciduous and coniferous) across the range of sites. As can be seen from Figure 5.16 the parameters were not significantly correlated (r=-0.017, P=0.896).

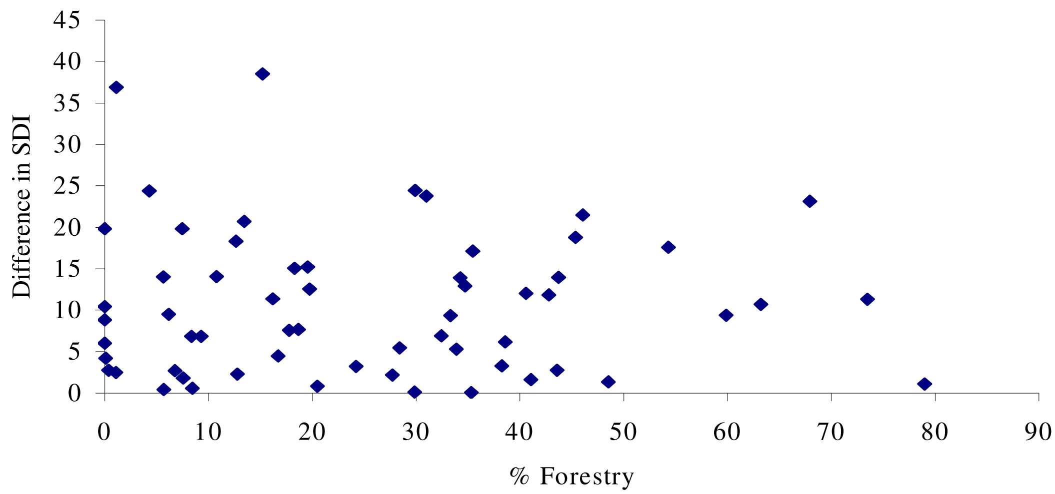


Figure 5. 16. Relationship between change in SDI between base and elevated flow and % catchment forest cover (n= 65).

Comparisons (Wilcoxon Rank Sign Test) of differences between base and elevated flow SDI at sites grouped according to dominant 7 soil type indicated significant differences for Gleysol (P =0.031), Histosol (P<0.001) (Histosol, Histosol-Blanket and Histosol-raised pooled) and Posdol-leptic (P =0.007). However, interaction with geology was not taken into account.

When data were ranked by distance from the sea, no significant trend was noted. The sampling point locations in relation to the prevailing winds (SW) did not appear to have a significant effect on SDI during changing flow conditions. In terms of change in SDI during changing flow conditions and the distance from the sea (SW), no significant correlation was found (r=-0.024, P =0.857), (Figure 5.17). However, the actual wind direction on individual dates was not taken into account, as no data were available.

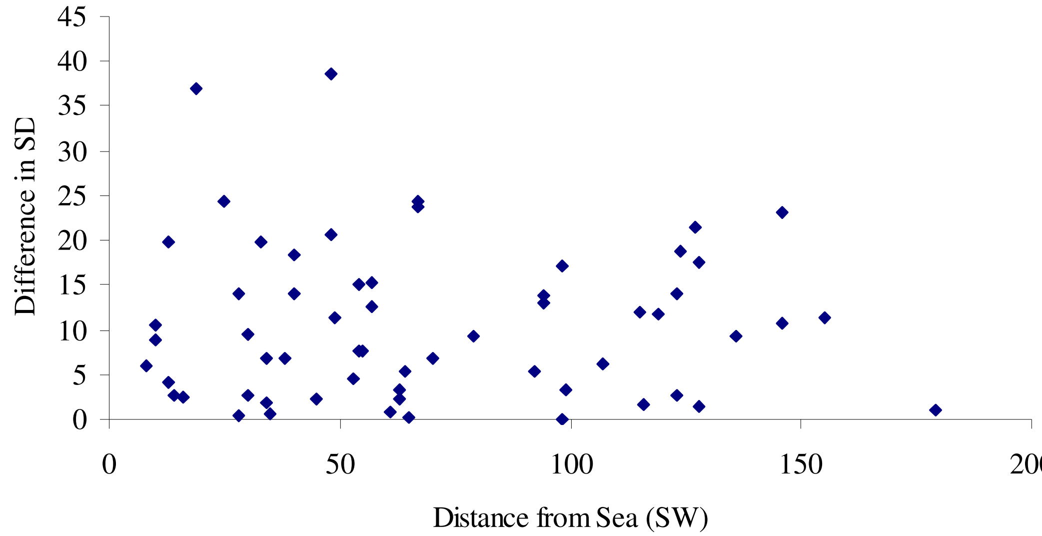


Figure 5. 17. Relationship between change in SDI between base and elevated flow and distance from the sea (n = 65).

There were too few forested sites to statistically test whether or not those in close proximity to the sea record greater changes in SDI than non-forested sites.

Analyses were carried out on Cl^- concentration between base and elevated flow ranked by the degree of total forestry cover. A two-way ANOVA using total forestry cover and flow condition as two possible factors affecting SDI showed no significant difference in the Index between non-forested and forested sites ($P > 0.05$, two-way ANOVA, Figure 5.18). This result held during flood conditions and when considering % coniferous cover only. A detailed analysis of Cl^- concentration ranked by total forest cover, showed that forestry had no significant effect on Cl^- during elevated flow events ($p > 0.05$, Wilcoxon Rank Sign Test).

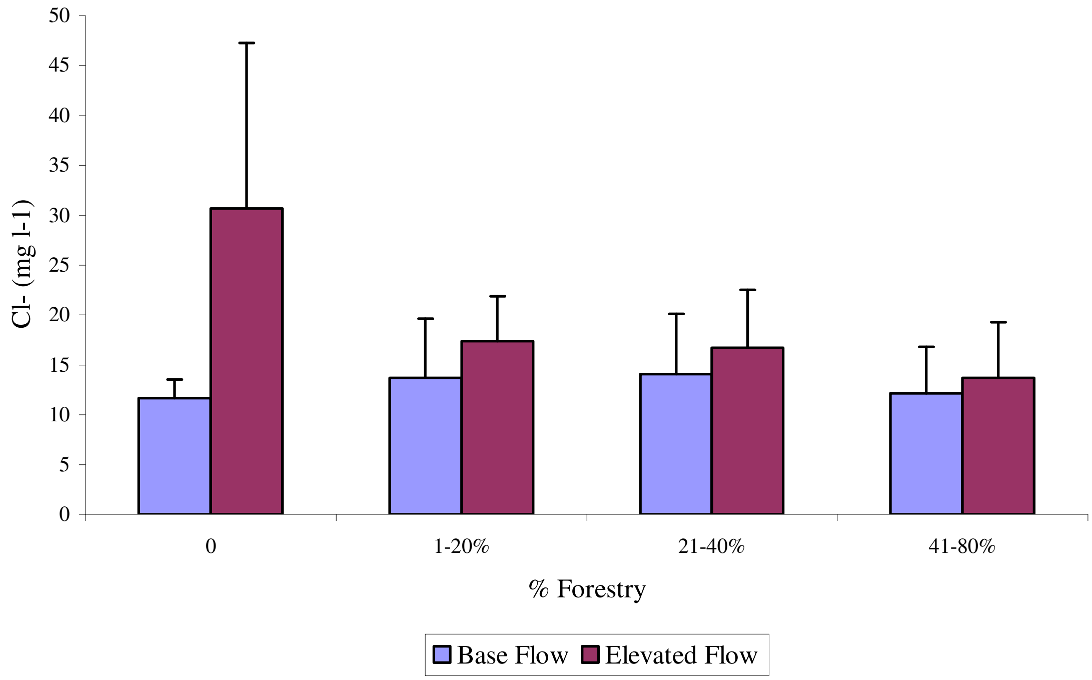


Figure 5. 18. Changes in chloride concentration, under base and elevated flow conditions, at different forest cover.

Of particular interest to this study is what governs the stability of SDI at some sites or variability at others. Figures 5.19 to 5.21 illustrate some typical patterns of change in cation composition. It can be seen that where SDI remain stable the relative proportions of the cations do not vary greatly (Figure 5.19) as in the well-buffered River Martin. The site illustrated in Figure 5.20 is more poorly buffered but overall the variation in SDI is less than 10 units. In contrast, SDI change at another site was greater due mainly to variation in the concentration of calcium (Figure 5.21). Changes in SDI between base and elevated flow, were unrelated to change in pH, alkalinity, hardness, calcium or sodium ($P>0.05$, Pearson correlation). The absence of clear relationships may be in part due to the fact that the majority of sites exhibited only small changes in SDI. For those sites showing stability of the index it is probable that rainfall simply dilutes the base cations but maintains the relative proportions of each. This issue is addressed in more detail in Section 5.3, which examines changes in SDI during a number of hydrological events.

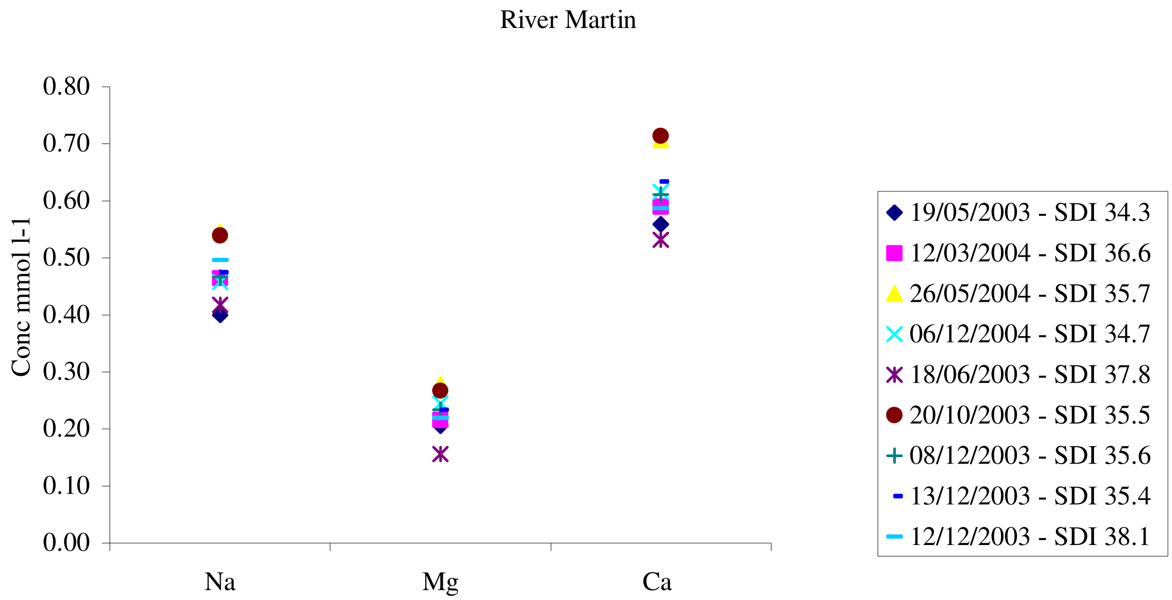


Figure 5. 19. Temporal variation in the concentrations of the major cations in the River Martin. (SDI values listed with the various dates).

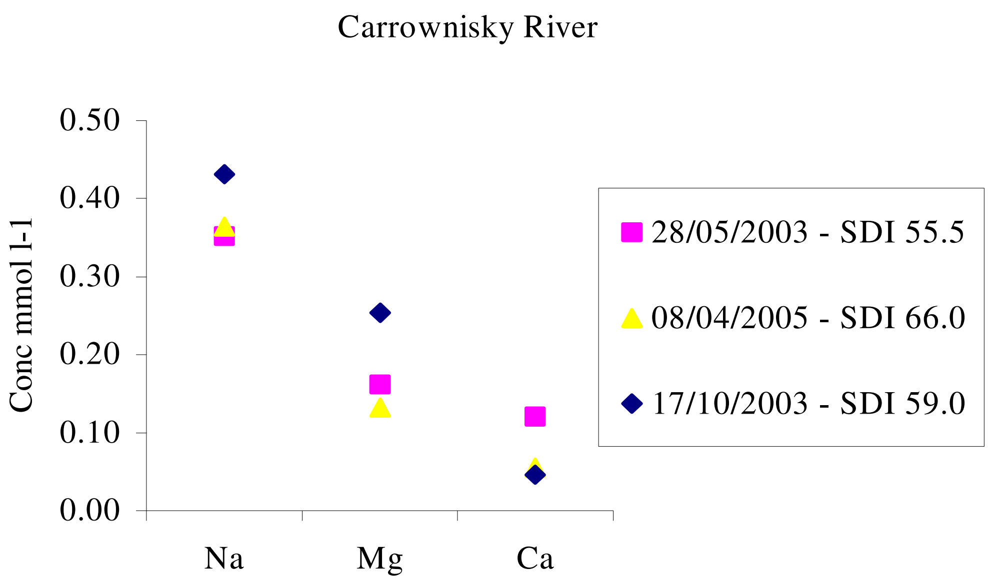


Figure 5. 20. Temporal variation in the concentrations of the major cations in the River Carrownisky. (SDI values listed with the various dates).

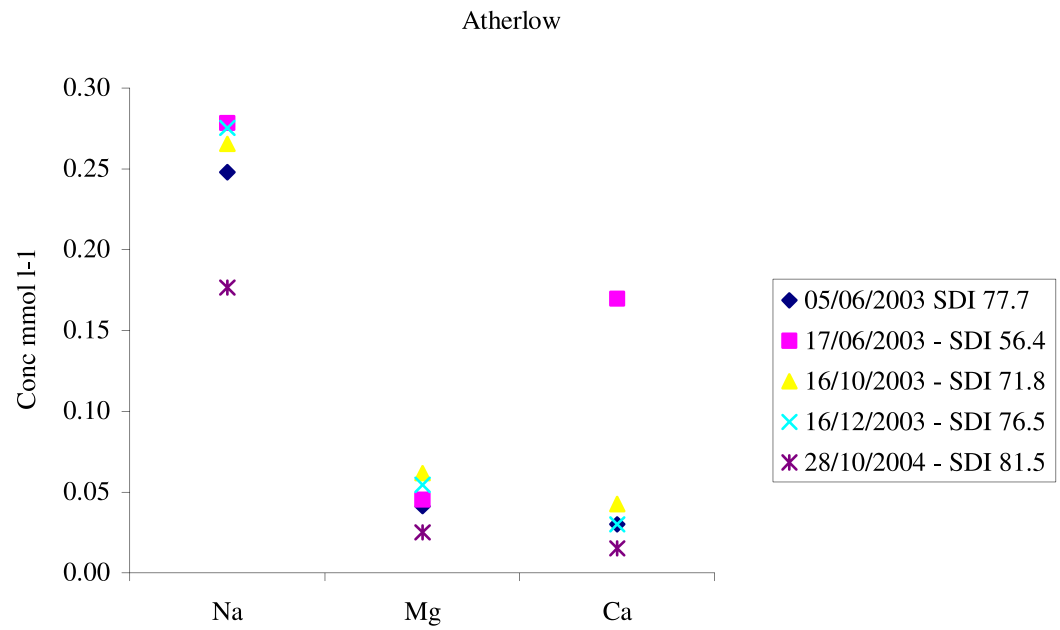


Figure 5. 21. Temporal variation in the concentrations of the major cations in the River Atherlow (SDI values listed with the various dates).

5.3 Variation in SDI during a number of hydrological events

A sub-set of sites was identified, based on SDI data from the extensive sampling and their degree of forest cover, and sampled during flood events in order to examine the temporal stability of the SDI and confirm whether a single sample is adequate to characterise acid sensitivity of the site. Events at both acid sensitive and moderately buffered sites were monitored. The dates and trends of all events monitored are given in Table 5.5. Changes in SDI and alkalinity at a number of events monitored in the Rivers Annalecka and Glendassan in Wicklow are illustrated in Figures 5.22 to 5.25. Flow was recorded at the Cork sites. Changes in flow and SDI for some of the more substantial events are shown in Figures 5.26 to 5.29. The Annalecka and Glendassan Rivers drain granite. Consequently, alkalinity fell close to zero or becomes substantially negative during flood events. The changes were typical of acid pulses (i.e. decrease in alkalinity of at least 50 ueq l^{-1} or 50%). Some of the events monitored were on reasonably buffered systems (e.g. River Dripsey and Glencullen). These did not show changes in alkalinity that would characterise an acid pulse (Table 5.5) despite a substantial rise in water level.

In general the pattern of change in both alkalinity and SDI differed (Figures 5.22 to 5.29). The coefficient of variation was highest for alkalinity (3.44- 836.41%) and relatively similar for pH (0.74-18.87 %) and the Sodium Dominance Index (2.21-20.5%). The value of 20.5% was taken from the Annalecka and represents a change from base flow SDI of 58.50 to the high flow value of 74.98. Coefficients of variation at other sites were substantially lower. Most events showed a SDI change of less than 20 units. However, during a number of events SDI changed by over twenty units, despite the low overall coefficient of variation. In fact the greatest change in both SDI and alkalinity occurred within the first few hours of the event. It should be noted that for many events recovery to base flow conditions were not captured. In some sites, such as the Annalecka, recovery may take several days after cessation of rainfall (Kelly-Quinn *et al.*, 1997a).

The two events from the Annalecka illustrated in Figures 5.22 and 5.23 show relative stability of the index despite the substantial change in alkalinity. Here the relative proportions of the major cations remained relatively stable despite a drop in their concentration. In contrast one of the events on the Glendassan River (Figure 5.24) showed a larger increase in SDI at the commencement of the event. This was the most substantial flood monitored with most of the rainfall concentrated in the first few hours. Unfortunately no actual flow measurements were available to support this observation. The Cork sites, although somewhat more buffered, show fairly similar patterns, i.e. some events where the SDI was relatively stable (Figure 5.26) and in others the change in the index occurred at the commencement of the event (Figure 5.29).

It appeared that the highest variation in SDI was most likely to be at the commencement of an event. The data collected for the Cork sites (Fig 5.26-Fig 5.29) included flow recording. Spearman rank correlation analyses indicated a significant (r_s=0.7-0.78, $P<0.01$) relationship between change in flow and change in the index. In fact this was the only significant relationship detected. Change in SDI was not related to a change in any of the other parameters measured. It thus appears that where water with a lower ANC enters the river during an event the relative proportion of calcium mainly changes. Complete ion chemistry for some events has permitted some evaluation of the processes responsible for the changes observed. In the Aghalode, for example, the dilution value was close to 100% which suggested that the base cations had simply diluted proportionally to alkalinity, this explains the small change in the index during this event (SDI range – 78.6-71.4). Dilution of this nature was also typical of the Glencullen River. All other events were probably influenced by a combination of dilution and acid titration. Drops in the alkalinity/∑BC suggest titration but as pointed out by (Lepori *et al.*, 2003) some of the change may be due to cation desorption in upper soils. Both the Glendassan and Annalecka events provide evidence of titrations. In the Glendassan this can be largely attributed to changes in organic anion. This is also the case for the Annalecka, but there are also inputs of sulphate at times during the event. So it appears that water with low ANC, low calcium and increased acid anion enters these systems. The rate at which it enters appears to influence the stability of the SDI. It may be that the altered hydrological path during heavy rainfall has resulted in reduced contact with the deeper layers of soils for buffering and recharge with calcium ions. A corollary of this effect was noted in Swedish streams, where base cation concentrations increased during base flow conditions (Fölster & Wilander, 2002).

Table 5. 5. Hydrochemical characteristics of the events monitored

Site Name	Forestry	Date		pH	Alkalinity mg l^{-1} $CaCO_3$	SDI
Annalecka	28%	20/4/'04	Max.	4.72	-0.99	74.94
			Min.	4.13	-3.10	58.50
			C.V.	4.78	40.22	20.50
Annalecka	28%	22/6/0'04	Max.	6.85	4.59	75.46
			Min.	4.45	-2.23	67.87
			C.V.	18.87	836.37	3.53
Glendassan	5%	22/6/'04	Max.	7.01	14.08	74.22
			Min.	5.17	-0.04	50.36
			C.V.	9.06	190.23	8.41
Glendassan	5%	14/3/'05	Max.	8.86	0.44	73.79
			Min.	5.64	0.08	65.69
			C.V.	11.77	108.18	2.63
Glencullen	0%	25/4/'05	Max.	7.63	16.48	58.10
			Min.	7.37	14.37	56.39
			C.V.	0.74	3.44	0.88
Glencullen	0%	28/4/'05	Max.	7.54	18.69	67.95
			Min.	7.15	12.33	57.67
			C.V.	1.64	11.12	4.74
Douglas	41%	13/4/'05	Max.	7.07	n/a	69.44
			Min.	6.17	n/a	51.34
			C.V.	3.96	n/a	12.06
Douglas	41%	28/2/'03	Max.	7.19	n/a	58.99
			Min.	6.80	n/a	47.46
			C.V.	1.60	n/a	8.79
Douglas Left	43%	13/4/'03	Max.	7.19	n/a	81.41
			Min.	6.20	n/a	63.04
			C.V.	5.12	n/a	9.78
Douglas Right	37%	13/4/'03	Max.	6.92	n/a	66.45

			Min.	6.26	n/a	49.06
			C.V.	3.62	n/a	12.89
Douglas Right	37%	28/2/'03	Max.	7.30	n/a	53.59
			Min.	5.97	n/a	40.07
			C.V.	4.68	n/a	8.70
Douglas Right	37%	3/6/'03	Max.	7.40	n/a	76.48
			Min.	7.02	n/a	72.99
			C.V.	2.25	n/a	2.21
Aghalode	50%	10/2/'05	Max.	6.92	10.12	78.64
			Min.	6.58	5.46	71.43
			C.V.	1.22	15.46	3.56
Aughboy	16%	10/2/'05	Max.	7.16	19.22	74.73
			Min.	6.83	8.28	66.15
			C.V.	1.55	26.10	4.23
Dripsey	23%	22/1/'04	Max.	n/a	37.00	43.43
			Min.	n/a	26.00	40.03
			C.V.	n/a	8.43	2.48
Dripsey	23%	30/1/'04	Max.	n/a	n/a	40.06
			Min.	n/a	n/a	35.69
			C.V.	n/a	n/a	2.77

n/a = not available

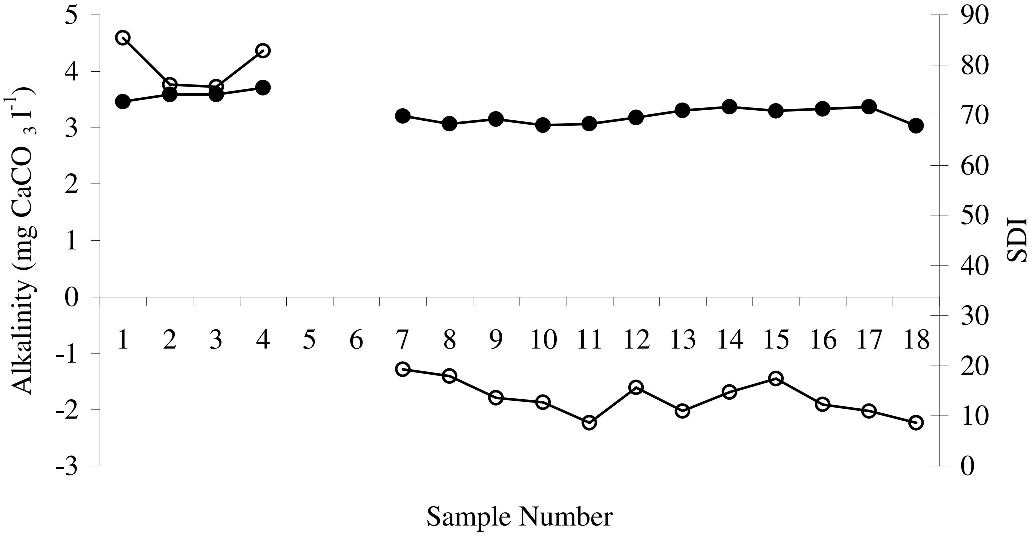


Figure 5. 22 Hydrochemical trends during an event on the Annalecka River (20/4/'04). SDI (filled circles) and alkalinity (open circles). (30% forest cover).

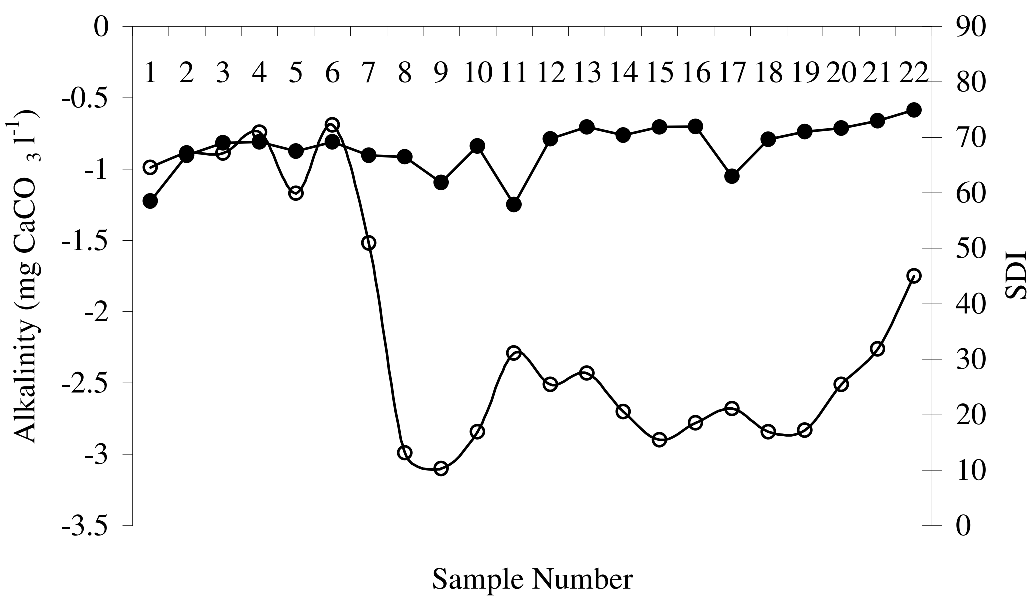


Figure 5. 23 Hydrochemical trends during an event on the Annalecka River (22/6/'04). SDI (filled circles) and alkalinity (open circles). (30% forest cover).

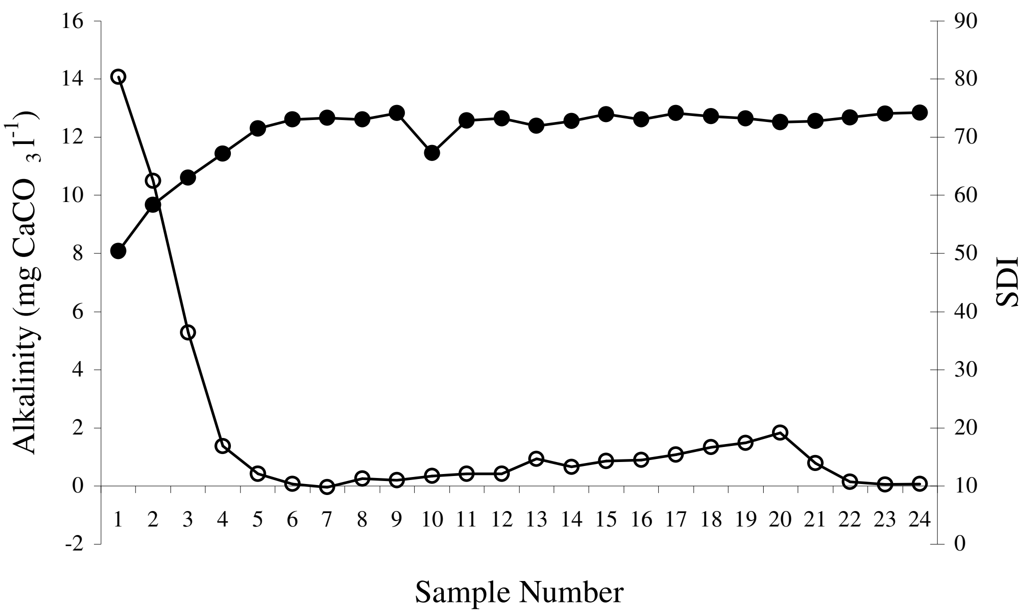


Figure 5. 24. Hydrochemical trends during an event on the Glendassan River (22/6/'04). SDI (filled circles) and alkalinity (open circles). (5% forest cover).

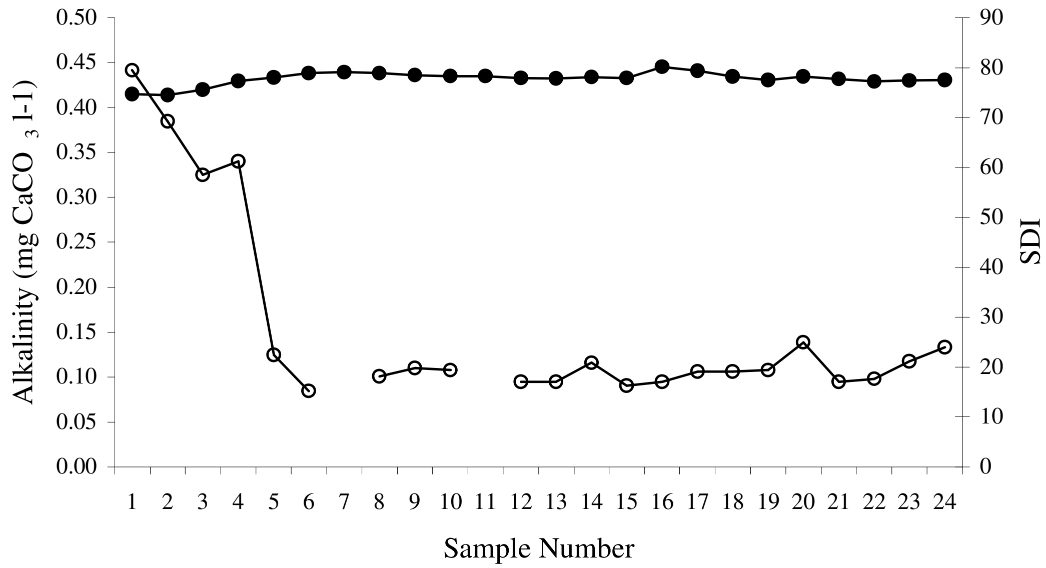


Figure 5. 25. Hydrochemical trends during an event on the Glendassan River (14/3/'05). SDI (filled circles) and alkalinity (open circles). (5% forest cover).

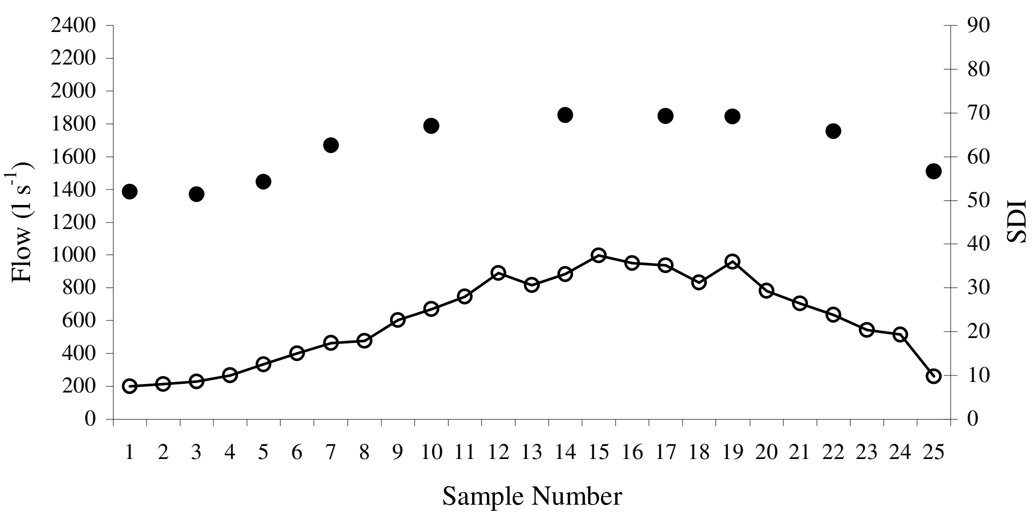


Figure 5. 26. Flow rate and SDI interaction during an event on the Douglas River (13/4/'03). SDI (filled circles) and flow rate (open circles). (Forest cover 41%).

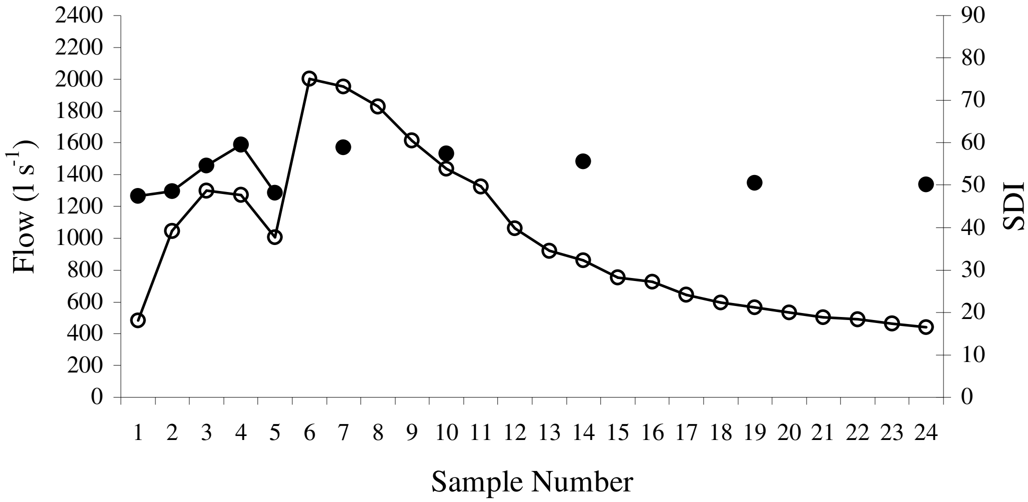


Figure 5. 27. Flow rate and SDI interaction during anevent on the Douglas River (28/2/'03). SDI (filled circles) and flow rate (open circles). (Forest cover 41%).

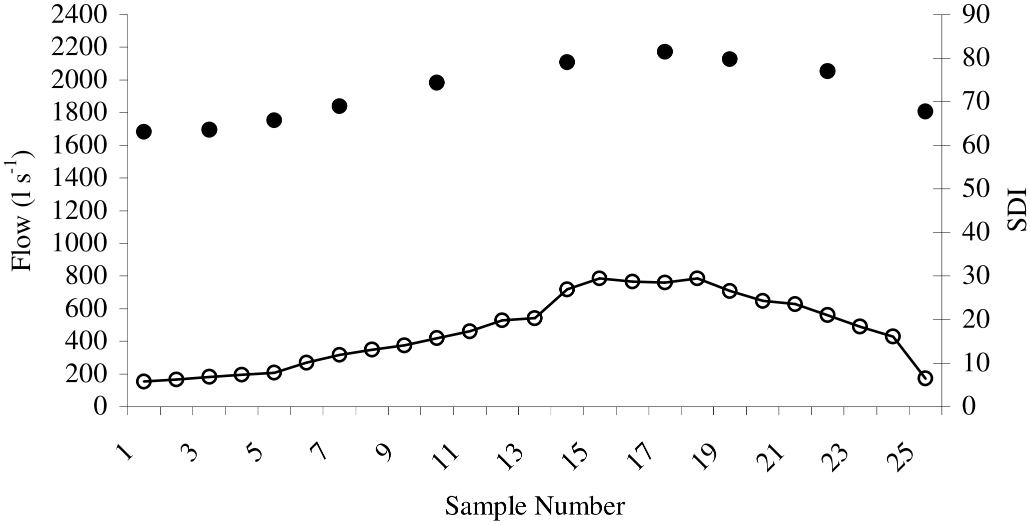


Figure 5. 28. Flow rate and SDI interaction during an event on the Douglas River left (13/4/'03). SDI (filled circles) and flow rate (open circles). Forest cover = 41%.

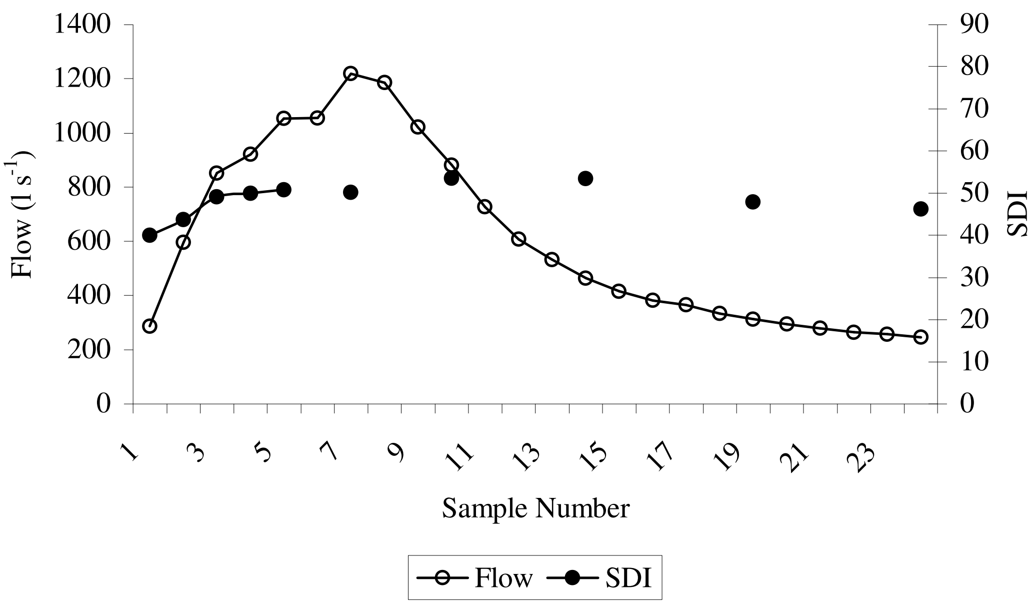


Figure 5. 29. Flow rate and SDI interaction during an event on the Douglas River (28/2/'03). SDI (filled circles) and flow rate (open circles). Forest cover = 41%.

Table 5. 6. Dilution and Titration (Alkalinity / ΣBC) values calculated for pulses monitored

River	Date	Phase	Dilution	Alkalinity / ΣBC
Annalecka	22/6/'04	Base Flow	-	1.16496
		Max. Flow	21.31	0.82967
Glendassan	22/6/'04	Base Flow	-	0.59450
		Max. Flow	79.10	0.00834
	14/3/'05	Base Flow	-	0.06113
		Max. Flow	6.23	0.00540
Glencullen	28/4/'05	Base Flow	-	0.43902
		Max. Flow	77.90	0.39413
Aughboy	10/2/'05	Base Flow	-	0.99774
		Max. Flow	46.13	0.60360
Aghalode	10/2/'05	Base Flow	-	0.88162
		Max. Flow	118.37	1.05113

5.4 Faunal sampling results

5.4.1 Taxon Numbers and Faunal Composition

A total of 237 taxa were recorded in the study representing a total of 75 families, both seasons inclusive. The total number of taxa recorded per site ranged from 33 to 78. Spring sampling yielded 205 taxa across 69 families, while 191 tax from 71 families were recorded in the autumn.

The Trichoptera was the most diverse group sampled with 48 species followed by the Coleoptera with 41 species. The Ephemeroptera were represented by nineteen species while eighteen plecopteran species were recorded. There were seventeen genera/subfamilies of Diptera. Two crustacean orders, namely Malacostraca and Entomostraca, with four and two representative species respectively were recorded from the two sampling periods while the Annelida were represented by six Hirundinae species and Oligochaeta. Fourteen gastropod species and two lamellibranch species were reported.

The following ten families were found in high abundances, Elmidae (Coleoptera), Baetidae and Heptageniidae (Ephemeroptera), the plecopterans Leuctridae, Nemouridae and Chloroperlidae and four trichopteran families: Hydropsychidae, Limnephilidae, Rhyacophilidae and Polycentropodidae. Of the nineteen ephemeropteran species noted in this study, *Baetis rhodani* (Pictet.) (Baetidae) was the most abundant and widespread, being present in all but one site (Site 208 Lugduff Stream (LUG1), Co. Wicklow). No other ephemeropteran were recorded in this acid-impacted stream. Another site, (Site 181, Vartry Feeder Stream 4 (V4), Co. Wicklow) only had a single *B. rhodani* specimen recorded, in autumn. Again no other mayfly species were recorded at the site. Both these sites have high percentage coverage of coniferous plantation forest in the catchment. Individuals of *Siphlonurus lacustris* Eaton (Siphlonuridae) and *Ameletus inopinatus* Eaton (Siphlonuridae) were noted at five sites. Four of these sites were in Co. Wicklow (Site 187, Glendassan Stream, (GDAS1); Site 191, Knockalt Stream, (KNOCK1); Site 211, Glencullen Stream (GCULL1) and Site 212, Glenealo Stream, (GLENEA1) and the final site was located in Donegal (Site 142, Cornvannoge Stream (CORN1).

Table 5. 7. A list of benthic macroinvertebrates occurring in >50% of total sites.

Family	Species	% of Sites Present	No. of Sites Present *
Oligochaeta	Oligochaeta indet.	100.00	65
Baetidae	*Baetis rhodani*	98.46	64
Simuliidae	Simuliidae indet.	98.46	64
Chironomidae	*Orthocladiinae* spp.	98.46	64
Chironomidae	Tanypodinae spp.	95.38	62
Rhyacophilidae	*Rhyacophila dorsalis*	92.31	60
Hydropsychidae	*Hydropsyche siltalai*	92.31	60
Elmidae	*Limnius volckmari*	92.31	60
Limoniidae	*Pediciinae* spp.	92.31	60
Nemouridae	*Protonemura meyeri*	89.23	58
Perlodidae	*Isoperla grammatica*	87.69	57
Chironomidae	Chironominae spp.	84.62	55
Chloroperlidae	*Siphonoperla torrentium*	83.08	54
Heptageniidae	*Ecdyonurus* spp.	83.08	54
Elmidae	*Elmis aenea*	83.08	54
Leuctridae	*Leuctra inermis*	80.00	52
Leuctridae	*Leuctra hippopus*	78.46	51
Heptageniidae	*Rhithrogena semicolorata*	78.46	51
Ephemerellidae	*Seretella ignita*	78.46	51
Empididae	Empididae indet.	78.46	51
Nemouridae	*Amphinemura sulcicollis*	76.92	50
Goeridae	*Silo pallipes*	76.92	50
Gammaridae	*Gammarus duebeni*	72.31	47
Dytiscidae	*Oreodytes sanmarkii*	63.08	41
Elmidae	*Esolus parralelepipedus*	58.46	38
Hydracarina	Hydracarina indet.	58.46	38
Baetidae	*Baetis muticus*	56.92	37
Sericostomatidae	*Sericostoma personatum*	55.38	36
Elmidae	*Oulimnius* spp.	55.38	36
Hydraenidae	*Hydraena gracilis*	53.85	35
Rhyacophilidae	*Rhyacophila munda*	52.31	34
Polycentropodidae	*Plectrocnemia conspersa*	52.31	34
Scirtidae	*Elodes* spp.	52.31	34

* 65 sites in total

The most commonly occurring plecopteran was *Protonemura meyeri* (Pictet) (Nemouridae), which was recorded at 15 sites in spring and 58 sites in autumn. *Isoperla grammatica* (Poda) (Perlodidae) was the next most frequently encountered plecopteran species, (57 sites) followed by *Siphonoperla torrentium* (Pictet) (Chloroperlidae) (54 sites both season's data).

Rhyacophila dorsalis (Curtis) (Rhyacophilidae) was the most commonly encountered trichopteran species along with *Hydropsyche siltalai* Döhler (Hydropsychidae) both found at 60 sites, and *Silo pallipes* (Fabricius) (Georidae) was recorded at 50 sites.

Of the Coleoptera, *Limnius volckmari* (Panzer) (Elmidae) (60 sites), *Elmis aenea* (Müller) (Elmidae) (54 sites), *Esolus parrallelepipedues* (Müller) (Elmidae) (38 sites), and *Hydraena gracilis* Germar (Hydraenidae) (35 sites) were the most common species.

The most commonly recorded dipteran, crustacean and molluscan taxa were Simuliidae and Orthocladiinae (Chironomidae) (64 sites), *Gammarus duebeni* Liljeborg (Amhipoda, Gammaridae) (48 sites) and *Ancylus fluviatilis* Müller (Gastropoda, Ancylidae) (39 sites).

The Ephemeroptera represented an increasing proportion of the community as one moved from sites with SDI>80 to those in the 30-40 SDI band (Figures 5.30 and 5.31). At SDI bands below 30, ephemeropteran representation was slightly reduced and an increase in the proportion of some groups, especially the Coleoptera, was noted. In contrast, Plecoptera demonstrated a trend of increasing proportion with increasing acid sensitivity (particularly at highly forested sites). While the proportion of crustacean and mollusca decreased predictably with increasing acid sensitivity, the representation of dipteran larvae generally increased. The pattern was similar for both seasons.

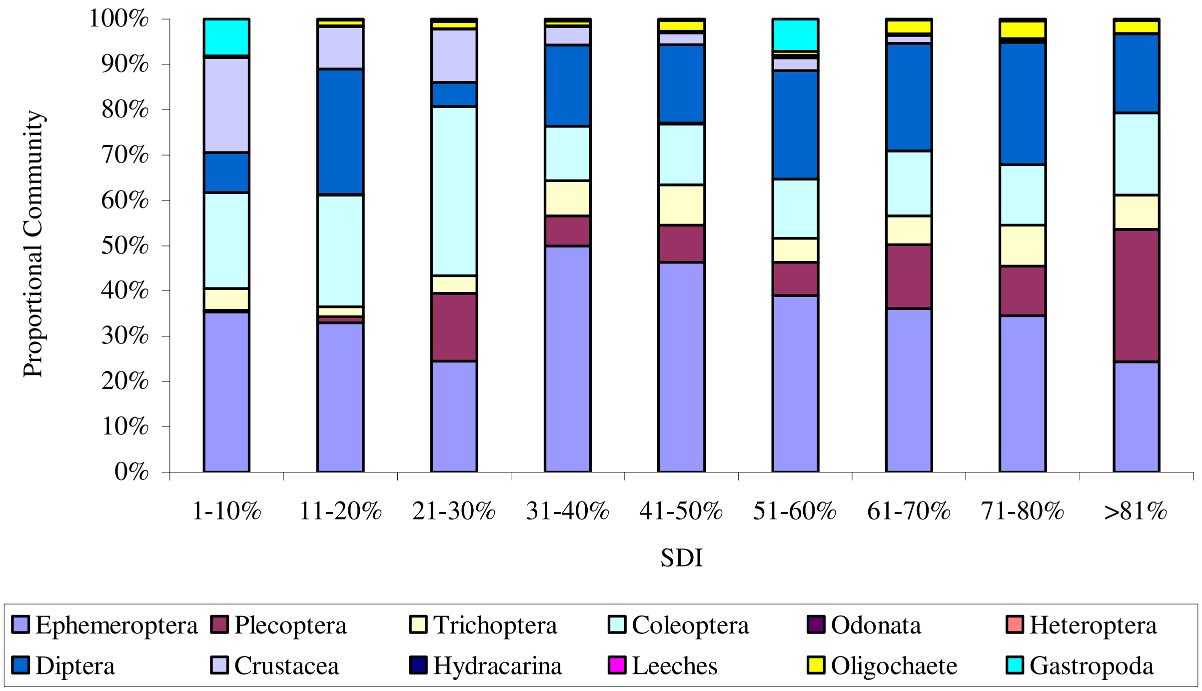


Figure 5. 30. Macroinvertebrate community composition over SDI gradient in spring (forested and non-forested sites

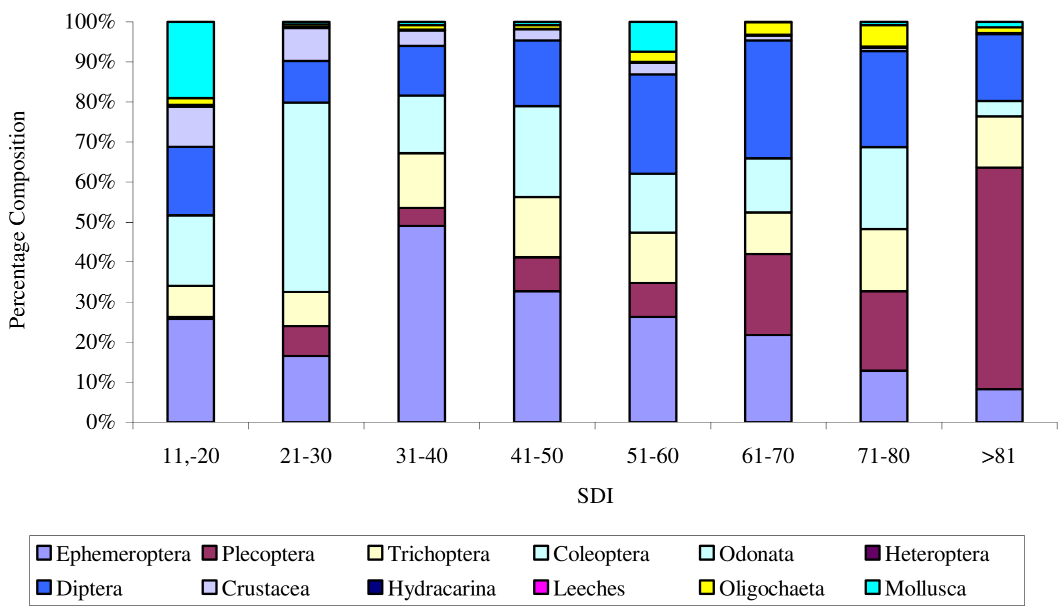


Figure 5. 31. Macroinvertebrate community composition over SDI gradient in autumn (forested and non-forested sites)

5.4.2 TWINSPAN analysis

TWINSPAN of the spring faunal dataset (non-forested sites) resulted in seven groups validated by MRPP (all less than P<0.05) (Figure 5.32a) and also for non-forested and forested sites (Figure 5.32b). In the case of the non-forested site analysis, Groups (1 to 6) had mean SDI values ranging from 50.1 to 74.9 and largely comprised of acid sensitive sites. Group 7 had a SDI mean of 21.6 (SDI range 7.6 to 59.7) and consisted mostly of acid tolerant sites. The chemical characteristics of the TWINSPAN site groupings are tabulated at the base of the dendrograms for each season (Figures 5.32a and 5.33).

At the first division, Group 7 (to the right of the dendrogram) was characterised by trends of higher abundances of *Athripsodes* spp., *Segmentia* spp., *Valvata* spp, and *Elmis aenea*. Other statistically significant indicators were *Protonemura meyeri*, *Perla bipunctata*, *Baetis scambus/fuscatus*, *Lepicostoma hirtum*, *Limnphilus lunatus*, *Elodes* spp., Limoniinae indet., Hexatominae indet., A*sellus aquaticus*, and *Potamorpyrgus antipodarium*.

At the second division, *Plectrocnemia* spp., and *Leuctra inermis* characterised site Groups 1 and 2, while Groups 3-6 were distinguished due to greater abundances of *Caenis rivulorum* and *Seratella ignita*. Group 2 was further distinct from Group 1 due to greater numbers of *Baetis muticus* at the third division. Group 1 had higher abundances of *Brachyptera risi* at the fourth division. Group 3 was distinguished from Groups 4-6 by greater abundances of *Leuctra* spp. At the third division, while Groups 4-6, noted higher numbers of *Esolus parallelepipedeus*. Figure 5.32b illustrated the Spring TWINSPAN for all sites (non-forested and forested) and no distinctive pattern was observed between non-forested and forested sites. However, as with the previous analysis the most sensitive (Group 7) and tolerant groups (Group 1) separated at the first level of division.

Analysis of autumn faunal data for the non-forested sites yielded relatively similar results. A total of seven groups were once again derived from TWINSPAN (Figure 5.33). Group 7 (comprising the right of the dendorgram) was characterised at the first division by higher abundances of gastropoda and *Asellus aquaticus*. The mean SDI values in Group 7 were 23.8 (range from 12.7 to 35.5). Groups 1-6 (on the left) made up a collection of moderately to highly sensitive sites grouping, initially characterised in the first division by a lower abundance of the mayfly, *Rhithrogena semicolorata*. Mean SDI values for Groups 1-6 ranged from 38.8 to 60.3.

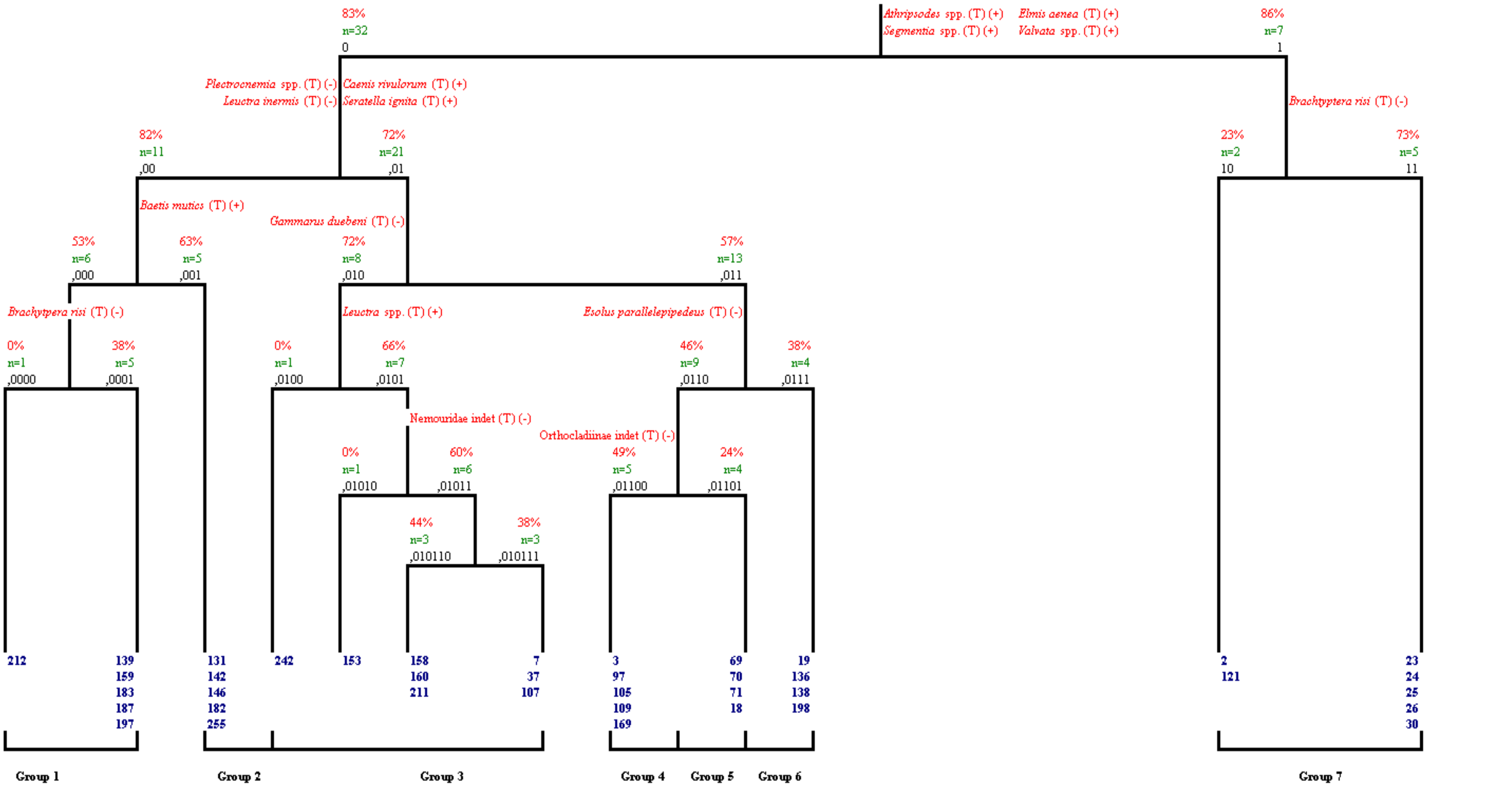


Figure 5. 32a. Spring TWINSPAN dendrogram - non-forested sites.

Table 5. 8. Spring TWINSPAN group characteristics. Mean values with ranges in brackets. Average slope, area and perimeter values represent

Site Number	SDI	pH	Alkalinity (mg $CaCO_3$ l^{-1})	Conductivity (uS/cm)	Total Aluminium (μg Al/l)	Area (km^2)	Perimeter (km)	Average Slope (%)	Altitdue (m.a.s.l.)	Distance to Source (km)
Group 1	74.94 (49.23-83.47)	6.52 (5.98-4.64)	3.81 (0.026-41.625)	34.50 (25-151)	96.56 (59.54-103.17)	6.46 (1.70-12.54)	11.49 (5.90-14.38)	15.95 (10.67-24.19)	181.88 (70.02-324.09)	4.86 (2.48-7.32)
Group 2	50.11 (27.04-67.56)	7.39 (6.82-7.66)	23.92 (7.16-40.666)	137.70 (52.80-352)	69.43 (40.70-78.80)	3.69 (0.79-9.05)	7.82 (4.54-12.21)	18.99 (9.17-16.75)	154.18 (99.65-220.49)	3.46 (2.19-4.83)
Group 3	41.24 (16.21-57.24)	7.33 (6.84-8.12)	54.86 (14.1523-118.75)	157.86 (67.67-310)	74.22 (50.122-85.86)	19.26 (2.14-43.95)	19.10 (6.19-30.08)	10.46 (3.28-17.48)	107.28 (51.89-191.11)	8.05 (2.97-13.99)
Group 4	54.14 (36.84-73.54)	7.13 (6.54-7.55)	22.86 (2.72-46.0)	131.17 (78.17-211.0)	116.70 (68.1-192.0)	23.07 (6.42-63.85)	22.29 (14.27-42.384)	12.02 (6.47-16.19)	87.12 (56.87-109.76)	9.83 (5.98-18.238)
Group 5	57.95 (47.58-77.61)	7.12 (6.90-7.45)	17.65 (7.16-34.11)	83.53 (53.77-127.90)	83.25 (68.1-89.2)	30.56 (6.34-46.39)	26.74 (12.30-36.30)	17.84 (13.27-24.27)	122.68 (51.63-160.49)	9.87 (5.15-14.98)
Group 6	70.12 (49.88-84.82)	6.36 (6.36-7.31)	3.17 (-0.13 - 111.071)	70.03 (62-74)	104 (53.12-104.0)	16.53 (1.36-26.42)	16.01 (7.27-24.08)	35.91 (9.20-107.69)	74.38 (9.15-105.09)	7.46 (3.62-11.22)
Group 7	21.60 (7.63-59.68)	7.75 (7.16-8.07)	213.30 (46.09-321)	469.0 (194.37-644.33)	175.57 (172.0-212.0)	52.11 (13.62-99.58)	36.70 (15.60-55.62)	3.84 (1.16-8.15)	66.58 (48.05-142.38)	14.96 (6.25-24.66)

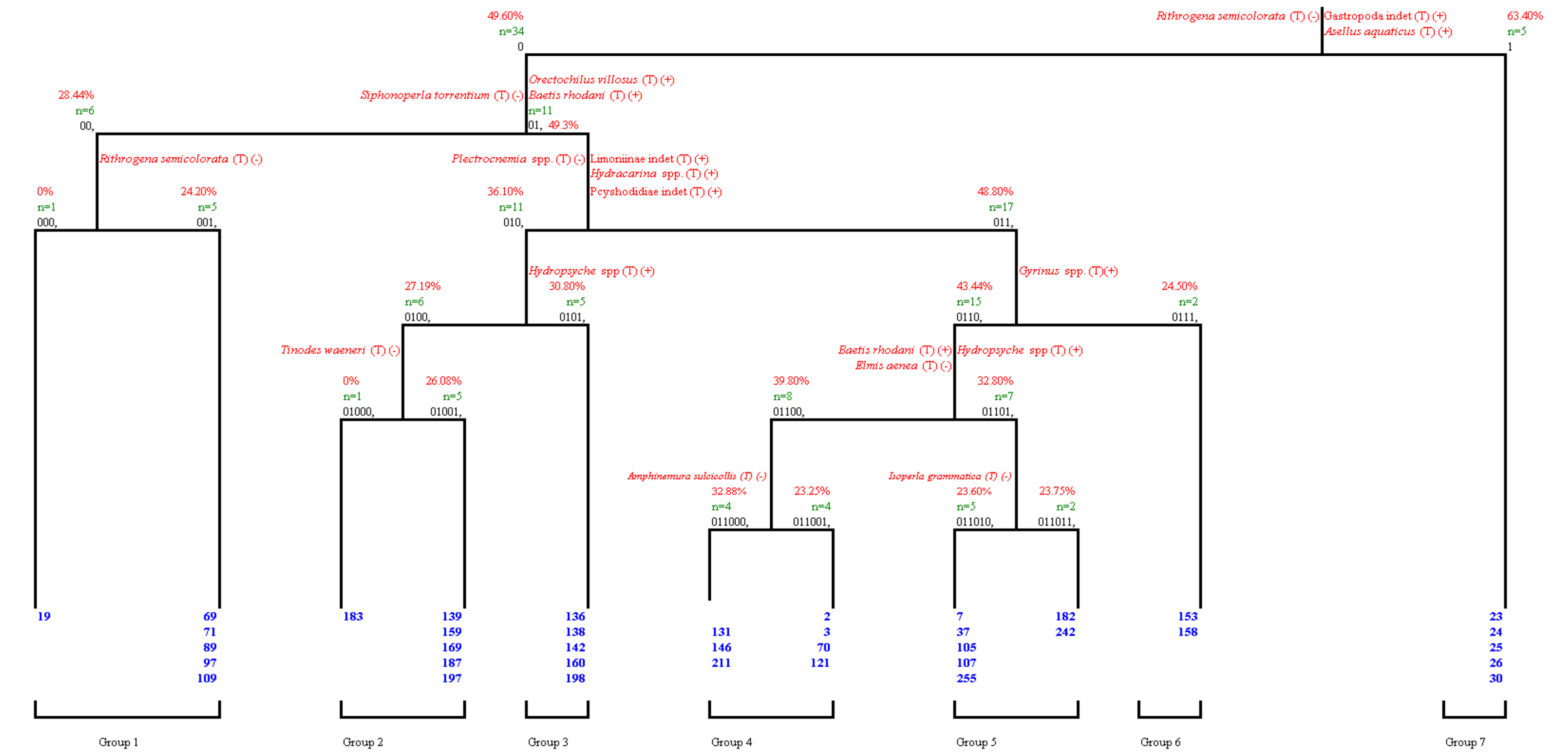


Figure 5. 33. TWINSPAN dendrogram of autumn data - non-forested sites.

Table 5. 9. Autumn TWINSPAN group characteristics. Mean values with ranges in brackets. Average slope, area and perimeter values represent catchment upstream of sampling points.

Group Number	SDI	pH	Alkalinity (mg $CaCO_3$ l^{-1})	Conductivity (uS/cm)	Total Aluminium (μg Al/l)	Area (km^2)	Perimeter (km)	Average Slope (%)	Altitdue (m.a.s.l.)	Distance to Source (km)
1	55.33 (49.51-72.10)	6.73 (5.91-7.29)	12.08 (-0.29-58.096)	76 (32-183)	87.49 (64.72-105.44)	0.72 (0.23-1.1)	11.49 (5.9-14.38)	15.95 10.67-24.19)	181.88 (70.02-324.09)	4.86 (3.24-7.32)
2	41.25 (24.10-60.65)	7.13 (6.26-7.90)	8.16 (8.16-115)	53 (53-225)	24.8 (24.8-79.14)	0.48 (0.1-0.96)	8.24 (4.54-12.21)	21.45 (16.29-36.3)	137.61 (99.65-161.74)	3.58 (2.19-7.83)
3	38.80 (23.36-55.78)	6.80 (6.01-8.38)	30.096 (47.85-170)	212.88 (94.50-478)	30.4 (29.60-70.38)	1.03 (0.8-1.64)	16.20 (6.19-30.08)	9.63 (3.28-17.48)	94.40 (43.45-137.42)	7.10 (2.97-10.86)
4	55.61 (39.33-72.41)	6.01 (5.76-7.25)	25.36 (2.78-30.12)	143.30 (89.10-212.00)	49.95 (20.00-46.45)	1.22 (0.81-1.23)	22.29 (15.09-42.38)	12.024 (6.48-20.54)	87.124 (58.12-109.76)	9.826 (5.98-18.24)
5	56.65 (45.05-66.16)	6.39 (6.22-6.55)	20.89 (12.15-37.11)	94.3 (71.5-139.8)	30.175 (20.0-41.5)	1.3275 (0.8-1.67)	26.74 (12.3-36.3)	17.84 (13.27-24.27)	122.68 (51.63-160.49)	9.87 (5.15-14.89)
6	60.26 (38.53-77.87)	7.11 (6.15-7.86)	4.17 (4.16-47.5)	62.9 (62.9-129)	119 (65.14-119.0)	0.9975 (0.13-1.41)	19.80 (7.27-26.42)	11.795 (9.2-16.08)	99.01 (53.27-130.00)	7.88 (3.62-11.22)
7	23.77 (12.73-35.48)	7.36 (6.36-7.96)	201.74 (17.14-282.00)	449.56 (152.90-579.00)	81.74 (51.10-102.00)	1.62 (1.13-2.00)	36.70 (15.60-48.59)	3.84 (1.16-8.15)	66.578 (48.05-142.38)	14.96 (6.25-24-66)

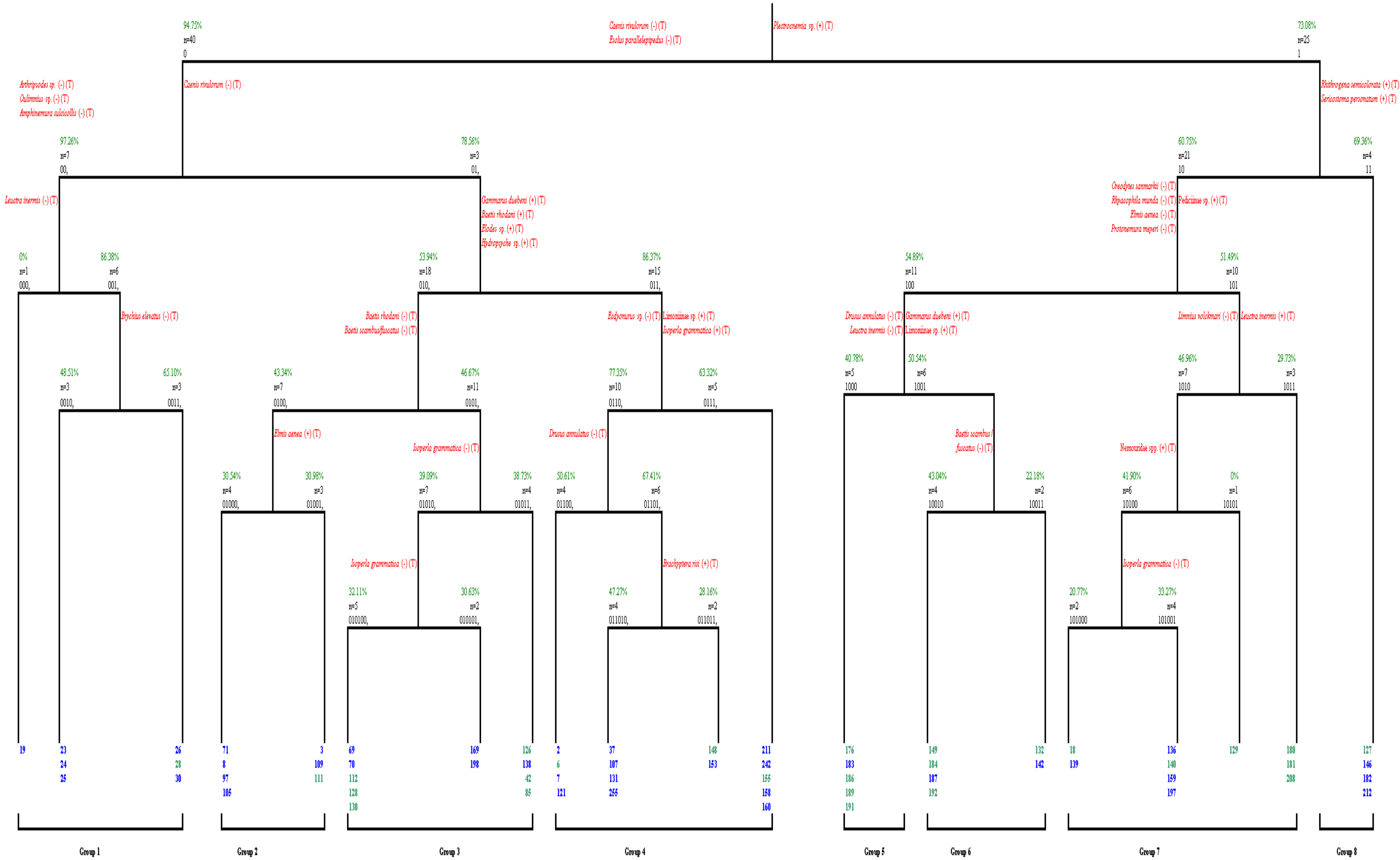


Figure 5. 32b. Spring TWINSPAN – Non-forested and forested sites (Blue – non-forested sites, green – forested sites).

5.4.3 Ordination analyses

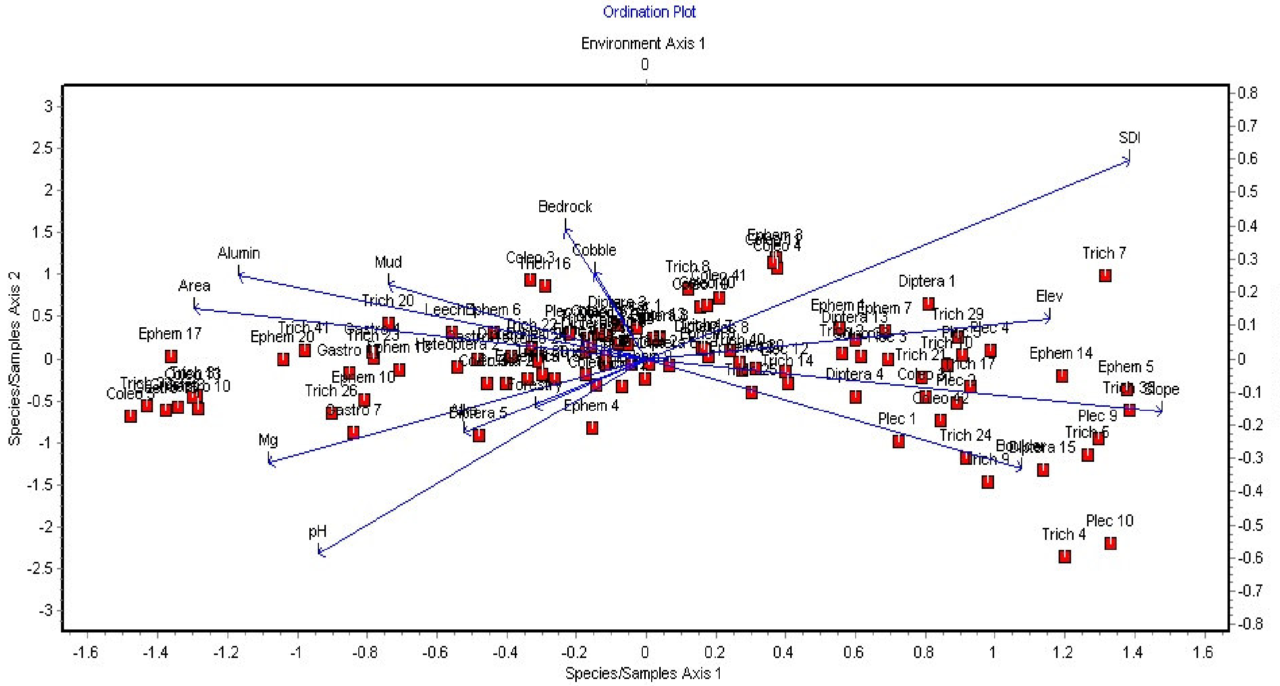
A Detrended Correspondence Analysis (DCA) was run on the faunal data from the present study in order to gain the length of the first gradient and thereby discern which multivariate ordination techniques were applicable. Ter Braak (1991) noted that a linear model (e.g. PCA) should be used when the gradient length is <2 standard deviation units, and a unimodal model (e.g. CCA) should be applied with gradient lengths >4 standard deviation units. However, when the value falls between 2 and 4, both models are applicable, although the unimodal methods are very robust and effective above 2 standard deviation units (Birks, 2000). The gradient length obtained for the faunal dataset was 2.72, as such both Principle Component Analysis (PCA) and Canonical Correspondence Analysis (CCA) models were appropriate but the latter was applied below.

5.4.3.1 CCA Ordinations

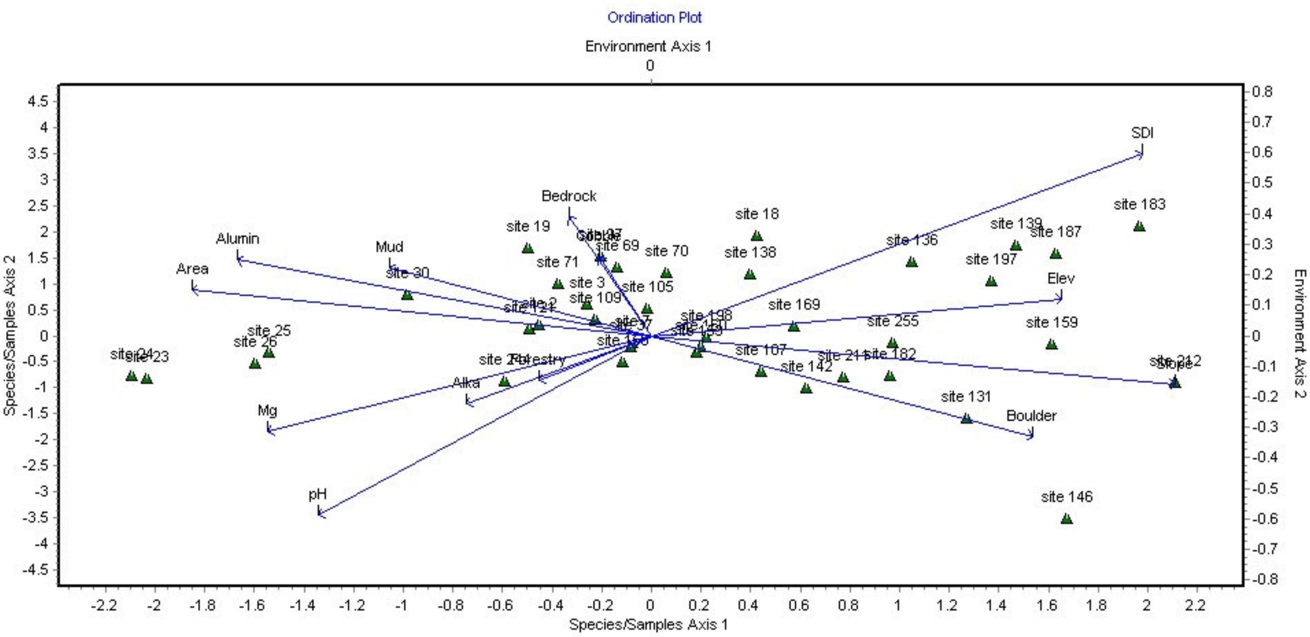
Canonical correspondence analysis (CCA) of the spring data – non-forested sites - demonstrated a significant correlation between the physico-chemical parameters and the faunal dataset (Table 5.10). A high degree of multicollinearity was noted among the 31 physico-chemical parameters. Highly correlated parameters were removed leaving 13 environmental parameters in the spring analysis using ECOM™ 2.0. The environment-species correlations for axes 1-4 were 0.912, 0.894, 0.932 and 0.854, respectively. However, despite the significant correlations, the eigenvalues were low (Table 5.10). All four axes explained 27.47% of the cumulative data variation. According to the ordination plots, SDI, elevation, slope and boulder substrate were strongly associated with the several taxa (eg. Ephem 5 & 7, *Ameletus inopinatus* and *Baetis vernus*, Plec 9, *Diura bicaudata*, Trich 24 & 35 – *Halesus radiatus* and *Stenophylax permistus* and Coleo 31, *Limnebius truncatellus*), (Figure 5.34 a), at the most acid sensitive sites (e.g. Site 183, Ballylow Brook, Site 187, Glendassan River and Site 136, Glen River), (Figure 5.34 b). Forward selection highlighted SDI (% variance 9.06%, P<001), slope (% variance, 8.76%, P<0.01) and mud substrate (% variance, 4.86%, P<0.01) as the three most important variables.

Table 5. 10. Spring data CCA summary.

	Axis 1	Axis 2	Axis 3	Axis 4	Total Inertia
Canonical Eigenvalues	0.188	0.105	0.084	0.072	1.636
% variance explained	11.50	6.39	5.15	4.43	
Cumulative % variance explained	11.50	17.89	23.044	27.47	
Multiple correlation Species-Environmental data	0.911	0.893	0.931	0.854	
Kendall-Rank Correlation Species-Environmental data	0.746	0.676	0.735	0.630	
Sum of canonical eigenvalues	0.728				
Sum of non-canonical eigenvalues	0.906				
Number of sites	39				
Number of species	103				
Number of environmental parameters	13				



a)



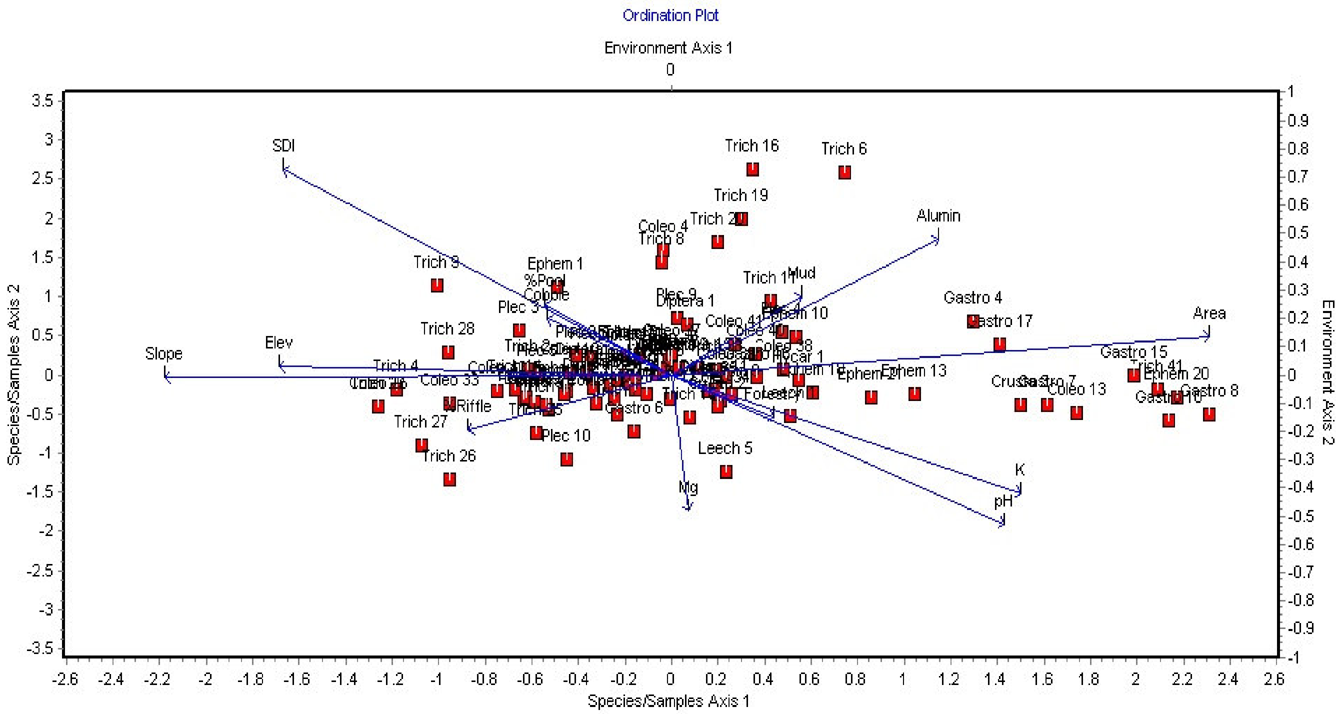
b)

Figure 5. 34. a) Non-forested sites CCA biplot of environmental and species relationship - Spring data - and **b)** Non-forested sites CCA biplot of relationship between environmental parameters and sampled sites - Spring data.

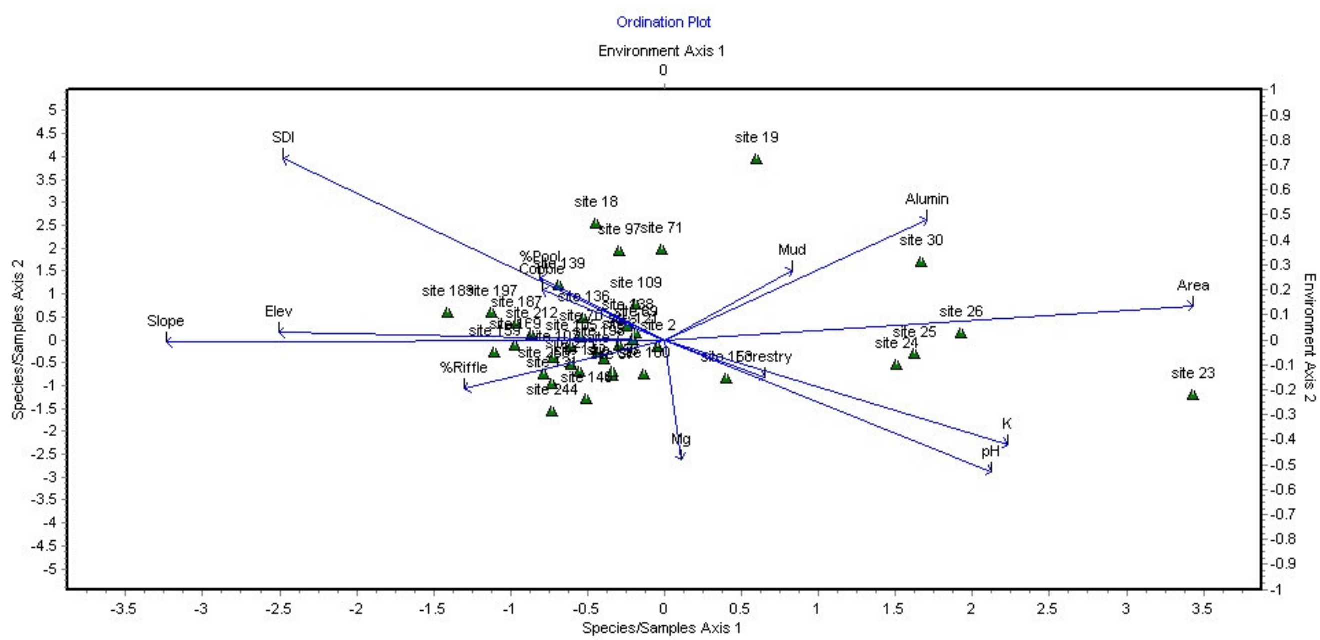
Once again the autumn data showed a high degree of multicollinearity among the 31 physico-chemical parameters. Highly correlated parameters were removed leaving 13 environmental parameters in the autumn analysis. Canonical Correspondence Analysis (CCA) of the data produced four axes with relatively high correlation values of 0.902, 0.934, 0.929 and 0.879, respectively. Again the eigenvalues were low. The total cumulative data variation explained after four axes was 29.19% (Table 5.11). As with the spring analysis, SDI, elevation and slope were important parameters were strongly associated with acid susceptible sites (Figure 5.35 a & b). Forward selection highlighted slope (% variance, 8.05%, $P<0.01$), SDI (% variance, 7.05%, $P<0.01$) and magnesium (% variance, 3.53%, $P<0.01$) as the three most important variables.

Table 5. 11. Autumn Data CCA summary.

	Axis 1	**Axis 2**	**Axis 3**	**Axis 4**	**Total Inertia**
Canonical Eigenvalues	0.223	0.120	0.094	0.077	1.769
% variance explained	12.642	6.810	5.352	4.392	
Cumulative % variance explained	12.642	19.452	24.805	29.196	
Multiple correlation Species-Environmental data	0.903	0.934	0.929	0.879	
Kendall-Rank Correlation Species-Environmental data	0.582	0.732	0.764	0.630	
Sum of canonical eigenvalues	0.822				
Sum of non-canonical eigenvalues	0.946				
Number of sites	39				
Number of species	93				
Number of environmental parameters	13				



a)



b)

Figure 5. 35. a) Non-forested CCA biplot of environmental and species relationship and **b)** non-forested CCA biplot of relationship between environmental parameters and sites - autumn data.

5.4.4 Relationships between SDI and faunal data

The relationship between this Index and various biological metrics were investigated.

Taxon numbers and abundances were examined over a gradient of sodium dominance with all sites grouped into SDI classes of 10-19, 20-29, 30-39, 40-49, 50-59, 60-69 and >70. SDI values from each class were compared with the taxon number or abundance in each case. The results for correlations of taxon richness and faunal abundance with SDI are shown for spring and autumn in Tables 5.12 and 5.13.

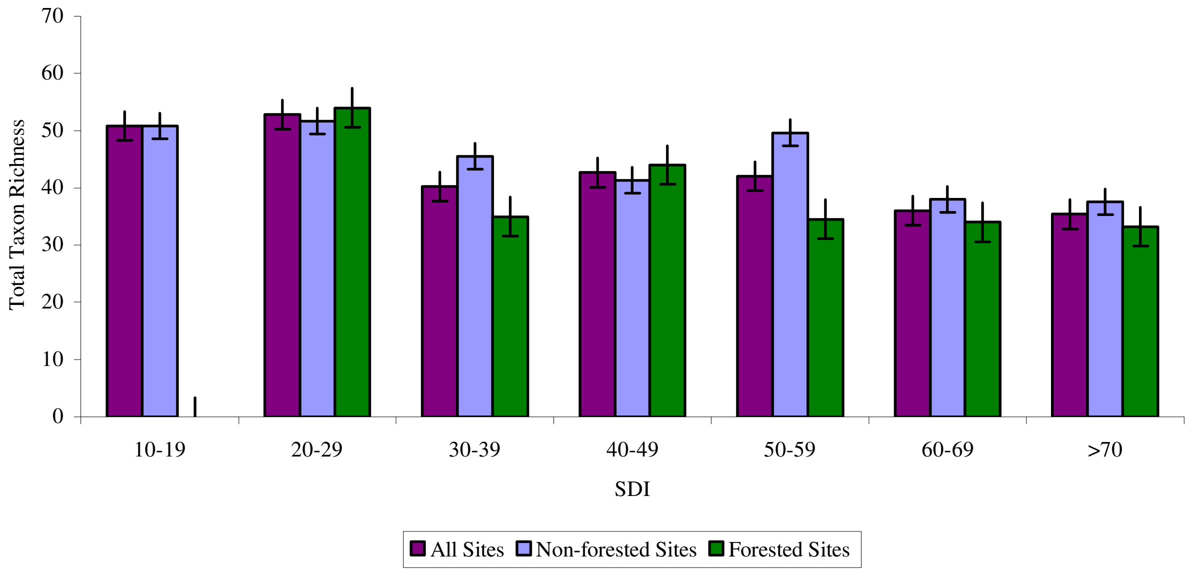


Figure 5. 36. Changes in total taxon richness across the SDI bands (Spring)

The total taxon richness in the spring dataset was significantly correlated with SDI for all sites combined for forested sites. As can be seen from Figure 5.36 the general trend was one of decreasing taxon richness with increasing SDI. The trend did not hold for the autumn data. The SDI correlation with ephemeropteran richness was only significant for the spring period (non-forested site data), while in the autumn it was with plecopteran taxon richness (Figure 5.37).

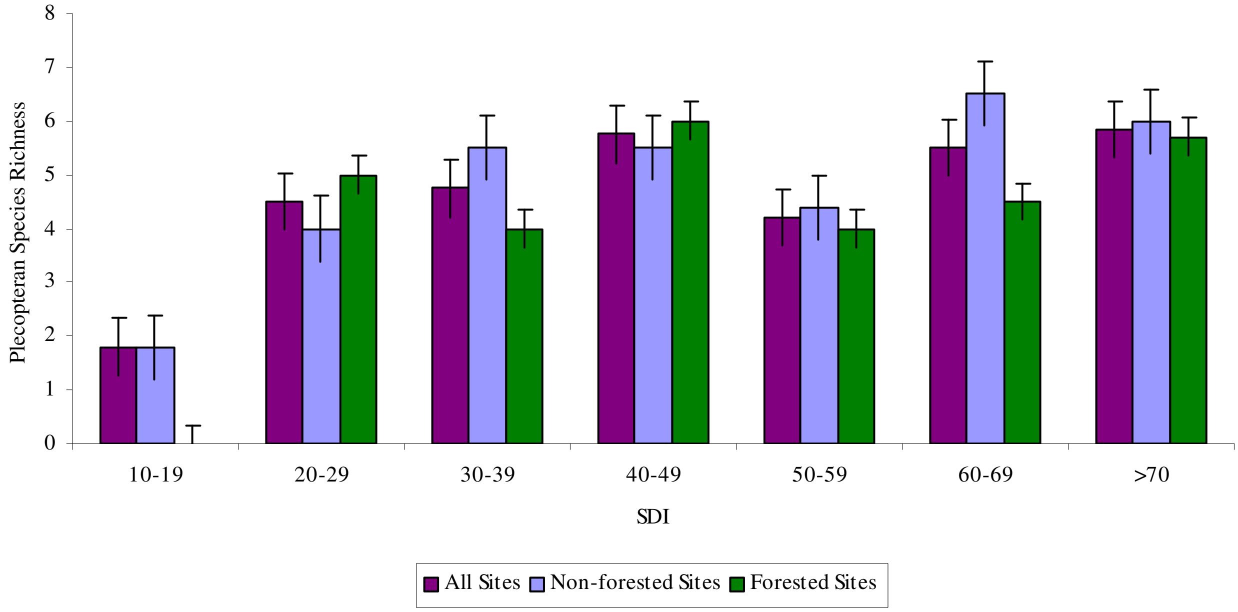


Figure 5. 37. Changes in plecoptera taxon richness across the SDI bands (autumn).

No other significant relationships were found in the autumn data. Trichoptera was the only group in the spring dataset, which showed a strong relationship for taxon richness (all combinations of data) with SDI (Figure 5.38).

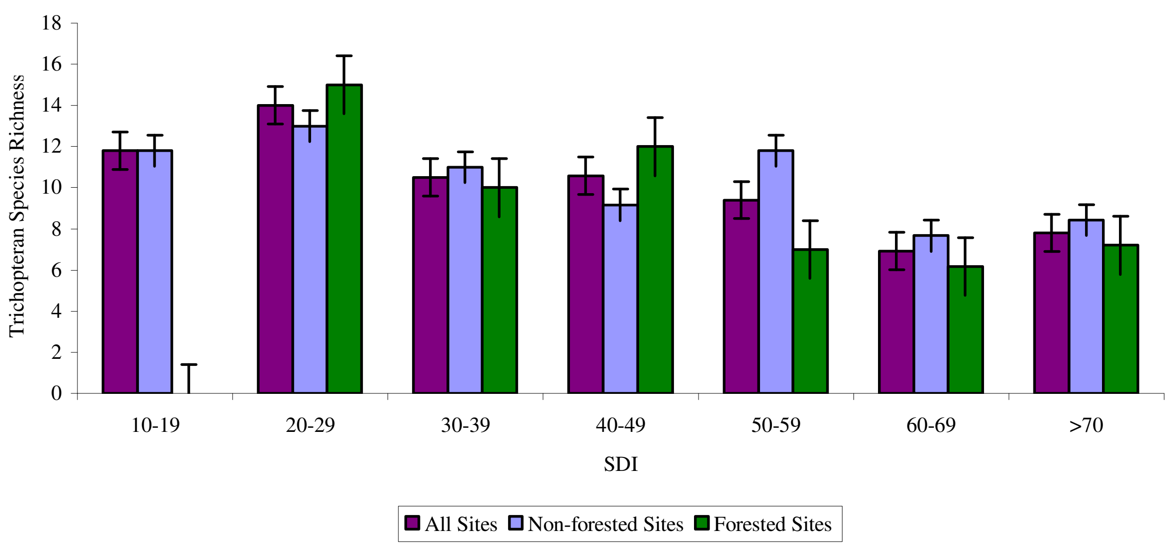


Figure 5. 38. Changes in trichopteran taxon richness across the SDI bands (spring)

Table 5. 12. Correlations of taxa number and faunal abundance with SDI for spring

Spring Parameters		Correlation	Regression	P-Value
Total Taxa Vs SDI	Non-forested	-0.792	R^2=0.627	P=0.034*
	Forested	-0.790	R^2=0.625	P=0.061
	All Sites	-0.859	R^2=0.738	P=0.028*
Total Number of Ephemeroptera Vs SDI	Non-forested	-0.868	R^2=0.753	P=0.011*
	Forested	-0.667	R^2=0.445	P=0.148
	All Sites	-0.795	R^2=0.633	P=0.059
Total Number of Plecoptera Vs SDI	Non-forested	0.214	R^2=0.046	P=0.645
	Forested	-0.797	R^2=0.583	P=0.058
	All Sites	-0.817	R^2=0.668	P=0.047*
Total Number of Trichoptera Vs SDI	Non-forested	-0.743	R^2=0.552	P=0.042*
	Forested	-0.887	R^2=0.786	P=0.018*
	All Sites	-0.916	R^2=0.840	P=0.010**
Ephemeropteran Abundance Vs SDI	Non-forested	-0.802	R^2=0.5646	P=0.051
	Forested	-0.478	R^2=0.2037	P=0.369
	All Sites	-0.851	R^2=0.696	P=0.020*
Plecopteran Abundance Vs SDI	Non-forested	-0.225	R^2=0.0597	P=0.598
	Forested	0.085	R^2=0.0118	P=0.838
	All Sites	-0.062	R^2=0.0052	P=0.877
Trichopteran Abundance Vs SDI	Non-forested	-0.753	R^2=0.5418	P=0.059
	Forested	-0.151	R^2=0.0166	P=0.808
	All Sites	-0.549	R^2=0.339	p=0.170

* significant to 0.05 level

** significant to 0.01 level

Table 5. 13. Correlations of taxa number and faunal abundance with SDI for autumn

Autumn Parameters		Correlation	Regression	P-Value
Total Taxa Vs SDI	Non-forested	-0.392	R^2=0.156	P=0.385
	Forested	-0.556	R^2=0.526	P=0.252
	All Sites	-0.677	R^2=0.571	P=0.144
Total Number of Ephemeroptera Vs SDI	Non-forested	-0.369	R^2=0.156	P=0.415
	Forested	-0.693	R^2=0.526	P=0.127
	All Sites	-0.755	R^2=0.571	P=0.083
Total Number of Plecoptera Vs SDI	Non-forested	0.823	R^2=0.817	P=0.023*
	Forested	0.138	R^2=0.000	P=0.794
	All Sites	0.753	R^2=0.854	P=0.051
Total Number of Trichoptera Vs SDI	Non-forested	-0.147	R^2=0.022	P=0.753
	Forested	-0.707	R^2=0.749	P=0.116
	All Sites	-0.765	R^2=0.844	P=0.076
Ephemeropteran Abundance Vs SDI	Non-forested	-0.525	R^2=0.425	P=0.226
	Forested	-0.210	R^2=0.060	P=0.689
	All Sites	-0.503	R^2=0.406	P=0.250
Plecopteran Abundance Vs SDI	Non-forested	0.375	R^2=0.508	P=0.407
	Forested	0.401	R^2=0.161	P=0.431
	All Sites	0.573	R^2=0.328	P=0.179
Trichopteran Abundance Vs SDI	Non-forested	-0.729	R^2=0.531	P=0.063
	Forested	0.526	R^2=0.276	P=0.284
	All Sites	-0.385	R^2=0.148	P=0.394

* significant to 0.05 level

** significant to 0.01 level

Analysis of variance (two-way) on the spring data showed differences in total taxon richness between SDI bands ($F_{6,50}$=2.721, P=0.023, Table 5.14). The same results were not found for the autumn data (Table 5.15). No significant effects of SDI were found when the analysis was run using spring and autumn ephemeropteran taxon richness. Plecopteran species richness demonstrated significant differences between SDI bands in both seasons (spring - $F_{6,50}$=3.732, P=0.004; autumn - $F_{6,52}$=4.108, P=0.002, Table 5.15), Tables 5.14 and 5.15), generally species richness increased with increasing SDI. Trichopteran richness differed between bands in the spring ($F_{6,50}$=3.749, P=0.004, Table 5.14) but was not repeated in the autumn. There was no significant interaction between forestry and SDI bands for these taxonomic groups.

In terms of abundance both the spring (Two-way ANOVA, $F_{6,50}$=2.721, P=0.023, Table 5.14) and autumn ($F_{6,52}$=3.354, P=0.007), data showed significant differences in total taxon abundance between SDI bands. Neither forestry nor the forestry SDI band interactions were significant. A similar finding applied to the Ephemeroptera in both seasons (spring - $F_{6,50}$=2.355, P=0.044; autumn - $F_{6,52}$=3.233, P=0.009, Tables 5.14 and 5.15). Plecopteran and trichopteran abundances showed no significant effect of forestry or SDI bands in the spring. However, significant differences in plecopteran ($F_{6,52}$=3.903, P=0.003, Table 5.15) abundance between SDI bands were detected in the autumn dataset.

In general, most of the significant differences in both taxon richness and abundances could be attributed to differences between the lowest SDI band (<20) and the two highest, 60-70 and >70 (Tables 5.14 and 5.15).

Table 5. 14. An analysis of a range of metrics across SDI bands in spring

Taxon Richness Parameters for spring		F - Test	P-Value
Difference in Total Taxon Richness			
	Forestry	F(1,50)=1.213	P=0.276
	SDI Bands	F(6,50)=2.721	P=0.023*
	Forestry x SDI Bands	F(5,50)=0.397	P=0.848
Ephemeropteran Species Richness			
	Forestry	F(1,50)=2.153	P=0.149
	SDI Bands	F(6,50)=1.764	P=0.126
	Forestry x SDI Bands	F(5,50)=0.384	P=0.857
Plecopteran Species Richness			
	Forestry	F(1,50)=0.722	P=0.400
	SDI Bands	F(6,50)=3.372	P=0.004*
	Forestry x SDI Bands	F(5,50)=0.462	P=0.803
Trichopteran Species Richness			
	Forestry	F(1,50)=0.064	P=0.951
	SDI Bands	F(6,50)=3.749	P=0.004*
	Forestry x SDI Bands	F(5,50)=0.662	P=0.654

* significant to 0.05 level

Abundance Parameters for spring		F - Test	P-Value
Difference in Total Taxon Abundance			
	Forestry	F(1,50)=1.213	P=0.276
	SDI Bands	F(6,50)=2.721	P=0.023*
	Forestry x SDI Bands	F(5,50)=0.397	P=0.848
Ephemeropteran Abundace			
	Forestry	F(1,50)=0.802	P=0.375
	SDI Bands	F(6,50)=2.355	P=0.044*
	Forestry x SDI Bands	F(5,50)=0.343	P=0.884
Plecopteran Abundance			
	Forestry	F(1,50)=0.002	P=0.969
	SDI Bands	F(6,50)=0.776	P=0.600
	Forestry x SDI Bands	F(5,50)=1.193	P=0.326
Trichopteran Abundance			
	Forestry	F(1,50)=0.608	P=0.439
	SDI Bands	F(6,50)=1.276	P=0.285
	Forestry x SDI Bands	F(5,50)=0.672	P=0.647

* significant to 0.05 level

Table 5. 15. Analysis of variance of metrics across SDI bands for autumn

Taxon Richness Parameters for autumn		F-Test	P-Value
Difference in Total Taxon Richness			
	Forestry	F(1,52)=2.767	P=0.102
	SDI Bands	F(6,52)=2.223	P=0.055
	Forestry x SDI Bands	F(5,52)=1.241	P=0.304
Ephemeropteran Species Richness			
	Forestry	F(1,52)=7.571	P=0.008*
	SDI Bands	F(6,52)=1.589	P=0.169
	Forestry x SDI Bands	F(5,52)=0.462	P=0.802
Plecopteran Species Richness			
	Forestry	F(1,52)=1.612	P=0.210
	SDI Bands	F(6,52)=4.108	P=0.002*
	Forestry x SDI Bands	F(5,52)=0.773	P=0.574
Trichopteran Species Richness			
	Forestry	F(1,52)=0.025	P=0.874
	SDI Bands	F(6,52)=0.850	P=0.538
	Forestry x SDI Bands	F(5,52)=2.001	P=0.094

* significant to 0.05 level

Abundance Parameters for autumn		F-Test	P-Value
Difference in Total Taxon Abundance			
	Forestry	F(1,52)=1.796	P=0.186
	SDI Bands	F(6,52)=3.354	P=0.007*
	Forestry x SDI Bands	F(5,52)=0.715	P=0.615
Ephemeropteran Abundace			
	Forestry	F(1,52)=4.625	P=0.036*
	SDI Bands	F(6,52)=3.233	P=0.009*
	Forestry x SDI Bands	F(5,52)=1.874	P=0.115
Plecopteran Abundance			
	Forestry	F(1,52)=0.110	P=0.915
	SDI Bands	F(6,52)=3.903	P=0.003*
	Forestry x SDI Bands	F(5,52)=0.918	P=0.447
Trichopteran Abundance			
	Forestry	F(1,52)=0.464	P=0.832
	SDI Bands	F(6,52)=1.263	P=0.266
	Forestry x SDI Bands	F(5,52)=0.446	P=0.814

* significant to 0.05 level

5.4.5 Other Biological Metrics and SDI

The relationships of three other metrics: Mean EPT (the sum of ephemeropteran, plecopteran and trichopteran abundance) (Figure 5.39) and mean E/P (ephemeropteran divided by plectopteran abundance) (Figure 5.41) and crustacaean/dipteran (C/D) (Figure 5.40), with SDI were examined within bands. An additional metric, was also tested. The C/D index, is a new index proposed because of the trends in the representation of the Crustacea and Diptera noted in Section 5.4.1.

The correlation between these metrics and SDI for spring and autumn faunal data are shown in Table 5.16. The relationship between EPT and SDI was significant for all sites (spring and autumn data) and non-forested sites considered separately (spring data). The relationship between SDI and C/D was significant for all sites combined and the non-forested sites in both seasons.

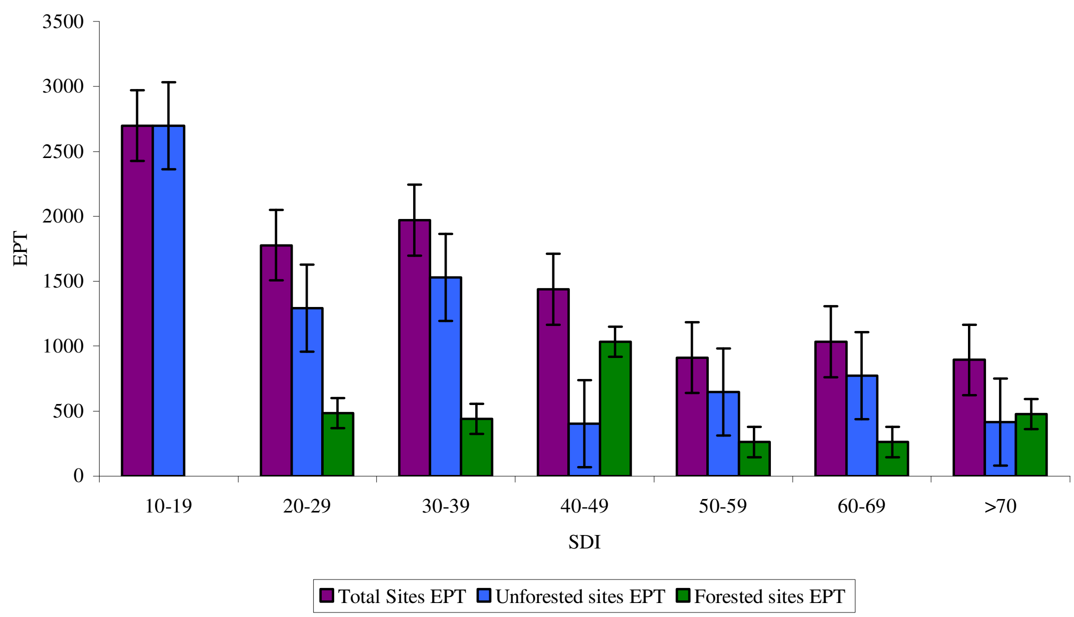


Figure 5. 39. Ephemeropteran/Plecopteran/Trichopteran (average for each site) metric along an SDI gradient (Spring)

Table 5. 16. Relationships for selected metrics with SDI For Spring And Autumn Faunal Data

Spring faunal data

Parameter		Correlation	Regression	P-Value
EPT Vs SDI	Non-forested	-0.87	R^2=0.875	P=0.011*
	Forested	-0.279	R^2=0.117	P=0.593
	All Sites	-0.939	R^2=0.906	P=0.005**
E/P Vs SDI	Non-forested	-0.213	R^2=0.0572	P=0.648
	Forested	-0.605	R^2=0.3675	P=0.202
	All Sites	-0.230	R^2=0.0706	P=0.611
C/D Vs SDI	Non-forested	-0.825	R^2=0.925	P=0.004**
	Forested	-0.716	R^2=0.565	P=0.110
	All Sites	-0.846	R^2=0.823	P=0.016*

* significant to 0.05 level
** significant to 0.01 level

Autumn faunal data

Parameter		Correlation	Regression	P-Value
EPT Vs SDI	Non-forested	-0.567	R^2=0.395	P=0.184
	Forested	0.038	R^2=0.030	P=0.942
	All Sites	-0.868	R^2=0.798	P=0.025*
E/P Vs SDI	Non-forested	-0.428	R^2=0.270	P=0.397
	Forested	-0.291	R^2=0.252	P=0.576
	All Sites	-0.439	R^2=0.346	P=0.383
C/D Vs SDI	Non-forested	-0.871	R^2=0.919	P=0.003**
	Forested	-0.886	R^2=0.914	P=0.011*
	All Sites	-0.920	R^2=0.988	P=0.019*

* significant to 0.05 level
** significant to 0.01 level

There was a significant difference in C/D values between the SDI bands (Kruskal Wallace, P<0.01). Pairwise comparison of the C/D values between classes show that C/D in SDI bands greater than >40 were significantly different from the values in the lower SDI bands. There were no significant correlation between E/P and SDI in this study (Table 5.16 and Figure 5.40 and 5.41).

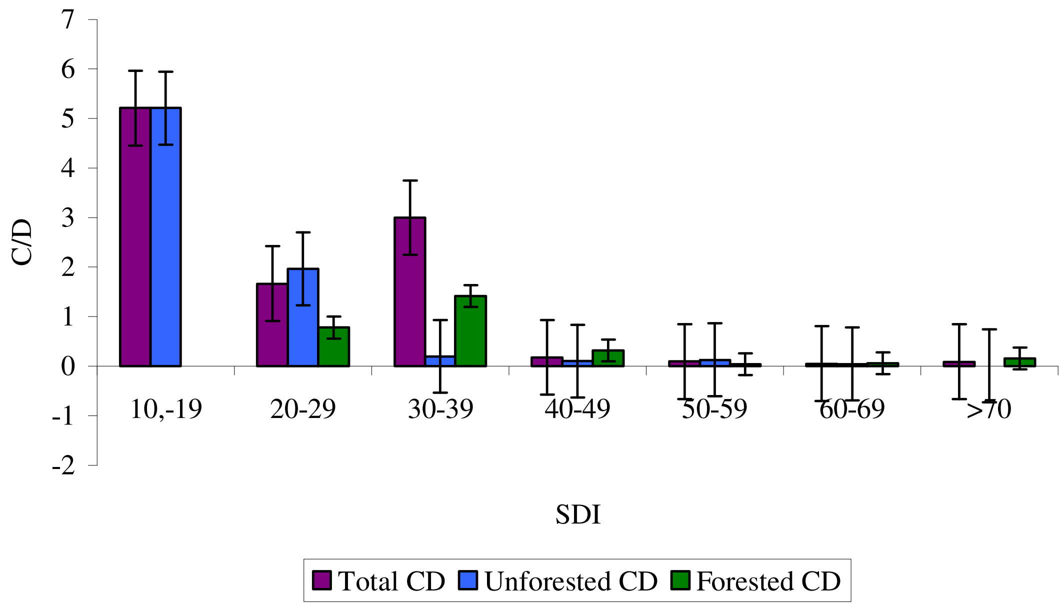


Figure 5. 40. Mean variation in the Crustacean/Dipteran Metric across the SDI gradient (Spring); ± S.E.

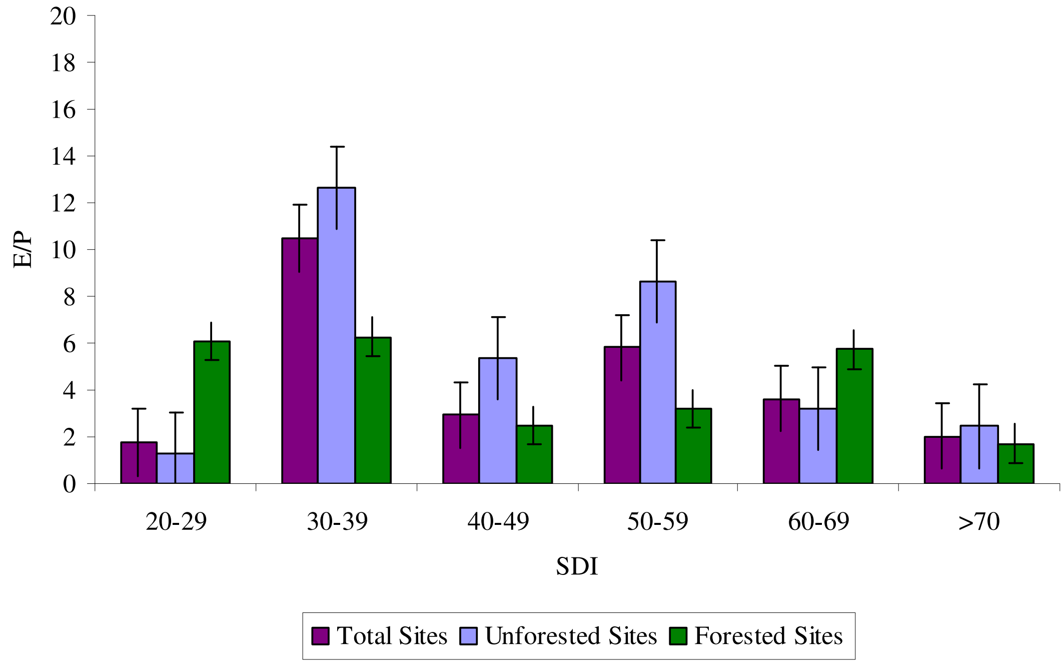


Figure 5. 41. Trends in E/P for spring data across the SDI bands.

6 DISCUSSION

The growing desire to develop plantation forestry further in Ireland has led to questions as to how to designate sites for future development. The protection of water quality, and in particular salmonid water quality, has become an important objective. One of the major issues associated with afforestation is the potential acidifying effect planting of trees will have water quality. A number of approaches have been used to classify and identify sites, which are sensitive/non-sensitive to forestry-mediated acidity. In view of the ecological importance of soft-waters for salmonid production, it is critical that measures are taken to avoid increased rates of acidification, particularly those relating to changes in land use. This necessitates the identification of acid-sensitive waters.

Alkalinity and acid neutralising capacity readings (ANC) are traditionally used to designate the likely impacts of acidification on catchments. The most commonly adopted indicators are pH (state) and alkalinity (sensitivity). Currently, the Irish Forest Service uses alkalinity readings in deciding whether to grant aid afforestation on potentially acid sensitive catchments. Grant aid is not provided for planting in areas where surface waters alkalinity values of < 8 mg $CaCO_3$ l^{-1} are recorded. However, planting in areas with alkalinity values > 15 mg $CaCO_3$ l^{-1} generally receives full grant aid. Between these levels partial grant aid for afforestation may be provided. Measures of alkalinity, hardness and pH methods are known to be extremely variable over time and are greatly influenced by stream flow rate and thus it became apparent that a more stable indicator of susceptibility to acidification was required. This project set out to test the applicability of SDI in providing this measure. It is also clear from this study that SDI is not altered by landuse of forest or non-forest.

Previous investigations into the use of Sodium Dominant (SDI) in Scotland outlined the calibration and relationships of the index to weathering rates, alkalinity and pH levels (Smart *et al.*, 1998; White *et al.*, 1998; White *et al.*, 1999). The potential of the index as a measure of acid sensitivity in upland freshwater streams in Ireland was tested by Kelly-Quinn and Ryan (2001) using a limited dataset. These authors noted strong relationships between SDI and alkalinity, and SDI and pH recorded during base flow and flood conditions. However, as these results were regionally based in Co. Wicklow on Ireland's east coast, and focussed on a low number of sites and limited geological types, they concluded that studies over a larger geographical and geological area would be beneficial.

SDI has shown great potential to deal with varying geologies underlying catchments and adverse temporal flows (i.e. spates or flooding) which occur following periods of rainfall and snowmelt (White *et al*. 1999) and compares well the Critical Load approach. While SDI appears not to be affected by marine aerosols in the present study, it was previously noted the critical loads (following simple mass balance equations) were significantly affected by sea salt deposition in areas with low weathering rates in western parts of the UK (Reynolds, 2000).

Sodium Dominance has been shown to accurately predict critical loads for streams on the Dee catchment in Scotland, for annual base flow data, single sample base flow data and single sample high flow data (Smart *et al*. 2000). The index also holds the advantage of being applicable to soil and freshwater acidification studies with no alterations in the approach or equation (White *et al*. 1998 and 1999), while separate critical loads equations are required for soil and freshwater studies (Aherne & Farrell, 2000).

Using data from Aherne and Farrell (2000), it was possible to calculate SDI for 155 lakes in an Irish study of critical loads. It was noted that SDI was significantly related to the Critical Loads results and that the relationships of SDI to other hydrochemical parameters identified by the authors mirror those gained for base flow sampling of river sites in the present study and that of SDI.

Curtis and Aherne (2003) examined surface water acidification in Irish lakes using critical loads and concluded that the lakes across Ireland were not under specific threat from anthropogenic acidification. However, they did highlight several areas of varying acid sensitivity. Aherne and Farrell (2000) noted that while atmospheric deposition was low in Ireland, there were periods of measurable concentrations. It was also suggested that the loads measured did have the potential to acidify poorly buffered surface waters (Aherne and Farrell, 2000), and to exacerbate acidification in forested areas (Farrell *et al.*, 2001).

The base flow relationships noted in this study indicated the strong potential of the index as an indicator of acid sensitivity in Ireland, as it less variable than pH or alkalinity. The results from over 200 sites across the country were in good agreement with those recorded for Co. Wicklow, Ireland, using fewer sites (Kelly-Quinn and Ryan, 2001). However, to test the validity of these results the index was tested for temporal variation in flood conditions. Of the over 200 site examined, a further 55 were examined at both high and base flows across a range of land use and SDI levels.

A strong relationship was found between Sodium Dominance Index and geology throughout the study. Not surprisingly the lowest SDI values were recorded on limestone, with values steadily increasing as one moves on to the more weather resistant rocks such as granite. However, within any geology type, no significant difference was found in the value of the SDI between the non-forested and forested sites, suggesting that the presence of forest on these sites, at least don't seem to reduce the sensitivity of the systems. However, few sites would have be deemed sensitive, based on their pH or alkalinity values. Therefore it might be difficult to detect such an effect acidification given the low number of potential sensitive sites.

Interestingly, however a linear relationship between pH and the SDI was found in this study, with sites of higher values associated with lower pH values and this pattern applied to both non-forested and forested sites. Low SDI sites (i.e. well buffered) were generally associated with high conductivities and *vice versa* with no clear separation of forested and non-forested sites in the overall pattern.

Not surprisingly, high alkalinity sites had low SDI values. However, here again there was no clear separation of forested and un-forested sites in the overall pattern. Accordingly, the SDI is giving similar outcomes, in terms, of designations and sensitivity. Land use does not seem to alter the values of SDI based on the data from this study, which suggests that SDI would be an effective acid sensitive designator of acidity, but not a detector of increased acidity. There was some scatter in the data at high conductivity sites, however once these were removed the relationship got stronger.

While there are limited data on the Acid Neutralizing Capacity for the study sites, it is clear from the in the analysis undertaken that that an .SDI Index value of 60% seems to be an indicative figure for sites at risk. In fact the data suggest that an SDI value of between 40 -60 identified sites which are at potential risk of acidification, while sites with values of greater than 60 are at risk of acidity. At this SDI value the ANC value approaching zero. This figure is significantly greater than the value of 40 for SDI previously reported on the limited dataset by Kelly-Quinn *et al.* (1999), but it appears to represent an important threshold in relation to ANC. In the same way, when SDI is plotted against alkalinity an SDI value of 60 seems to be the threshold for the identification of sensitive sites.

As with the extensive hydro-chemical data, there were high correlations between SDI and pH, alkalinity, hardness for the group of sites selected for examination at base flow and elevated flow. There was however, variation in all parameters between base flow and elevated flow, but the extent of variation was less for SDI. In fact the coefficient of variation for SDI was much less when compared to alkalinity and pH. Also, no relationship between the SDI and forest presence, distance from sea or distance form south west.

In general the SDI seemed stable when compared between high and low flow, however there was some evidence at some sites of significant percentage change in SDI in mixed geology catchments during extremely high flows. Of particular interest were those sites on mixed geology: as low flow is probably influenced by reach geology/soil, whereas the high flow is more influenced by watershed characteristics.

Of particular interest to this study is what appears to govern the stability of SDI at some sites or variability at others. It appears that where SDI remain stable the relative proportions of the cations do not vary greatly as in the well-buffered systems like River Martin, Co Cork. In contrast, SDI change at other sites was greater due mainly to variation in the concentration of calcium. Change in SDI between base and elevated flow, was found to be unrelated to change in pH, alkalinity, hardness, calcium or sodium. The absence of clear relationships may be in part due to the fact that the majority of sites exhibited only small changes in SDI. For those sites showing stability of the index it is probable that rainfall simply dilutes the base cations but maintains the relative proportions of each.

The hydrological events were opportunistically sampled, involving sites from both acid sensitive and moderately buffered areas. Changes in SDI and alkalinity were noted at a number of events monitored in the Rivers Annalecka and Glendassan in Wicklow and on the Rivers Douglas, Martin and Dripsey in Cork. The Annalecka and Glandassan Rivers drain granite and alkalinity fell close to zero or became substantially negative during flood events. The changes were typical of acid pulses (i.e. decrease in alkalinity of at least 50 μeq l^{-1} or 50%). Some of the events were on reasonably buffered systems (e.g. River Dripsey and Glencullen) and do not show the change in alkalinity that would characterise an acid pulse despite a substantial rise in water level.

In general the pattern of change in both alkalinity and SDI during the monitored events were fairly similar. As with the base and elevated flow data, the coefficient of variation was highest for alkalinity (3.44- 836.41%) and least for pH (0.74-18.87 %) and Sodium Dominance Index (2.21-20.5%). In fact a single high value of 20.5% was taken from the Annalecka (and represents a change from base flow SDI of 58.50 to the high flow value of 74.98. The coefficient of variation values for other sites were substantially lower.. Most events showed a SDI change of less than 20 units. However, during a number of events SDI changed by over twenty units, despite the low overall coefficient of variation. In fact the greatest change in both SDI and alkalinity occurred within the first few hours of an event. It should be noted that for many events the recovery to base flow conditions was not captured. In some sites, such as the Annalecka, recovery may take several days after cessation of rainfall (Kelly-Quinn *et al.*, 1997b).

Two of the events from the Annalecka show relative stability of the index despite the substantial change in alkalinity. Here the relative proportions of the major cations remained relatively stable despite a drop in their concentration. In contrast one of the events on the Glendassan River showed a larger increase in SDI at the commencement of the event. This was the most substantial flood monitored with most of the rainfall concentrated in the first few hours. The Cork sites, although somewhat more buffered, show fairly similar patterns, i.e. some events the SDI was relatively stable and in others where a change in the index occurred at the commencement of the event.

It appears that the highest variation in SDI is most likely to be at the beginning of the flood event. The data collected for the Cork sites included flow recording. A significant relationships between change in flow and change in the index was found in this study. In fact this was the only significant relationship detected. Change in SDI was not related to a change in any of the other parameters measured. It thus appears that where water with a lower ANC enters the river during an event the relative proportion of calcium mainly changes. Complete ion chemistry for some events has permitted some evaluation of the processes responsible for the changes observed. In the Aghalode, for example, the dilution value is close 100% suggesting that the base cations have simply diluted proportionally to alkalinity, this explains the small change in the index during this event (SDI range – 78.6-71.4). Dilution of this nature was also typical of the Glencullen River. All other events were probably influenced by a combination of dilution and acid titration. Drops in the alkalinity/∑BC suggest titration but as pointed out by Lepori, *et al*. (2003) some of the change may be due to cation desorption in upper soils. Both the Glendassan and Annalecka flood events provide evidence of titrations. In the Glendassan, this could be largely attributed to changes in organic anion. This is also the case for the Annalecka, but there were also inputs of sulphate at times during the event. So it appeared that water with low ANC, low calcium and increased acid anion enters these systems. The rate at which it enters appears to influence the stability of the SDI. It may be that rapid surface flow during heavy rainfall reduced contact with the deeper layers of soils for buffering and recharge with calcium ions. A corollary of this effect was noted in Swedish streams, where base cation concentrations increased during base flow conditions (Fölster & Wilander, 2002).

These results suggested that dilution of basic cations was driving changes in the sodium dominance index.

While SDI is calculated using cation concentrations originating from geochemical weathering, it can also be used to show sea salt effect with increasing sodium levels in coastal areas (White *et al*. 1998). Sea spray effects have been noted particularly during storm events on Ireland's west coast with the use of monitoring chloride concentrations (Allot *et al.*, 1990; Kelly-Quinn *et al.*, 1997b). However, while SDI can detect acid sensitivity in catchments induced by low base cation contributions or through sea spray effects, the index does not distinguish between the two parameters. Monitoring of chloride and examining ion ratios is necessary to identify such differences.

One difficulty in assigning levels of sodium dominance to catchments in Scotland lies in the salting of roads in winter months (Smart *et al*. 2003). However, those authors noted that the index was most effective in upland areas where little traffic persists on mountainous roads and little road salting occurs during the year. Little or no salting takes place on upland roads in Ireland, in fact sand is more commonly sued in gritting roads during winter.

6.1 Fauna and Sodium Dominance Index

The total of 237 taxa were recorded in the study representing a total of 75 families, inclusive of both seasons is broadly typical of upland streams in Ireland and suggest that the quality for the sites were good. Of the nineteen ephemeropteran species noted in this study, *Baetis rhodani* (Pictet.) (Baetidae) was the most abundant and widespread species, being present in all but one site (Site 208 Lugduff Stream, Co. Wicklow). However, no other ephemeropteran was noted in this acid-impacted stream. Here again no other mayfly species were present at the site. Both these sites have high percentage coverage of coniferous plantation forest in the catchment. Individuals of Siphlonurus lacustris Eaton (Siphlonuridae) and Ameletus inopinatus Eaton (Siphlonuridae) were noted at five sites. Four of these sites were in Co. Wicklow (Site 187, Glendassan Stream, Site 191, Knockalt Stream, Site 211, Glencullen Stream and Site 212, Glenealo Stream, and the final site was located in Donegal (Site 142, Cornvannoge Stream). These data confirm earlier work by Kelly-Quinn et al. (1998), that some of these sites are acidic.

The Ephemeroptera represented an increasing proportion of the community as the SDI varied from >80 to those in the 30-40 SDI band. Below this, ephemeropteran representation was slightly reduced because of the increasing diversity of some groups, especially the Coleoptera. In contrast, Plecoptera demonstrated a trend of increasing abundance with increasing acid sensitivity (particularly at highly forested sites). A TWINSPAN analysis for the spring faunal dataset yielded seven validated groups: those with mean SDI of 21.6 (SDI range 7.6 to 59.7) representing the mostly acid tolerant sites, and a second group with a higher mean SDI values ranging from 50.1 to 74.9, largely acid sensitive conditions. Although these bands overlap in the 50-60 SDI, there is a suggestion that this might represent some threshold SDI value of biological significance. Interestingly an analysis of autumn faunal data for the non-forested sites yielded relatively similar results, suggesting that this pattern may be applicable year around. However, as shown below this was not the case for taxon richness and for ephemeropteran richness. This suggests that it may not be possible to designate acid sensitive sites year around but only in spring, as employed using current methods, if exclusively biological methods are used for assessment.

A general trend of decreasing taxon richness with increasing SDI with found throughout the data set in the spring, but not for autumn data, suggesting some sort of graded response of stream macroinvertebrates to SDI. However, while this general pattern appeared there was some variation across season and land use. For example, the correlation with ephemeropteran richness and SDI was only significant for the spring period (non-forested site data). The autumn sampling indicated the best relationship with plecopteran taxon richness. From the spring data, total taxon richness showed no significant differences between non-forested and forested sites along an SDI gradient. No significant difference in ephemeropteran richness was noted between SDI bands for non-forested sites but a difference was significant for the forested site. In terms of plecopteran richness no significant differences were noted between non-forested and forested sites. A significant difference was detected between SDI bands for trichopteran taxon richness again at non-forested site. Significant differences were also noted in total abundance of macroinvertebrates and Ephemeroptera along the SDI gradient for both the non-forested and forested sites. In spring a significant difference was noted for total taxon richness between non-forested and forested sites in the 20-29 SDI band. Using spring abundance data, total abundance differed between non-forested and forested sites at the 60-69 SDI band This suggest that there maybe significant influence of life-history traits on the data presented here and further work involving replication of season is required to fully elucidate the patterns emerging.

While the relationship between EPT and SDI was significant for all sites and non-forested sites considered separately, it did not hold for forested sites in spring. For the autumn data the relationship was significant for all sites combined. The relationship between SDI and crustacaean/dipteran, (C/D) a new index, was significant for all sites combined and the non-forested sites in both seasons. Pair-wise comparison of the C/D values between classes suggested that C/D in SDI bands greater than >40 were significantly different from the values in the lower SDI bands. The most likely explanation here is that the C/D ratio represents the sum of the biological significant cations present for exoskeleton formation and are thus indicative of soft acid sensitive waters.

7 Conclusions

In conclusion, based on the present large-scale study, the SDI clearly offers a valuable and effective alternative indicator of stream sensitivity to acidification and hence for the assessment of possible sites for afforestation. The variation in SDI across a range of geologies and land use and in relation to changes in stream flow was significantly lower than found with other indicators of sensitivity at the catchment scale. The index is more stable than alkalinity, in the majority of hydrological events. However, at the beginning of extreme events, the SDI can show some change and this is the only stage in the hydrological event that should be avoided. SDI will diagnose the acid susceptibility of a catchment or sub-catchment at base flow, whereas the current approach using alkalinity readings (Anon 1995) can sometimes indicate moderate sensitivity (8-12 mg $CaCO_3$ l^{-1}) at base flow. Therefore, when used alone, alkalinity readings could allow grant aid and increased forestry plantations on catchments, which could be deemed acid sensitive by SDI. There was however, some variation in the SDI at the individual site scale. However this variation seems to decline after about 5-6 hours of elevated flow, when it again shows less variation than pH or alkalinity. It appears that a thresh hold level of SDI of 50-60 is indicative of sensitivity to acidification as measured by ANC and alkalinity.

Some evidence of a response in biology across the SDI bands was detected. TWINSPAN distinguished between those sites with mean SDI values > 60 and those < 20, between these two extremes, the site grouping were characterised by a mix of SDI values. However there were no consistent differences between the fauna from forested and non-afforested sites. Further work is required to validate these data within each catchment in the context of risk assessment under the Water Framework Directive.The links with the fauna will require further analysis and more detailed consideration. In particular the contribution of river typology (RIVTYPE after Kelly-Quinn *et al.*, 2004) may well help to elucidate more fully the relationship between SDI and fauna and this may lead to both the identification of indicator species, ideally with a graded response to the SDI index. Given the errors associated with the measurement of pH, compared to base cations, SDI is perhaps a more reliable measure of acid sensitivity.

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