Effects of broadleaf woodland cover on streamwater chemistry and risk assessments of streamwater acidification in acid-sensitive catchments in the UK

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Submitted for the degree of Doctor of Philosophy

School of GeoSciences

The University of Edinburgh

May 2007

Declaration

I certify that the work described in this thesis is my own, except where otherwise stated, and that has not been previously submitted for a degree at this, or any other university.

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Abstract

Acidification of surface waters has been recognised as the major water quality problem in the UK uplands. The adverse effects of conifer afforestation on streamwater chemistry and ecology are well documented in acid-sensitive catchments and have mainly been attributed to the enhanced deposition of atmospheric pollutants onto conifer canopies (the “scavenging effect”). Currently, international and national policies promote the expansion of native broadleaf woodland in the UK. Pollutant deposition onto broadleaf canopies is considered less than onto the more aerodynamically rough conifers, but there is concern that large-scale broadleaf planting could delay the recovery of acidified waters or lead to further acidification in most sensitive areas. However, there has been limited investigation of the influence of broadleaf woodland cover on streamwater chemistry in the UK.

To investigate the effect of woodland cover 14 catchments with different (0-78%) percentages of broadleaf woodland cover were identified in representative acid-sensitive areas in north-western and central Scotland (Glen Arnisdale and Loch Katrine area) and northern and south-western England (Ullswater area and Devon) using spatial datasets in a GIS. Streamwater was sampled at high flow from the catchment outlets in winter and spring 2005 and 2006 and was analysed for major cations, anions and trace metals using standard methods. The number of samples ranged from two in the Glen Arnisdale catchments to 10 in the Loch Katrine area catchments which were sampled more intensively.

Significant positive correlations were found between percentage broadleaf woodland cover and streamwater NO_3 ($r_s = 0.51$) and soluble Al ($r_s = 0.64$) concentrations. The greater NO_3 leaching to streamwater in the three most forested catchments ($\geq 50\%$) was probably due to enhanced N deposition onto woodland canopies and nitrification by alder in the Ullswater area forested catchments. Streamwater NO_3 concentrations equalled or exceeded non-marine SO_4 in the above catchments indicating that NO_3 was the principal excess acidifying ion in catchments with greater woodland cover.

The woodland effect on streamwater chemistry in the study catchments was masked to some extent by variability in acid deposition climate and soil type composition. Seasalt inputs were found to be a more important control than woodland cover for streamwater chemistry in the maritime Glen Arnisdale catchments.

A risk assessment of acid-sensitivity in the study catchments was conducted by calculating streamwater critical load exceedances using the Steady-State Water Chemistry (SSWC) and First-order Acidity Balance (FAB) models and modelled pollutant deposition for 1995-97 and 2002. Critical loads were exceeded by 0.01 to 1.74 keq H ha^{-1} yr^{-1} in two catchments which had woodland covers $\geq$ 50% and in the Devon control catchment. The remaining 11 study catchments were assessed to be not at risk of acidification, probably due to significantly reduced non-marine S deposition from 1986 to 2001, but seasalt inputs to the Glen Arnisdale catchments might cause acidic streamwater episodes. Acid-sensitivity was also assessed using macroinvertebrates sampled in 11 of the study catchments and the results generally agreed with the critical load assessments. More detailed estimates of the enhancement of dry S and N deposition onto birchwoods in the Loch Katrine area catchments using calculated roughness length within FRAME showed that it posed no risk for streamwater acidification in these catchments because of the high rainfall environment. However, in acid-sensitive areas of the UK with lower rainfall and closer to major pollution sources, enhanced pollutant scavenging by broadleaf woodland canopies could pose a greater risk of acidification to freshwaters.

The finding that almost all study catchments with woodland covers less than 30% are well protected from acidification suggests that this is a sensible threshold value for use in risk assessments of the effects of broadleaf woodland planting conducted within the Forests and Water Guidelines. The results of a sensitivity analysis of the Guidelines' methodology, conducted using parameters such as numbers and timing of streamwater sampling, different runoff estimates and critical acid neutralising capacity values, showed that the Guidelines should be able to protect sensitive freshwaters from acidification in areas where broadleaf woodland is expanding.

Acknowledgements

Firstly, I would like to thank my supervisors in the University of Edinburgh, Dr. Kate Heal and Dr. Neil Stuart, for their guidance and input during the course of the PhD. Special thanks to Kate for her assistance with fieldwork, especially for driving me around while recovering from my bike accident. I would also like to thank Dr. Tom Nisbet of Forest Research for his contribution and guidance during this project.

I would also like to thank Andy Gray, John Morman, Dr. Peter Anderson, Dr. Lorna Eades and Dr. Joanna Cloy of the University of Edinburgh for their invaluable help with sample analysis, and Dr. Massimo Vieno for his assistance with modelling pollutant deposition. Special thanks to Andy for access to his huge jazz collection.

I am grateful to the Greek State Scholarships Foundation (IKY) for funding this project. I would also like to thank the following for additional funding and assistance with the research: The University of Edinburgh Development Trust, Forestry Commission; the Eden Rivers Trust; the Environmental Change Research Centre, University College London; Dr. Allan Lilly (The Macaulay Institute, Aberdeen); Dr. Barry Gardiner (Forest Research, Edinburgh); Dr. Ron Smith (Centre of Ecology and Hydrology, Edinburgh); Russell Lamont (Forest Enterprise, Aberfoyle); the catchment landowners.

Special thanks to Daniel, George and Julia for their help during fieldwork and the numerous and never-ending discussions over coffee and drinks.

I would especially like to thank my family in Greece for their guidance and encouragement, without which completing this PhD would have been impossible. Special thanks to Evangelia - without your support I couldn’t have done it.

This thesis is dedicated to my father, Leonidas, and mother, Olga, whom I know would be very proud to see me complete a PhD.

“Να φοβάσθε τον άνθρωπο του ενός βιβλίου...”

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Chapter 1 Introduction

Freshwaters in the UK uplands have suffered from acidification, due to a combination of high acid deposition and the occurrence of soils with low soil buffering capacity, with adverse impacts on the aquatic ecology and biology. Extensive conifer afforestation in the UK uplands has been associated in the past with increased acidity in water and depletion of salmonid populations, due to the ability of the aerodynamically rough conifer canopies to enhance the deposition of acidic pollutants. Currently, national policies promote the expansion of native, mainly broadleaf woodlands aiming to enhance the biodiversity and ecological quality of forest ecosystems in the UK. However, effects of the broadleaf woodland expansion on streamwater chemistry and particularly on streamwater acidification are largely unknown.

The purpose of this research was to investigate effects of broadleaf woodland cover on chemical indicators of streamwater acidification and assess acid-sensitivity in catchments with different proportions of broadleaf woodland cover in acid-sensitive areas in the UK. This chapter presents the rationale behind the research and outlines the thesis structure. After describing the background of the effects of surface water acidification and the role of conifer afforestation in the acidification of surface waters in the UK uplands, consideration is given to the risks of acidification posed by the expansion of broadleaf woodlands. Then, the main research aims are presented and the chapter concludes by briefly outlining the thesis structure and content of subsequent chapters.

1.1 Surface water acidification

Increases in surface water acidity have been observed since the late 1960s in large areas of Scandinavia, north, west and central Europe, the eastern USA and Canada. The acidification in lakes and streams in these regions was attributed to the increases in anthropogenic emissions of sulphur (S) and subsequent wet and dry S deposition to ecosystems caused by an exponential increase in coal and oil burning and long range transport of pollution occurring in the Northern Hemisphere after the Second World War and until about 1980 (Driscoll et al., 2001). The acidification of freshwaters depends on the interaction between direct acid deposition and soil chemical processes and the areas worst affected were all characterised by base-poor silicaceous geological formations, with soils of low base saturation and subsequently low ability to neutralise acidic inputs (Soulsby, 1997).

1.1.1 Evidence of surface water acidification

The clearest evidence for the acidification of surface waters was provided by detailed palaeoenvironmental reconstructions which showed that surface water acidification generally began in the latter half of the 19th century following marked increases in fossil fuel burning after the industrial revolution (Battarbee and Charles, 1986). Analysis of diatom assemblages indicated that decreases in lake water pH in the UK and Norway began between 1850 to 1930, post 1945 decreases in pH were found in lakes in Sweden, Finland, Denmark, the Netherlands, Belgium and some parts of western Germany, while pH decreases in lakes in eastern USA and Canada occurred between 1930 to 1970 (Battarbee and Charles, 1986). Assessments of diatom assemblages in lake sediment cores in UK lakes showed that sites in upland regions of England, Scotland and Wales with low pH (<5.5), high sensitivity to acidification (calcium concentration <50 μeq l^{-1}) and moderate or high acid deposition (> 0.5 g S m yr^{-1}) had undergone major changes in diatom flora since about 1850 (Battarbee et al., 1988). Reconstructions at the acidified sites indicated that most had a pH of about 6.0 prior to 1850 and the pH decline ranged from 0.5 to 1.5 units since 1850. In contrast, little change had occurred in diatom flora at non-sensitive sites in areas of high deposition or at very sensitive sites in areas of low deposition.

1.1.2 Impacts of surface water acidification

Freshwater acidification has resulted in adverse impacts on aquatic ecology and biology with the first manifestation being the depletion of salmonid fish stocks in acidified lakes and rivers. Driscoll et al. (2001) report that in a survey of 1469 lakes in the Adirondack region, eastern USA, at least one fish species was caught in 1123 lakes (76%), while no fish were caught in 346 lakes (24%). The 346 fishless lakes had significantly (*P*<0.05) lower pH, Ca concentrations and acid neutralising capacity (ANC) values, as well as higher concentrations of the toxic inorganic monomeric aluminium (Al) compared to lakes with fish. In the same survey, of the 53 fish species recorded, almost half (26) were absent in lakes with pH<6.0, including important recreational fish such as Atlantic salmon and tiger perch, indicating that increases in surface water acidity were related to reductions in species diversity (Driscoll et al., 2001). A survey of 1000 lakes in Norway also found that fish losses correlated well with low pH values and Ca concentrations and high labile Al concentrations in lake water (Rosseland and Henriksen, 1990). In Wales, significant reductions in trout populations were observed in 102 acidic streams between 1984 and 1995 (Stevens et al., 1997). Apart from fish reductions, surface water acidification has also resulted in reported losses or reductions in species diversity of algae, macroinvertebrates and amphibians in North America (Mielre et al., 1986), reductions in macroinvertebrate diversity in Wales (Stevens et al., 1997) and complete loss of freshwater snails in Norway (Økland, 1992). Jenkins and Ferrier (2000) also report studies from the UK linking surface water acidification with the loss of acid-sensitive macrophytes and declines in the distribution of the natterjack toad. Main processes of impacts of acidified waters on biota include the dissolution of snail shells (Ribi et al., 1986), freshwater fish embryonic mortality and inhibition of hatching (Keinänen et al., 2004) and respiration dysfunctions at gill surfaces and ion regulatory disturbances in fish related to Al toxicity (Alstad et al., 2005).

Acidification of surface waters has been recognised as the main water quality problem in the UK uplands and was attributed mainly to increased deposition of atmospheric pollutants resulting in detrimental effects for the aquatic ecology and biology (Langan and Soulsby, 2001). In Wales, over 12 000 out of 24 000 km of river length are estimated to have been impacted by acidification, while acidification in Scotland has been identified as the main cause of pollution in 17% (504 km) of polluted streams, with around 400 km of the acidified rivers being in the west region of Scotland (Jenkins and Ferrier, 2000). Although the economic impact of acidification is difficult to estimate, the actual capital loss in net economic value of fisheries in Wales alone in 1990 was probably £1-5M and the potential loss was £5-25M (Jenkins and Ferrier, 2000). Despite the imprecision of these estimates, they provide an indication of the economic costs to local communities caused by atmospheric deposition.

1.1.3 Effects of conifer afforestation on surface water acidification

Land-use, especially forest, may exacerbate acidification in sensitive surface waters. Deposition of atmospheric sulphur and nitrogen (N) is strongly influenced by the height and structure of the land's vegetation cover. In areas of high acid deposition, dry and occult (cloud water) deposition can be enhanced by forests (termed the scavenging effect), due to the greater turbulence caused by the stand structure (Fowler et al., 1989), and subsequently contribute to surface water acidification. The scavenging effect increases with the height and therefore the age of the forests and with altitude (Nisbet et al., 1995). Areas most affected by acidification have soils with small base cation pools which are rapidly depleted in response to acidic deposition, resulting in the acidification of soils and freshwaters. Forests on those areas could increase the sensitivity of freshwaters to acidification.

Conifer cover in the UK uplands, in the form of commercial conifer plantations, increased greatly since the 1930s and is usually found on land sensitive to acidification, at high altitude and thin, base-poor soils. Following a Forestry Commission and Department of Environment (DoE) workshop in 1990, it was suggested that forestry had a minimal impact on acidification in areas of low acid deposition (Nisbet et al., 1995). However, in areas of high acidic deposition forest can significantly contribute to acidification due to the enhanced capture of atmospheric pollutants by conifer canopies. Conifers are considered to acidify soils and drainage water more than deciduous trees (Neal, 2002; Nisbet et al., 1995), mainly because conifers are more efficient at scavenging atmospheric pollutants and at the same time their roots have less cation exchange capacity than broadleaves resulting in lower soil buffering capacity.

1.1.3.1 Studies of the effect of conifers on surface water acidification

There has been detailed investigation of the effect of conifer afforestation on surface water chemistry in the UK uplands. A study of streams and lochs in Galloway, south-west Scotland, found that water acidity and sulphate (SO_4) concentrations were significantly higher in catchments with conifer forest cover and this was attributed to the enhanced pollutant deposition onto the conifer canopies (Harriman et al., 1987), but catchment variability in geology, soils, topography and deposition levels prevented attributing the changes in streamwater chemistry solely to a forest effect. Ormerod et al. (1989) attempted to eliminate these confounding influences in the context of the 1984 Acid Waters Survey by analysing a large water chemistry dataset from 113 streams in upland Wales, separated into three acid-sensitivity classes by water hardness. The analysis found that pH declined and Al increased significantly in streamwater with increasing percentage conifer forest cover across all classes but, due to a large scatter in the dataset, only 11% of the variation in pH and 30% of that for Al was accounted for by forest cover. Thus, the fitted regressions between percentage forest cover and streamwater pH and Al were considered unreliable for predicting the extent and magnitude of a forest acidification effect. Significant positive relationships were also found between percentage forest cover and the predominantly atmospherically-derived solutes sodium (Na), chloride (Cl) and marine and non-marine SO_4. In the subsequent 1995 Acid Waters Survey of Wales, percentage conifer cover was significantly negatively correlated with streamwater pH and significantly positively correlated with streamwater Na, Cl, marine and non-marine SO_4 and Al concentrations in 91 streams grouped according to water hardness (Stevens et al., 1997). Relationships between forest cover and streamwater Al were stronger in the lower hardness group and for winter samples and Al concentrations tended to increase only when conifer cover exceeded 30 to 40%. Highly significant positive relationships between area-weighted mean forest age and streamwater Na, Cl, marine and non-marine SO_4 concentrations were only found in the >30 years age cover category, indicating that enhanced capture of seasalts and atmospheric pollutants may not be significant until time after canopy closure at 15-20 years of age (Stevens et al., 1997). Streamwater nitrate (NO_3) concentrations increased significantly with plantation age in both the 1984 (Reynolds et al., 1994) and 1995 Acid Waters Surveys (Stevens et al., 1997).

Nisbet et al. (1995) investigated the impact of afforestation on streamwater chemistry in a forested tributary in the Loch Dee catchment, south-west Scotland, using precipitation and streamwater chemistry data corresponding to a period of forest growth from an age of 6 to 17 years at which a substantial part of the forest reached canopy closure. The impact of the forest on streamwater chemistry was investigated by evaluating and comparing trends in streamwater chemistry to those in an adjacent moorland catchment. The study did not identify a clear forest acidification effect mainly because the increased scavenging of dry and occult deposition by the growing forest was estimated to be small at that site (<10%). The small forest scavenging effect was attributed to the relatively low altitude of the site (<450 m) which resulted in small contributions of occult deposition, combined with low concentrations of sulphur dioxide (SO_2). However, the authors suggested that these results did not provide evidence that afforestation will not have an effect on streamwater chemistry elsewhere because the scavenging effect is considered highly catchment-specific, depending on the interaction between pollutant climate and loadings, the location and extent of forest cover and catchment buffering capacity (Nisbet et al., 1995). Overall, the results of the above studies suggest that the effect of conifers on streamwater chemistry in acid-sensitive areas is well-established, but there are few studies on broadleaf woodland effects.

1.2 Broadleaf woodland expansion and implications for surface water acidification

1.2.1 Changing pollutant emission and forestry policy in the UK

Reducing emissions of acid pollutants has been recognised as the principal way of solving the problem of acidification. In the UK, S emissions and deposition have declined since the late 1960s and N emissions since the late 1980s (NEGTAP, 2001). The European Union has agreed to further S and N pollutant reductions by 2010 to facilitate the recovery of acidified terrestrial and aquatic ecosystems (Jenkins and

Cullen, 2001). Conifer afforestation has also declined in the UK since the late 1980s but planting of broadleaves has gradually increased since the late 1970s as the result of policies and initiatives to restore native broadleaf woodlands and improve the conservation status and habitat value of forested ecosystems (Rollinson, 2000). Despite the decline in emissions of acid pollutants there is concern that increasing forest cover from the expansion of broadleaf woodlands could delay the recovery of acidified surface waters, or even lead to further acidification, in the most sensitive areas. Reductions in S emissions have not led to clear improvements in the acid status of surface waters in afforested catchments in south-west Scotland, suggesting that forestry could confound chemical recovery from acidification in this region (Helliwell et al., 2001). Pollutant deposition is expected to be less on broadleaf woodland than on the more aerodynamically rough conifer canopies (Neal, 2002), but the impact of large-scale broadleaf planting schemes may still exert a significant impact on the most acid-sensitive freshwaters (Alexander and Cresser, 1995). For example, targets for new woodland planting published in 1996 aim to double woodland cover in England and increase it in Wales by 50% over the next 50 years, most of which will be achieved by new broadleaf planting (Farmer and Nisbet, 2004). The Forestry Commission has also recently announced plans to restore around 8500 ha of natural habitats around Loch Katrine, in the Loch Lomond and the Trossachs National Park in north-central Scotland, over the next 10 to 20 years. The scheme includes at least 2000 ha of native woodland habitat and aims to create Scotland's biggest native woodland comprising mostly broadleaved trees rather than conifers (Forestry Commission, 2005).

1.2.2 Studies of the effects of broadleaves on streamwater chemistry

Despite the change in planting preferences from conifers to native broadleaves in the UK, past research has exclusively focused on the acidification of surface waters by conifer afforestation and there is a lack of knowledge and understanding of the potential impacts that native broadleaf woodland restoration may have on river water quality. One of the few studies of broadleaf trees examined precipitation, throughfall and streamwater chemistry in a lowland ash forested catchment in south-central England (Neal, 2002). Despite the low altitude, local SO_4 and NO_3 inputs to the site from deposition were high due to the proximity to pollutant sources (light industry and brick and cement works). NO_3 was effectively taken up by vegetation, but SO_4 was enriched in throughfall probably due to gaseous S deposition onto the forest and subsequent washoff. However, the underlying soils were rich in base cations and consequently streamwater had a moderately high alkalinity (~490 μeq l^{-1}) and pH (~7.9). Therefore, any incoming acidity was buffered by soil preventing soil and water acidification (Neal, 2002). The soil buffering capacity was also augmented by the ability of ash to effectively cycle divalent cations through root mycorrhizal fungi. The study concluded that lowland broadleaf woodland plantations on base-rich soils would not cause streamwater acidification, despite possible enhanced deposition on woodland canopies. Furthermore, selection of broadleaf tree species, such as ash, may well enhance acid neutralisation and improve surface water quality. However, these results also highlight the uncertainty in any predictions of the effects of new broadleaf woodland planting in acid-sensitive areas at higher altitudes, where soils are thinner and base cation-poor and waters have low alkalinity and ANC values.

1.2.3 The role of broadleaf woodland expansion in current UK and EU policies

Investigating the effects of new broadleaf woodland planting on surface water chemistry is also relevant due to present land management in the uplands in which extensive areas are being converted to continuous cover forestry (CCF) (Reynolds, 2004). CCF aims to maintain a continuous, uninterrupted forest cover which would consist of a range of tree species of different age, thus moving from current homogeneous, even-aged to mixed age stands. The overall effect of CCF on long-term water acidification will depend on the balance between base cation removal in forest products, possible enhanced deposition of atmospheric pollutants due to the rough forest canopy, the choice of tree species and the overall effect on nitrogen cycling (Reynolds, 2004). Thus, research on the effects of different broadleaf trees on water chemistry is necessary for predicting the impact of CCF in the UK uplands. Effects of new woodland planting on diffuse pollution, such as acidification, also need to be quantified in the context of current European legislation. The European Water Framework Directive (2000/60/EC) requires Member States to achieve good ecological and chemical quality in surface and ground waters by 2015 (Farmer and

Nisbet, 2004). Research on the impacts of broadleaf woodland planting on streamwater chemistry is therefore necessary for the successful delivery of the objectives of the Directive.

1.2.4 Assessing the risk of surface water acidification from new broadleaf woodland planting

The recognition that forests and their management can affect the quality of surface waters led to the publication of the Forests & Water Guidelines by the Forestry Commission in order to provide guidance on how forests should be designed and forestry operations conducted to protect and enhance the water environment (Forestry Commission, 1991). The latest (4th) edition of the Forests & Water Guidelines (Forestry Commission, 2003) takes into account the scavenging of atmospheric pollutants by forest canopies when considering new planting and restocking plans. Until the most recent edition of the Forests & Water Guidelines only the effects of conifer afforestation on surface water acidification were considered, because broadleaved woodland is generally believed to pose less of an acidification threat due to the smaller scavenging effect (Nisbet, 2001). However, because national forestry strategies now strongly promote the expansion of native woodlands, the impact of larger broadleaf woodland planting schemes was also included in the most recent edition. The Guidelines use the critical loads approach (Henriksen et al., 1986) for identifying areas at risk of acidification and suggest that for catchment areas inside a critical load exceedance square or contiguous square, a catchment-based critical loads assessment is carried out when more than 10% of the catchment area is to be planted with conifers or more than 30% with broadleaves. The threshold value for conifer afforestation is based on the results of extensive research on the relationship between conifer plantations and the acidification of surface waters. However the 30% threshold value is a best estimate adopted by the Guidelines since there has been limited research on the effects of broadleaves on surface water acidification.

1.3 Research aims

This research aims to fill the research gap concerning the effects of broadleaf woodland cover on streamwater chemistry in view of changing forest planting policies and increasing broadleaf woodland planting in acid-sensitive areas of the UK. The specific research objectives are to:

1) Investigate associations between the proportion of broadleaf woodland cover within acid-sensitive catchments with streamwater chemistry indicators of acidification, focusing on atmospherically-derived species;

2) Assess the risk of acidification in catchments with different proportions of broadleaf woodland cover using the critical loads approach and modelled deposition data as used in the context of the Forests and Water Guidelines;

3) Evaluate the effectiveness of the Forests and Water Guidelines methodology for identifying catchments at risk of acidification where broadleaf woodland is expanding.

The catchments selected for the study were located in representative acid-sensitive areas in the UK and were covered by the main tree species currently used in new broadleaf woodland planting. Therefore the study results should be representative of UK conditions and of particular relevance to the majority of acid-sensitive areas in the UK uplands. The research results will assist in the prediction of different broadleaf woodland planting schemes and forestry management plans on streamwater chemistry in acid-sensitive areas. In addition, the research results will inform the Forests and Water Guidelines methodology used for the protection of acid-sensitive waters from the expansion of broadleaf woodlands.

1.4 Thesis structure

Chapter 2 expands on the general introduction to acidification presented in this chapter by describing the main processes causing surface water acidification, including those related to forest cover. The pollution climate in the UK is described along with the mechanisms of acid deposition and the interactions of acidic inputs with soil chemical properties leading to the acidification of water. The planned expansion of broadleaf woodlands in the UK is also discussed to demonstrate the importance of this research to land-use policy in the UK. The chapter concludes with brief descriptions of the Forests and Water Guidelines methodology and the critical loads concept used by the Guidelines.

Chapter 3 presents the methodology used to identify the study catchments, and also describes the topography, land-use, geology and soil types of the study catchments. The streamwater sampling and chemical analysis programme is briefly described, along with flow monitoring in a selected catchment, the statistical methods used to analyse the streamwater chemistry data, details of a macroinvertebrate survey conducted in 11 of the study catchments and the description of the two critical load models used to assess acid-sensitivity in the study catchments.

The streamwater chemistry and macroinvertebrate survey results and statistical analyses are presented and discussed in Chapter 4. Chapter 5 provides the results of the critical loads calculations and an assessment of the sensitivity of these calculations to different parameter inputs inherent in the critical load model formulations. The results are discussed in the context of the changing pollution climate and acidic deposition in the UK and the influence of broadleaf woodland cover on catchment acid-sensitivity is highlighted.

A case study was undertaken to investigate the extent and impact of pollutant scavenging by forest canopies. Chapter 6 describes this case study in which dry pollutant deposition onto birch canopies was modelled in a sub-group of the study catchments, and discusses the effects of the modelled pollutant estimates on acid-sensitivity in these catchments.

The effectiveness of the Forests and Water Guidelines methodology for identifying catchments at risk of acidification from broadleaf woodland expansion is discussed in Chapter 7. The effect of different parameters on critical loads calculations was assessed, including numbers and timing of sampling and measured catchment runoff.

Conclusions drawn from the research are outlined in Chapter 8, in particular the streamwater chemistry parameters which are more likely to be influenced by the broadleaf woodland expansion and the extent to which this expansion could lead to further acidification or delay chemical and biological recovery in the most acid-sensitive areas. The possible implications of the changing deposition climate and climate change in general are also outlined, and finally specific areas of further research are suggested.

Chapter 2 Processes and policies influencing the effect of broadleaf woodland cover on streamwater acidification

This chapter describes the processes causing surface water acidification in the UK, including the sources of atmospheric pollutants, the deposition mechanisms of different pollutants and the way acidic inputs interact with soils to cause soil and water acidification. Information on present forest cover in the UK is given along with the driving policies promoting the expansion of broadleaf woodlands and the practices used to plan this expansion. The processes by which woodlands could influence surface water chemistry and acidification are then described and the chapter concludes by briefly describing the methodology used by the Forests and Water Guidelines for identifying areas at risk of acidification where broadleaf woodland is expanding.

2.1 Processes influencing surface water acidification

A summary of the mechanisms of acid deposition and the interactions with the soil complex that lead to surface water acidification is shown in Figure 2.1.

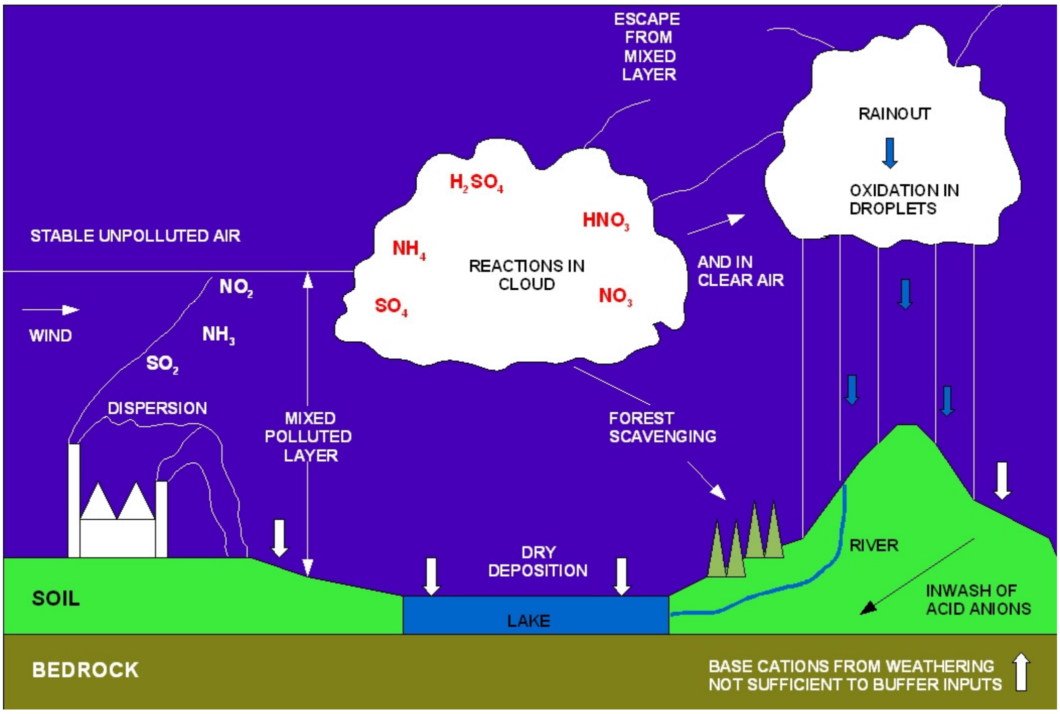

Figure 2.1 Diagrammatic representation of the mechanisms of acid deposition and surface water acidification (Modified from: http://www.freshwaters.org.uk)

2.1.1 Deposition of acidic atmospheric pollutants

Surface water acidification is caused by the atmospheric inputs of acidity from deposition. Acid deposition is the transfer of strong acids and acid-forming substances from the atmosphere to the surface of Earth. The composition of acid deposition includes ions, gases and particles derived from the following: sulphur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3) and particulate emissions of acidifying and neutralising compounds (Driscoll et al., 2001). S and N oxides can be transported long distances in the atmosphere and can be oxidised by reaction with free hydroxyl (OH) radicals, formed from the reaction of ozone with sunlight, to form sulphate (SO_4) and nitrate (NO_3).

2.1.2 Sources of acidic atmospheric pollutants in the UK

Emissions of acidifying atmospheric pollutants in the UK are compiled from a combination of reported and estimated emissions from major pollution sources derived from the National Atmospheric Emissions Inventory (NAEI) (King et al., 2006). The primary emissions of S are mainly in the form of SO_2, with only a small proportion already oxidised to SO_4. In the UK, SO_2 in the atmosphere comes from direct emissions mainly from fossil fuel combustion, while "natural" S contribution from sea-spray is significant in areas subject to maritime influence (RGAR, 1997). Coal-fired power stations contribute around 70% of UK SO_2 emissions. Annual UK emissions of SO_2 peaked in 1970 at 3259 kTonnes S and declined to 563 kTonnes S in 2001 (Fowler et al., 2005).

The major sources of oxides of N are motor vehicles, which account for about 50% of UK emissions. Fuel combustion in power plants, industry and the domestic sector contributes most of the remaining 50%, although a small proportion is also emitted from the soil as nitric (NO) and nitrous oxide (N_2O). Annual emissions of N oxides in the UK peaked in the 1980s at around 850 kTonnes N and have declined to 511 kTonnes N in 2001 (Fowler et al., 2005). Emissions of NH_3 arise primarily from agriculture and more intensive animal and poultry management practices have led to increases in emissions in recent years (Jenkins and Ferrier, 2000). NH_3 emissions from farm buildings and slurry applications are large point sources which are very variable with time. NH_3 emission estimates in the UK are the least certain of the pollutants causing acidification but they reached approximately 300 kTonnes N annually in the late 1980s and have fallen slightly to 261 kTonnes N in 2001 (Fowler et al., 2005).

Emissions of hydrogen chloride (HCl), which is predominantly derived from coal combustion, have been high in the past in the UK and have contributed greatly to soil and freshwater acidification. However, HCl emissions have declined in line with the total mass of coal burnt, and are largest in central England, where most major coal-fired power stations are located (RGAR, 1997). The contribution of HCl emissions and deposition to acidification is considered to be very small in the northern and western areas of the UK where not many major sources of HCl exist, and in these areas seasalts are the dominant source of Cl in water.

The annual atmospheric budget for non-marine S and oxidised N for the UK indicates that only about 25% of the emissions are deposited in the UK with the remaining 75% being transported and deposited outside the UK, indicating that the UK is a major net exporter of acidic pollutants (Jenkins and Ferrier, 2000). In contrast, about 66% of UK NH_3 emissions are deposited within the UK. The relative amount of pollutant import, mainly transported from North America across the Atlantic, compared to the sum of national pollutant emissions and import is around 17%, 20% and 12% for reduced and oxidised N and S, respectively (NEGTAP, 2001).

2.1.3 Pollutant deposition mechanisms

Pollutant compounds can be deposited on the ground surface in rainwater and snow (wet deposition), cloud water (occult deposition) and directly onto plant and other surfaces (dry deposition). Acid deposition in the UK mainly consists of wet deposition of the ions SO_4, NO_3 and ammonium (NH_4) and dry deposition of the gases SO_2, NO_2, nitric acid (HNO_3) and NH_3 and deposition of aerosols containing SO_4, NO_3 and NH_4. Deposition of seasalts containing SO_4 can also contribute to surface water acidification in areas subject to high marine inputs.

2.1.3.1 Wet deposition

Wet deposition is simply the process whereby pollutants are removed from the atmosphere by precipitation. The process contributing the majority of pollutants in rain and snow is nucleation scavenging, in which aerosols containing the pollutant act as the condensation nucleus around which cloud droplets form (NEGTAP, 2001). A substantial fraction of the mass of the atmospheric aerosol is present as ammonium sulphate ($(NH_4)_2SO_4$) which is formed by the uptake of NH_3 by pre-existing aerosol particles of H_2SO_4 (Metcalfe et al., 1999). Ammonium sulphate is largely removed from the atmosphere by rain and has an atmospheric lifetime of several (5-10) days. As a result, ammonium sulphate particles may be transported hundreds of kilometres from pollution sources. Apart from ammonium sulphate, aerosol ammonium nitrate (NH_4NO_3) is also present in the atmosphere which is formed by the condensation of NH_3 and HNO_3 onto pre-existing aerosol particles and is largely removed by rain

(Metcalfe et al., 1999). Other minor contributors to wet deposition include diffusion and impaction of aerosols onto cloud and rain droplets. SO_2 is relatively insoluble in cloud water, but photochemical reactions lead to the conversion of the gas to soluble SO_4 aerosol, while a similar reaction converts N oxides to aerosol NO_3. The movement of precipitation through the atmosphere allows the entrainment of other gases and particles so that precipitation removes most aerosols (1.0 to 2.0 µm in diameter) containing SO_4 and NO_3 (Soulsby, 1997). Snowflakes, due to their large surface area are particularly effective at entraining material when they fall. The hydrolysis of SO_2 and NO_x (NO and NO_2) in clouds leads to the formation of sulphuric (H_2SO_4) and nitric (HNO_3) acid, which are responsible for most deposited acidity in the UK.

2.1.3.2 Orographic enhancement and occult deposition

Wet pollutant deposition in upland hills (typically 300-1000 m in the UK) is subject to orographic enhancement due to the "seeder-feeder" effect, where precipitation from the high level (seeder) cloud effectively washes out aerosol phase pollutant-derived ions (SO_4, NO_3 and NH_4) from hill (feeder) clouds increasing the amount and concentrations of ions reaching the ground (Metcalfe et al., 1999). Hill clouds are formed above the uplands as the air is forced to rise by the topography, and contain larger concentrations of anthropogenic ions than high level clouds because they form largely within the boundary layer which contains large concentrations of pollutant-derived aerosols. In addition, the direct deposition of cloud droplets, containing large concentrations of liquid phase pollutant ions, to vegetation represents an important contribution to deposition totals in upland areas in the western UK which are in cloud for a significant fraction of time, especially at elevations above 600 m (NEGTAP, 2001). The deposition of fine mist and fog droplets (occult deposition) on the surfaces of trees may increase solute concentrations above the levels in direct rainfall (Fowler et al., 1988).

2.1.3.3 Dry deposition

Direct dry deposition of dust and gases can occur on suitable surfaces via settling under the force of gravity, or impaction onto surfaces by winds. Gaseous S and N compounds differ in their reactivity with natural surfaces. In terms of S pollutants, SO_2 is quite readily dry deposited and deposits at high rates (RGAR, 1997). The dominant component of dry deposition of oxidised and reduced N is NO_2 and NH_3, which both deposit onto natural surfaces at significant rates. NH_3 can be readily taken up by damp soils and vegetation resulting in an atmospheric lifetime for NH_3 of a few hours or less in the atmospheric boundary (Metcalfe et al., 1999). Other contributors to dry deposition of N include HNO_3, which is the most reactive N compound and deposits on to all natural surfaces at the rate which turbulence in the atmosphere can transport the gas to the ground, and NO, which deposits at a very limited rate on to natural surfaces. Dry deposition is particularly important in forested areas since the deposition of material is enhanced on tall, aerodynamically rough forest canopies.

2.1.3.4 Seasalt deposition

The spatial distribution of precipitation chemistry largely reflects the proximity of a given area to the various hydrochemical or pollution sources. The marked east-west gradients in the deposition of the major pollutant-derived ions contrast with the deposition of marine derived ions, mainly chloride (Cl) and sodium (Na) (NEGTAP, 2001). In western Britain, the ionic composition of precipitation is dominated by seasalts, which provide most of total SO_4 deposition along the west coast, while most SO_4 in eastern areas comes from anthropogenic sources. Therefore, the relative contribution of marine and pollutant-derived ions to precipitation chemistry is spatially variable within the UK. Atmospheric concentrations of anthropogenic-derived pollutants in the UK are also temporally variable, with higher concentrations during winter months, due to high precipitation totals and to the westerly direction of weather systems that can bring high concentrations of marine-derived ions (Cl) and pollutants (especially SO_4) from North America in precipitation (Soulsby et al., 2002).

2.1.3.5 Pollutant deposition in the UK

Total anthropogenic (non-marine) S deposition in the UK was 524 kTonnes in 1987, of which wet and dry S deposition comprised 233 and 291 kTonnes, respectively (Fowler et al., 2005). Total S deposition declined to 205 kTonnes in 2001, with higher reductions in dry S deposition. For oxidised N, wet deposition in the UK has remained fairly stable at around 100 kTonnes per annum from 1986 to 2001, and total (wet and dry) oxidised N deposition was 206 kTonnes in 2001 (Fowler et al., 2005). Deposition of reduced N, especially by dry deposition, is more difficult to quantify and total (wet and dry) annual deposition is currently estimated to be around 120 kTonnes.

The most recent maps of wet and dry non-marine S and total oxidised and reduced N deposition in the UK for 2004 are shown in Figure 2.2. These maps are derived from measurements of precipitation composition and atmospheric chemistry (SO_2, particulate SO_4 and NO_2) made by the Acid Deposition Monitoring Network (ADMN), which are then interpolated (using the kriging method) across the UK (Vincent and Lawrence, 2007). The high rainfall areas in north-western and central Scotland, north-western England, Wales and south-western England receive the highest wet S and oxidised N deposition loads, while dry S and N deposition is greatest in areas closest to major pollution sources such as in the Midlands and south-eastern England (NEGTAP, 2001). Reduced N deposition loads are more spatially variable and largely follow the pattern of emissions from major sources.

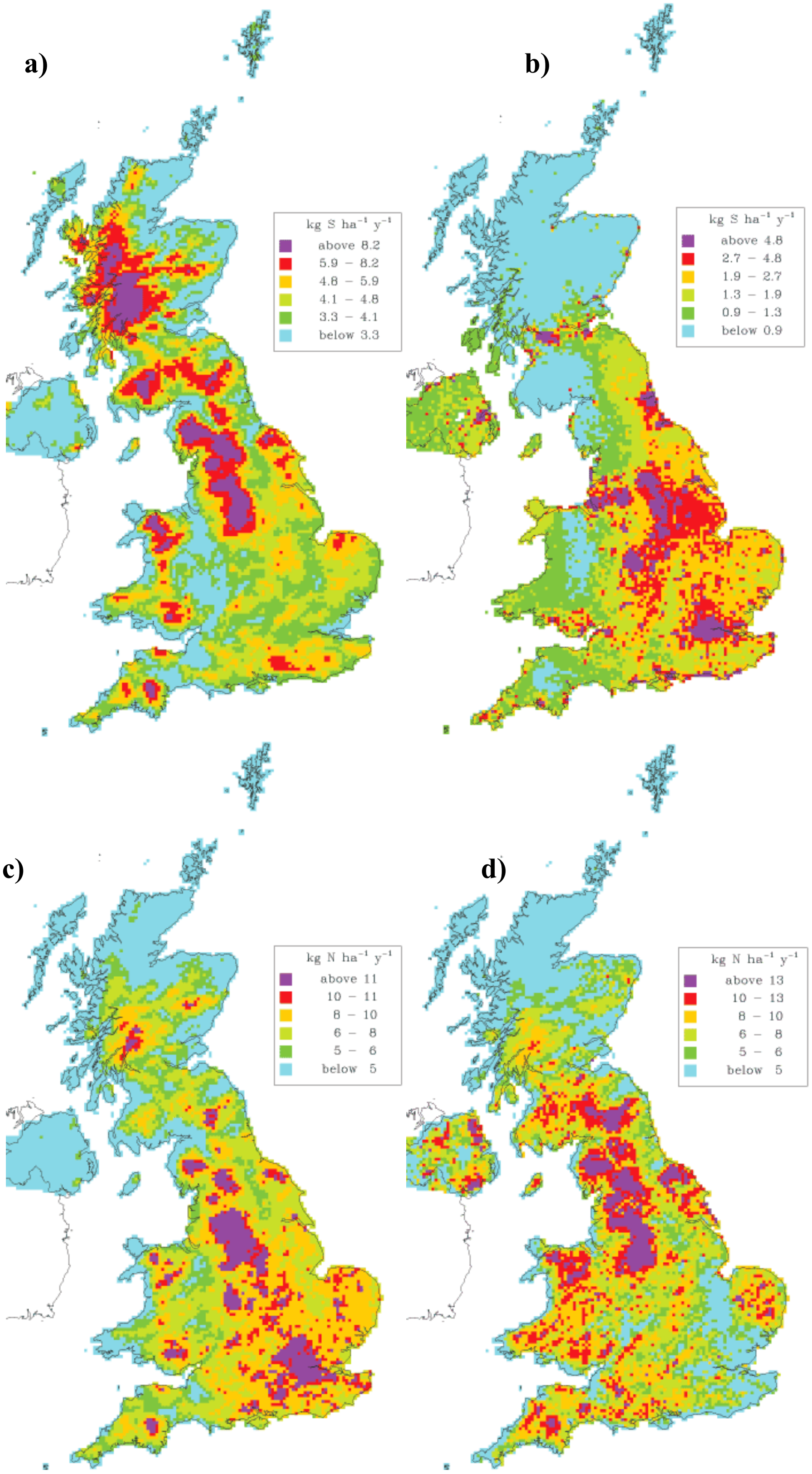

Figure 2.2 Maps of a) wet and b) dry non-marine S deposition and total deposition of c) oxidised N and d) reduced N in the UK for 2004 (source: CEH, 2004)

2.2 Soil processes controlling surface water acidification

The rate of release of base cations from mineral weathering in soils regulates water chemistry in the long term (Soulsby et al., 2002). The following sections describe the soil processes controlling the acidification of surface waters.

2.2.1 Cation exchange

Chemical weathering of soil parent material results in the production of clay minerals that have negatively charged surfaces (Johnson et al., 1993). The small size of clay particles (<2 μm) creates a large surface area on which chemical reactions occur. The breakdown of organic matter also affects soil properties, as humic substances are also negatively charged with a large surface area. These negatively charged surfaces form the soil cation-exchange complex which adsorbs cations from percolating water. The total quantity of cations that can be adsorbed by a given soil mass is referred as the Cation Exchange Capacity (CEC). When the soil parent material has abundant supplies of base cations, calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) are the dominant cations adsorbed onto exchange sites. The proportion of the CEC that is satisfied by these base cations is known as the base saturation, expressed as a percentage. Where resistant alumino-silicate minerals dominate the parent material and the supply of weatherable minerals is reduced, base saturation declines and Al and H^+ increasingly dominate the cation-exchange complex. This is because cations of a higher valence (Al^{3+}) and small radius (H^+) are preferentially retained by the exchange complex. The relative strength of cation adsorption is generally regarded as:

$$Al^{3+} > H^{+} > Ca^{2+} > Mg^{2+} > K^{+} > NH_4^{+} > Na^{+}$$

Equilibrium is maintained between the adsorbed cations and the composition of the soil water. Thus cations can move between percolating water and the cation-exchange sites until a new equilibrium is established. In calcareous soils with a high base saturation the exchange will mainly involve the displacement of base cations such as Ca, while Al may be released in more acidic soils.

2.2.2 The "mobile anion" effect

The process by which deposition of S and N compounds causes the acidification of soils and surface waters is commonly referred as the "mobile anion" effect. In this process, the deposition of non-marine anions (SO_4, NO_3 and to a lesser extent Cl) cause decreased surface water alkalinity, increased hydrogen ion concentrations and increased inorganic Al concentrations. Anions are widely believed to take part in only limited interactions with charged soil surfaces and are not retained in soils (Mulder and Cresser, 1993). Thus anions are considered mobile and can be transported via hydrological pathways to surface waters with the effect on acidification of surface waters being determined by the nature of the cations associated with the anions. Incoming sulphuric and nitric acid from atmospheric deposition disassociate into H^+ and SO_4 and NO_3, respectively. In soils with a high CEC, H^+ initially displaces available base cations which form neutral salts with the anions and are leached to surface waters (Soulsby, 1997). As the soil base cations are depleted, the soil buffering capacity is eventually exhausted so that the CEC becomes dominated by H^+ and Al^{3+} and the deposited anions are transported in association with hydrogen and Al ions causing an increase in surface water acidity and Al concentrations. Overall, the acidification effect of the deposition flux of a given anion is a function of the size of the base cation pool, which is related to the bedrock geology and the supply of base cations from weathering. The acidifying effect of SO_4 is greater than NO_3 due to the production of two hydrogen ions from the disassociation of H_2SO_4, compared to only one hydrogen ion produced from that of HNO_3 (NEGTAP, 2001). Inputs of reduced N (NH_3 and NH_4) from atmospheric deposition can contribute to soil and water acidification by the "mobile anion" effect if they are oxidised to NO_3 by soil micro-organisms (Driscoll et al., 2001).

The "mobile anion" effect is complicated by internal chemical and biological processing of anions within terrestrial and aquatic ecosystems. SO_4 is retained in soils to a small degree and is usually in excess of biological requirements. Soil retention of SO_4 is controlled by adsorption by sesquioxides of iron (Fe) and Al in the soil that are abundant, for example, in the B horizons of podzolic soils in the UK uplands (NEGTAP, 2001). This process is concentration dependent, with the capacity of the soil to adsorb/desorb SO_4 changing with the soil solution SO_4 concentration. Microbial reduction of SO_4 to sulphide is an important process in anaerobic soils, particularly in wetlands and bogs, resulting in the formation of pyrite (FeS_2) and/or the loss by volatilisation of hydrogen sulphide or other gaseous compounds (NEGTAP, 2001). S storage in wetlands and peatlands is reversible if the system is allowed to dry out allowing re-oxidation of sulphides. Nevertheless, ion budget studies have shown that surface water SO_4 concentrations have risen in line with increased non-marine S deposition, indicating that the effect of S retention on streamwater chemistry is negligible (Jenkins and Ferrier, 2000).

The acidifying effect of the main forms of N deposition (NH_3, NH_4 and NO_3) depends on the N transformations that occur in the soils. N leaching to groundwater and surface waters is usually limited by efficient ecosystem retention of NO_3, and usually N deposition is immobilised and retained by carbon-rich soils, or mineralised by soil micro-organisms (Helliwell et al., 2001). However, in upland ecosystems in the UK with thin mineral soils of low N retention capacity there is evidence of N saturation (Soulsby et al., 2002), where atmospheric N inputs exceed the biological demand and any excess N is then leached from the soil to surface waters (Aber et al., 1989). Under these conditions, all reduced N inputs in excess of biological demand are transformed to NO_3 and are leached to water. The timing of NO_3 breakthrough is related to the amount and duration of N deposition inputs, the amount of N stored in the soil and the severity of catchment acidification as measured by soil pH and Al leakage. It has been suggested (Rasmussen, 1998) that N cycling may become uncoupled resulting in significant NO_3 leaching to water at high N deposition rates (>25 kg N ha^{-1} yr^{-1}). N addition experiments have also demonstrated that the added NO_3 can be mobile in soils during dormant seasons and even under N limited conditions in soils with high C/N ratios (Gundersen, 1998).

2.2.3 Effects of seasalts

Much of the western UK is subject to high levels of marine ion deposition. The major impact of marine ion deposition, generally termed the “seasalt effect”, is the alteration of cation-exchange equilibria within the soil (Evans et al., 2001). This is a transient process, in which episodic inputs of marine base cations, primarily Na and Mg, cause the displacement of base cations, hydrogen ions and inorganic monomeric Al from the soil cation-exchange leading to the episodic acidification of runoff. It is suggested that the sites most sensitive to seasalt inputs are those at an intermediate distance from the coast, such as in central and south-west Scotland, north-west England and north Wales, because background concentrations of Cl at these sites are relatively low and occasional major seasalt inputs can generate very large proportional changes in the concentrations of Cl and other marine ions (Evans et al., 2001).

2.2.4 Trace metals

Trace metals are important in the biogeochemistry of forest and aquatic ecosystems as many are required micronutrients for plant or animal life. However, at elevated concentrations of availability, certain trace metals may be toxic (e.g. Al, lead (Pb), and mercury (Hg)) (Driscoll et al., 1993). Atmospheric deposition may serve as an important source of trace metals (such as cadmium (Cd), copper (Cu), Pb, zinc (Zn) and Hg) to forest ecosystems. Altitude and vegetation characteristics are particularly important influences on metal deposition due to increased concentrations in cloud and fog water, relative to bulk precipitation. The main source for other trace metals (e.g. Al, manganese (Mn) and Fe) is internal release from catchment soils by processes such as weathering, mineralization and desorption from soil/sediment surfaces.

Acidic atmospheric deposition may facilitate leaching of trace metals from soils in acid-sensitive regions with adverse impacts on surface water quality (Driscoll et al., 1993). These effects are particularly evident at high elevations due to increased amounts of precipitation and the scavenging of acidic aerosols by forest canopies, as well as the presence of shallow soils with limited ability to neutralise acid inputs. The geochemistry and bioavailability of trace metals are strongly influenced by speciation. Trace metals can exhibit a variety of aqueous and particulate species (Driscoll et al., 1993). For example, Al in water occurs in three fractions: particulate Al, organic monomeric Al (organic complexes of Al) and inorganic monomeric Al (inorganic complexes of Al including aquo Al, OH^-, F and SO_4 complexes). The speciation of dissolved Al is particularly significant because inorganic forms of Al are potentially toxic to plants and aquatic organisms, while organic and particulate forms are not considered toxic (Driscoll et al., 1980).

2.3 Pollution abatement policies

2.3.1 S and N protocols

The recognition of the continental scale of the problems resulting from the deposition of S and N oxides and the requirement for international solutions resulted in the establishment in 1979 of the Convention on Long Range Transboundary Air Pollution (CLRTAP) under the auspices of the United Nations Economic Commission for Europe (UN/ECE) (Gregor et al., 2001). The Convention adopted its first protocol in 1985, which set targets for reducing national emissions of S by 30% by 1993, based on a datum of 1980. The Protocol on Further Reductions of Sulphur Emissions (Second S Protocol), signed in 1994, agreed a further reduction in S emissions for the UK of about 70% by 2005 and 80% by 2010 (based on 1980 levels). The most recent Protocol to abate acidification, eutrophication and ground-level ozone was adopted in Gothenburg in 1999 (Jenkins and Cullen, 2001). This recognised the combined effects of four key atmospheric pollutants: S, NO_x, volatile organic compounds (VOCs) and NH_3, and sets emission ceilings. In the UK, implementation of the Protocol will involve reductions from 1990 levels of around 20% in S and 55% and 80% in NO_x and NH_3 emissions, respectively, by 2010.

Since the mid-1980s, total UK S emissions have decreased by 60% (Fowler et al., 2005) and, due to this, catchment acidification is expected to decline in the future. However, soil acidification is only reversed slowly, delaying rapid improvement in streamwater chemistry (NEGTAP, 2001). At the same time, the deposition of NO_3, NH_3 and NH_4 has not shown significant reductions similar to S. Ammonia emissions are more difficult to quantify than NO_x emissions because of the diversity of diffuse sources, but are thought to have increased with agricultural intensification. As a result, both the absolute and relative contributions of N species to acid deposition have increased in recent years, and are at least partially offsetting the beneficial effects of reduced S deposition (Curtis et al., 1998).

2.3.2 The critical loads concept

The concept of critical loads was introduced in 1988 by the UN/ECE CLRTAP as a tool for the development of abatement strategies and international agreements on the reduction of regional air pollutants which cause acidification in forest soils and surface waters (e.g. SO_x) and eutrophication in terrestrial ecosystems, freshwaters and marine waters (e.g. NO_x) (Gregor et al., 2001). The critical loads approach was formally adopted in the Second S Protocol (1994) with the aim of for the first time to protect the areas most vulnerable to acidification. A critical load is defined as the "quantitative estimate of exposure to one or more pollutants below which significant harmful effects of specified sensitive elements of the environment do not occur according to present knowledge" (Bull, 1993). With regard to acid deposition, a critical load is "the highest deposition of acidifying compounds that will not cause chemical changes leading to long term harmful effects on ecosystem structure and function according to present knowledge".

Critical loads have been calculated to avoid acidification of forest soils, groundwater and surface water. For UK freshwaters, the critical loads concept defines the maximum pollutant load which will maintain an ANC, defined as the difference between the sums of base cations and acid anions in streamwater, above zero (equating with water pH>5.3) in order to protect salmonid fish, in particular brown trout (Salmo trutta) (Nisbet, 2001). Models used to calculate critical loads for UK freshwaters include the diatom model (only for lakes) (Battarbee et al., 1995), the Steady-State Water Chemistry model (SSWC) (Henriksen et al., 1986) and the First-order Acidity Balance (FAB) model (Posch et al., 1997).

2.4 Expansion of broadleaf woodlands in the UK

2.4.1 Background to forest cover in the UK

Over the past 5000 years almost 90% of the UK's native woodland cover has been lost. The main reasons for this have been agricultural development, timber harvesting, heavy grazing and climate change, but the relative importance of these causes remains controversial (Hester et al., 2000). In a UK context, the term native woodland is used to refer to woodland that directly descends from the trees that spread over the British Isles after the last glaciation ended 11 000 years ago (Brown, 1997). Based on this definition, the types of woodland that are regarded as native are: upland birchwoods; upland oakwoods; native pinewoods; upland mixed ashwoods; wet woodlands; lowland mixed deciduous woods and lowland wood pasture and parkland.

Part of the lost woodland cover has been replaced by plantations of fast-growing conifer species on low value farmland in the uplands (Robinson et al., 2000), as part of the government's policy after the 1st World War to encourage home-grown timber production in order to reduce reliance on timber imports and provide a source of employment in rural areas (McIntosh, 1995). The extensive conifer plantations relied on one or two exotic species and tree planting operations were conducted either by direct state activity through the Forestry Commission (FC) or as private forests receiving indirect state incentives in the form of tax benefits and subsidy (Mather, 1993). From 1950 to 1990, the area of new conifer plantations created in the UK was 1.13 millions of ha, of which 69% were planted in Scotland (Forestry Commission, 2006). However, during the past decade the restoration and expansion of native, broadleaf and Scots pine woodlands has become a conservation priority and planting preferences have changed from conifer plantations to native tree species (McIntosh, 1995).

Figure 2.3 shows the area covered by conifers, broadleaves and total woodland in England, Wales and Scotland.

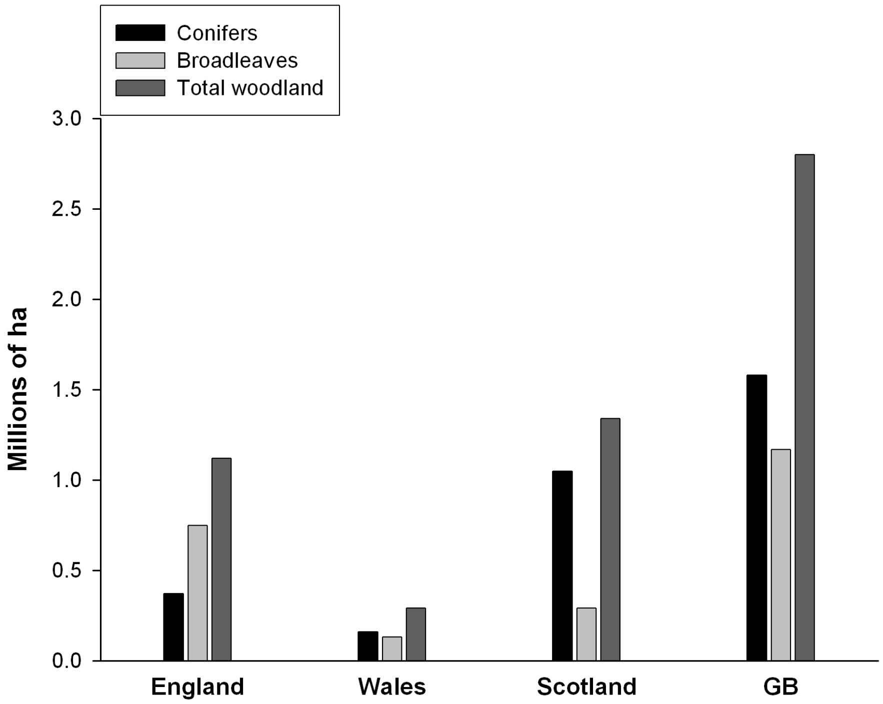

Figure 2.3 Area covered by conifers, broadleaves and total woodland in England, Wales and Scotland (Forestry Commission, 2006)

Forests in the UK cover 2.85 millions of ha equating to 11.8% of the total land area (Forestry Commission, 2006). Conifer forests cover an area of 1.58 millions of ha providing 58% of the present forest cover, while broadleaf woodland comprises 1.17 millions of ha or 42% of total forest cover. Conifer forests predominate in Scotland, while most broadleaf woodlands are found in England. Planting of new broadleaf woodland in the UK has increased from around 250 ha in 1978 to 9360 ha in 2006 (Forestry Commission, 2006). The main broadleaf species planted are birch (*Betula* spp.), beech (*Fagus sylvatica*), oak (*Quercus* spp.) and ash (*Fraxinus* spp.). Currently, oak provides the largest area of broadleaf woodlands (223 000 ha), followed by birch (160 000 ha) and ash (129 000 ha).

2.4.2 Policy drivers for broadleaf woodland expansion

The milestone in the recognition of the importance of native woodlands at a global scale was the United Nations Conference on Environment and Development held in Rio de Janeiro, Brazil in 1992 which resulted in the UN Convention on Biological

Diversity (CBD). In particular, Article 8f of the Convention urges countries to restore and rehabilitate degraded ecosystems and promote the recovery of threatened species through the development and implementation of plans and management strategies (Newton and Kapos, 2000). Since the 1992 Conference, the UK and other European governments have built on the Rio principles and are committed to implementing them (Rollinson, 2000). At the Ministerial Conference on the Protection of Forests held in Helsinki in 1993, guidelines for the sustainable management of forests and for the conservation of the biodiversity of European forests were agreed, while the declaration and resolutions of the pan-European Ministerial Conference on the protection of forests in Europe were agreed at the Ministerial Conference on the Protection of Forests held in Lisbon in 1998.

The UK's response to these international and European agreements was the development and publication of the UK Biodiversity Action Plan in 1994 (Rollinson, 2000) which aims to conserve and enhance biological diversity within the UK. In addition, the publication of the UK Forestry Standard (Forestry Commission, 1998) outlined a comprehensive approach towards sustainable forestry in the UK by providing guidance on forest management practices such as the creation of native woodlands and management of existing semi-natural woodlands. Finally in the publication "A better quality: a strategy for sustainable development in the UK" (Anon, 1999), it was stated that the UK's strategy for sustainable development should rely on the expansion of native woodland area, the better management of existing woodlands and the conservation of natural capital (biodiversity, air, soil and water).

Following these developments, a large number of projects aiming to restore native woodlands have been initiated during the past decade in the UK by numerous governmental agencies and environmental non-governmental organizations (NGOs), often operating in partnership. These include agencies such as the Forestry Commission as well as NGOs such as the Royal Society for the Protection of Birds (RSPB) and the Woodland Trust (Newton et al., 2001). In addition, major financial incentives were introduced in 1988 for new (non-Forestry Commission) broadleaf woodlands planting through the range of grants available under the Woodland Grant Schemes.

2.4.3 Planning the expansion of broadleaf woodlands

The expansion of broadleaf woodlands can be achieved either by restoring degraded woodland ecosystems or by re-creating new woodlands on sites that were covered by forest historically (Brown, 1997). In practice, native woodland restoration plans require the use of both approaches. The Forestry Commission is using the concept of Forest Habitat Networks (FHN) as the ecological basis for planning woodland expansion. In this concept, new broadleaf woodland planting should reconnect existing semi-natural woodland remnants, reduce fragmentation and provide a link with riparian forests, with the aim of increasing the ecological value and improving the biodiversity of forests in the long term (Peterken, 2000). FHN also aim to provide linkage with existing conifer plantations in order to lead to a long-term transition from conifer plantations towards semi-natural mixed forests of enhanced ecological quality. FHN form the basis for the change in forestry management towards Continuous Cover Forestry (CCF), where the forest canopy is maintained at a range of tree heights without clearfelling (Farmer and Nisbet, 2004). FHN have been implemented in the Local Forestry Framework for the restoration of native woodlands at a landscape scale in the Cairngorms and the Middle Clyde area in Scotland (Forestry Commission, n.d.), and also similar projects in England, such as in the North York Moors (Peterken, 2002). With expansion of broadleaf woodland in the UK, there is need to assess its effect on streamwater chemistry, especially in upland areas which are sensitive to acidification.

2.5 Processes controlling the effect of forests on streamwater chemistry

Forests have the potential to influence surface water chemistry through a range of processes. The composition of precipitation that reaches the ground (throughfall and stemflow) can change dramatically after contact with plant surfaces and movement through vegetation canopies to the soil. The processes related to the effects of forest cover on streamwater chemistry are described below.

2.5.1 Scavenging of pollutants

Deposition of atmospheric pollutants on forest canopies can be enhanced due to the capture of gases and aerosols (the scavenging effect) as a result of the aerodynamic roughness of the forest structure, which enhances turbulent air mixing (Fowler et al., 1989). Pollutant gases in the atmospheric boundary layer are advected by wind and transported to terrestrial surfaces by turbulence. The turbulence generated by frictional drag at the edge of the airflow above surfaces with different aerodynamic roughness will lead to different rates of exchange with the atmosphere (Metcalfe et al., 1999). Since forests exert much greater drag on the airflow than other land covers, such as grassland, rates of dry deposition are greater onto forests. Forests are also particularly effective at scavenging acidic pollutants in cloud water due to the condensation of cloud droplets on the rough tree canopies (Nisbet et al., 1995). The extent of scavenging depends upon a number of interacting factors, including climate, altitude, atmospheric pollution and canopy architecture and trapping characteristics (Alexander and Cresser, 1995). Higher rates of pollutant scavenging by forest canopies are expected in areas of high elevation, where high winds occur and which are cloud-covered for a substantial proportion of the time and also in areas close to major pollutant sources. The chemical composition of air is also important for pollutant scavenging as pollutants vary in their capacity for dry deposition as described in Section 2.1.3.3. Conifer forests are more aerodynamically rough than the usually more open broadleaf woodlands, and thus scavenging has been found to be greater onto conifer canopies. For example, in a literature review Alexander and Cresser (1995) report a study in central Germany where S deposition increased from 24.5 kg ha^{-1} yr^{-1} in the absence of trees to 44.2 and 75.4 kg ha^{-1} yr^{-1} under beech and spruce canopy, respectively, with the additional S inputs attributed to enhanced S deposition in gaseous or aerosol form on forest canopy. Rates of dry deposition (especially for NH_3) have also been found to increase at forest edges (NEGTAP, 2001) and thus some enhancement of pollutant scavenging is expected as forest edge length increases. Broadleaf woodlands usually have a larger edge length (for the same woodland size) than conifer plantations, but any effects of woodland edge on dry deposition rates would greatly depend on the local pollution climate (Neal, 2002).

2.5.2 Changes in throughfall chemistry

Precipitation can wash out the products of dry and occult deposition that have accumulated on the forest canopy and thus resulting in increased solute concentrations in throughfall. The effect of different tree species on throughfall chemistry was reported in studies in the Llyn Brianne catchment, mid-Wales. Concentrations of base cations (Ca, Mg, Na and K), SO_4 and dissolved organic carbon (DOC) in bulk precipitation were two to ten times lower than throughfall under a Sitka spruce canopy (Soulsby and Reynolds, 1992) and two to six times lower than under an oak canopy (Soulsby and Reynolds, 1994). The highest increases in throughfall solute concentrations were for the mainly atmospherically-derived ions Na, Cl and SO_4, under the canopy of both spruce and oak. In contrast, NO_3 concentrations in throughfall for both tree species were half those in bulk precipitation due to NO_3 retention by the foliage. Nitrogen is a nutrient that is usually limited and required by vegetation and thus can be absorbed and retained by the vegetation canopy. Nutrients can also be leached from the vegetation and returned to the soil. Stemflow, although a relatively minor component of the canopy water balance in forests, has high solute concentrations and can result in a disproportionate chemical flux into a restricted area around the base of the tree (Levia Jr. and Frost, 2003).

Increases in solute concentrations in throughfall below forest canopies are also caused by a concentration effect, which results from the interception of precipitation and evaporation of moisture back into the atmosphere, leaving dissolved chemicals in the intercepted precipitation on the vegetation canopy (Soulsby, 1997). The changes in the chemical composition of throughfall are greater in coniferous species, mainly because deciduous trees intercept a lower proportion of the annual precipitation (15 to 25%) than conifers (25 to 35%) (Ward and Robinson, 2000). The higher interception losses and canopy storage by coniferous species are due to the larger surface area of conifer needles compared to leaves, the retention of needles through winter and the open texture of conifer canopy which allows better air circulation (Ward and Robinson, 2000).

2.5.3 Forest effects on soil chemistry

Pollutant scavenging and the subsequent leaching of acid anions under forest canopies can lead to soil acidification by reducing the available cation pool. The chemical characteristics of surface soil horizons under different tree species depend on litter quality and nutrient status of the tree, root nutrient uptake and leaching, the interception of atmospheric pollutants and the soil biological community (Hagen-Thorn et al., 2004). Soils under conifer trees are generally more acidic than under broadleaf trees because conifers are faster-growing and have a higher base cation demand, the pH of needles is lower than leaves and there is a higher flux of acid anions under conifers. Moreover, increased N availability from excess N deposition onto forests can stimulate forest growth and further exacerbate soil acidification due to increased base cation demand (Sogn and Abrahamsen, 1998). On the other hand, N leaching from forests to surface water increases with age because mature forest stands have reduced N requirements from the soil pool (Emmett et al., 1993) and can lead to soil acidification through the leaching of base cations from the soil pool, with NO_3 acting as the mobile anion.

Streamwater chemistry in forested catchments can also be affected by the chemistry of forest litter. It is widely agreed that annual litter mass production is the same for all tree species, conifers or broadleaves, and that leaf litter is more nutrient-rich than branch material regardless of vegetation type or stand age (Alexander and Cresser, 1995). However, seasonal nutrient fluxes to the forest floor or to streams may occur, for example litter fall in autumn for broadleaves. In addition, the pH of runoff flowing through or over surface forest horizons could be affected by the pH of litter, and this process could be important especially for overland flow following rainfall events, and contribute to the lowering of streamwater pH in such conditions. The pH measured in water is higher for litter from broadleaf trees than for conifers, as reported in Alexander and Cresser (1995), and, hence, depending on the litter mass present, the pH of drainage waters could increase in broadleaf woodland soils.

2.5.4 Forest effects on hydrological pathways

The effect of vegetation on water chemistry does not end when the water reaches the ground because vegetation changes the physical and chemical properties of underlying soils. The differences between solute and sediment loads in the different flow pathways (overland flow, throughflow and baseflow) are due to the different residence times of water in the soil (Soulsby, 1997). Trees alter the pathways of water flow and the rates of water flux through the creation of drier soil conditions under established vegetation and a decrease in soil moisture (Gilvear et al., 2002). At the same time, the texture and structure of soils are altered by forest rooting which enhances the effective thickness of the upper more permeable soil horizons (Robinson et al., 2003). Deep, permeable soils can absorb and store large quantities of water, producing more even temporal patterns of runoff. Although overland flow is relatively uncommon in well-vegetated areas in temperate climates, due to the high soil infiltration capacity that enables most of the rainfall to be absorbed, spatial and temporal variations in infiltration capacity occur during high rainfall events (Robinson et al., 2003). Under such conditions, when water moves mainly as overland flow or near-surface throughflow, water acidity can increase due to the limited contact time of water with the soil-exchange complex. In contrast, low flows are more influenced by soil chemical processes because the water has more time to interact with the soil matrix (Soulsby, 1997). Broadleaf trees have usually deep root systems which can promote higher infiltration rates and consequently reduce overland flows (Papamichos, 1996), but this depends on the extent of woodland cover, the depth of the soil horizons and the site topography. The effect of broadleaf woodland cover on flow patterns will be less in high rainfall areas with steep gradients and thin soils where rainfall events can cause overland or near-surface flow and lead to increases in acidity in streamwater.

2.6 Guidelines for the protection of acid-sensitive freshwaters from new broadleaf woodland planting

The Forests and Water Guidelines (Forestry Commission, 2003) contain best practice guidelines for minimising the effect of forestry activities on the freshwater environment in the UK. The Guidelines use the critical loads methodology and the provisional critical loads exceedance map for UK freshwaters (ECRC, 2001) shown in Figure 2.4 to determine freshwaters at risk of acidification from the scavenging effect due to new woodland planting or restocking plans in acid-sensitive areas. The map was derived from calculating critical loads with the Steady-State Water Chemistry (SSWC) model (Henriksen et al., 1986) from the chemical analysis of water samples from the most sensitive water body, usually a lake, within each 10 km x 10 km grid square, and comparing these with the modelled atmospheric deposition of non-marine S and N for 1995-1997. Excess of atmospheric N inputs are determined from measured NO_3 concentrations in runoff because it is assumed that most of the N deposition is retained by vegetation and soils. The use of modelled non-marine S deposition for 1995-97 for identifying areas at risk of acidification allows for a safety margin since pollutant non-marine S deposition has declined in the last 15 years in the UK and is expected to further decline in the future (Fowler et al., 2005). The Guidelines recognise that, due to factors related to sampling and scale, waters bordering the exceedance squares could also possibly be at risk. Therefore, the impact of new planting in adjacent squares also needs to be considered.

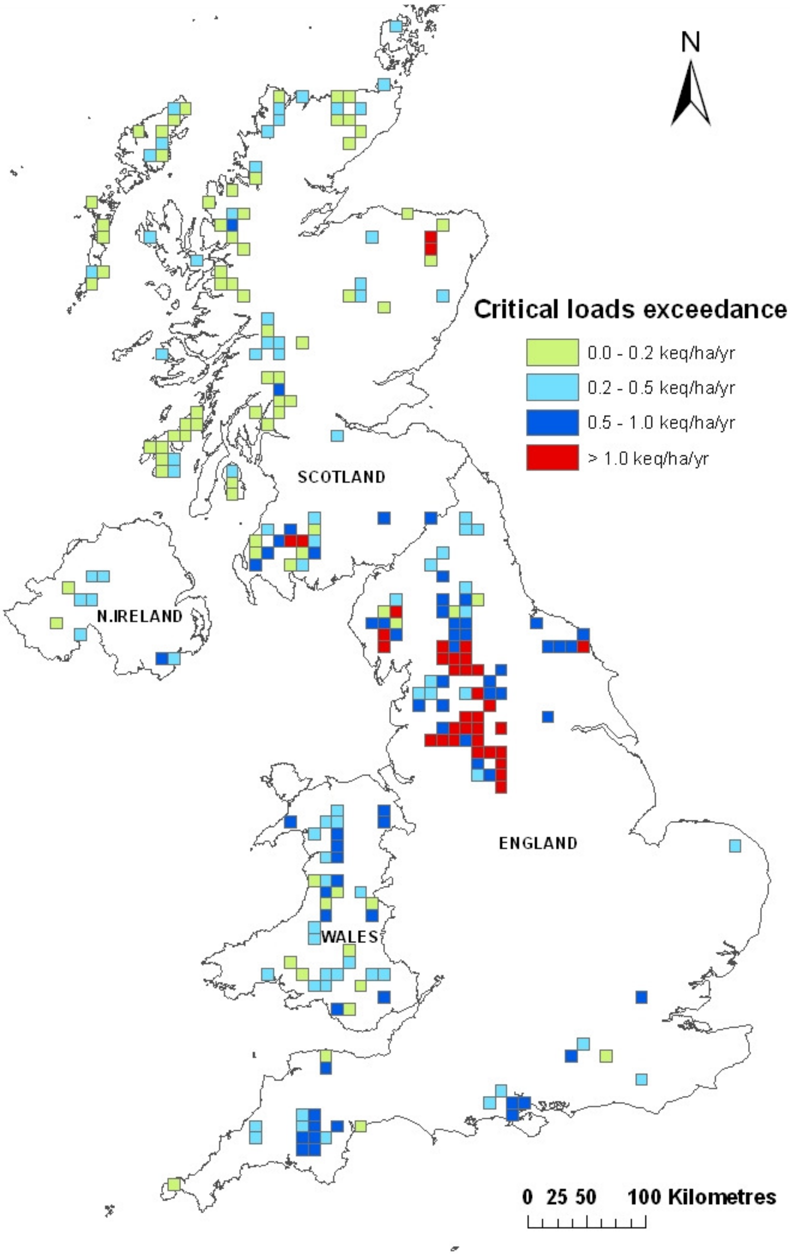

Figure 2.4 Critical load exceedance squares (10 km x 10 km) of acidity (keq H ha^{-1} yr^{-1}) for freshwaters in the UK by non-marine S and N deposition for 1995-97 (ECRC, 2001)

The indicative nature of the 10 km^2 scale critical load exceedance map requires that a more detailed catchment-based assessment is conducted to determine the actual susceptibility of individual waters to a forest scavenging effect within both exceeded and not exceeded/adjacent squares. For new proposed planting, the need for a more detailed assessment is based on factors such as the size of the planting scheme, species mix, the present proportion of forest cover in a catchment and the sensitivity of catchment geology and soils. The procedure followed for undertaking catchment-based assessments is shown in Figure 2.5. For catchments with acidic geology and poorly-buffered soils where new planting is planned, the Guidelines require a site-specific critical load assessment when more than 10% of the catchment area is to be planted with conifers or more than 30% with broadleaves within a critical load exceedance, or adjacent square. Streamwater critical loads are calculated using the results of the chemical analysis of one to three water samples collected from the main watercourse receiving drainage from the area proposed for new woodland at high flows, preferably between January and March, when streamwater tends to be more acidic. Where the estimated pollutant deposition exceeds the critical load calculated for the specific catchment, approval of a planting grant is unlikely until there are further reductions in pollutant emissions and consequent deposition.

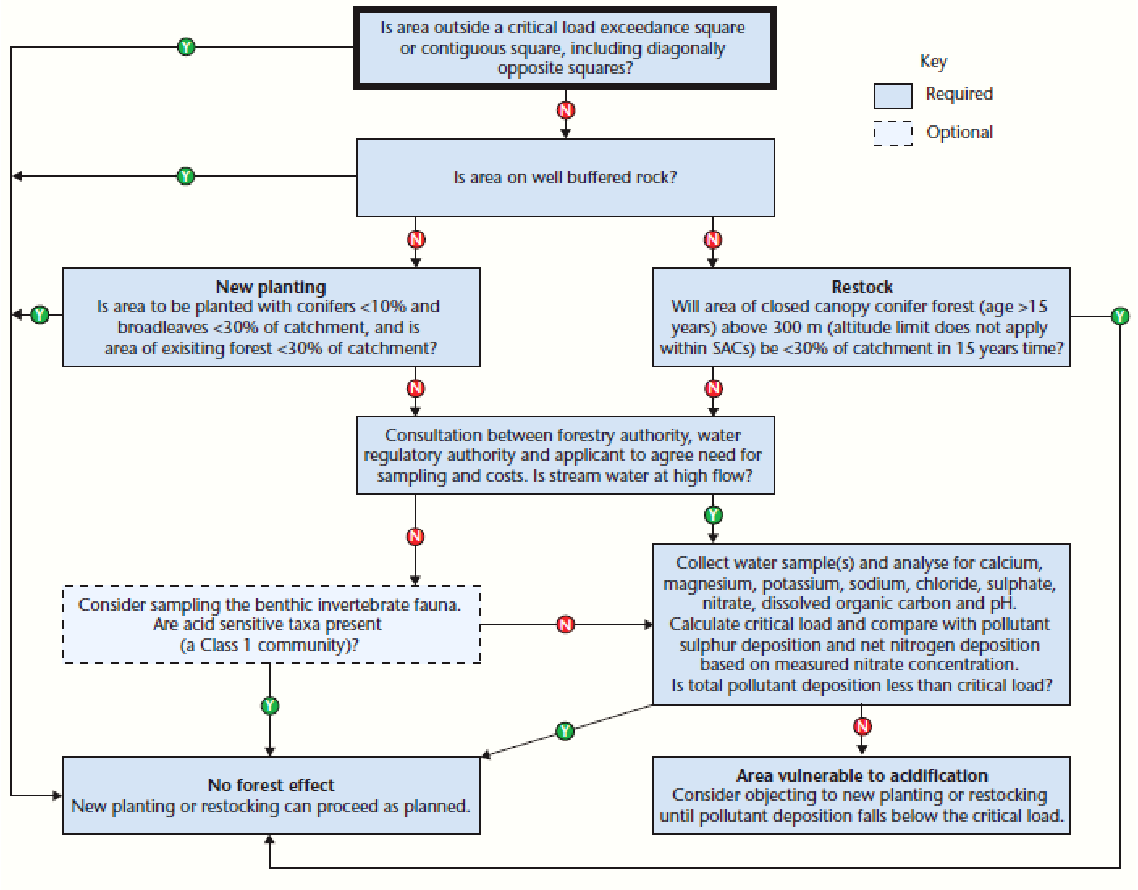

Figure 2.5 Decision tree for undertaking catchment-based critical loads assessments in areas where new woodland planting is planned (Forestry Commission, 2003)

2.7 Contribution of this research

Most research has focused on the effects of conifer afforestation on surface water acidification in the UK uplands, hence there is a lack of studies investigating the associations between different proportions of broadleaf woodland cover and streamwater indicators of acidification. This research contributes to the knowledge concerning the effects of land-use change, in particular the expansion of broadleaf woodlands, on streamwater chemistry in acid-sensitive catchments. It will also address factors influencing acid-sensitivity and assess the effectiveness of the risk assessment methodology currently used for the protection of sensitive freshwaters from broadleaf woodland expansion.

Streamwater chemistry, and consequently streamwater acidification, depends on the complex interactions between factors related to geological, soil and deposition processes, which are integrated within the critical loads concept. Therefore, the adoption of the critical loads approach in the research methodology enabled the selection of study areas with similar acid-sensitivity status, which enabled this study to focus solely on the investigation of broadleaf woodland cover effects on streamwater chemistry, whilst minimising the effect of other confounding factors.

Chapter 3 Catchment selection and streamwater chemistry analytical methodologies

The project followed the methodology recommended by the Forests and Water Guidelines for identifying catchments at risk of acidification in sensitive areas covered with broadleaf woodlands. The first stage was to select catchments with different percentages of broadleaf woodland cover in acid-sensitive areas of the UK. Section 3.1 describes the main spatial datasets used within a Geographical Information System (GIS) and the methods used to identify candidate catchments with different proportions of broadleaf woodland cover.

Section 3.2 presents a summary of the characteristics of the study catchments. Section 3.3 outlines the sampling strategy employed for the collection of streamwater samples from the study catchments and briefly describes the analytical methods used to determine streamwater chemical parameters. Also, this section describes the flow monitoring in a selected study catchment and the macroinvertebrate survey conducted in 11 of the study catchments. Section 3.4 describes the data analysis methods used, including the statistical methods used for the analysis of the streamwater chemistry data and analysis of macroinvertebrate data. Section 3.5 concludes with the description of the critical load models used to assess acid-sensitivity in the study catchments.

3.1 Catchment selection

3.1.1 Datasets

The analysis of spatial datasets held within a GIS to identify study catchments is summarised in Figure 3.1. The main datasets used in the initial catchment selection process were the Steady-State Water Chemistry (SSWC) model Critical Load (CL) exceedance 1995-97 dataset for UK freshwaters (ECRC, 2001) and the National Inventory of Woodlands and Trees-Interpreted Forest Type (NIWT-IFT) (Woodland Surveys, 2002). Both datasets were provided under licence by Forest Research (FR) in digital format as ArcGIS shapefiles (.shp).

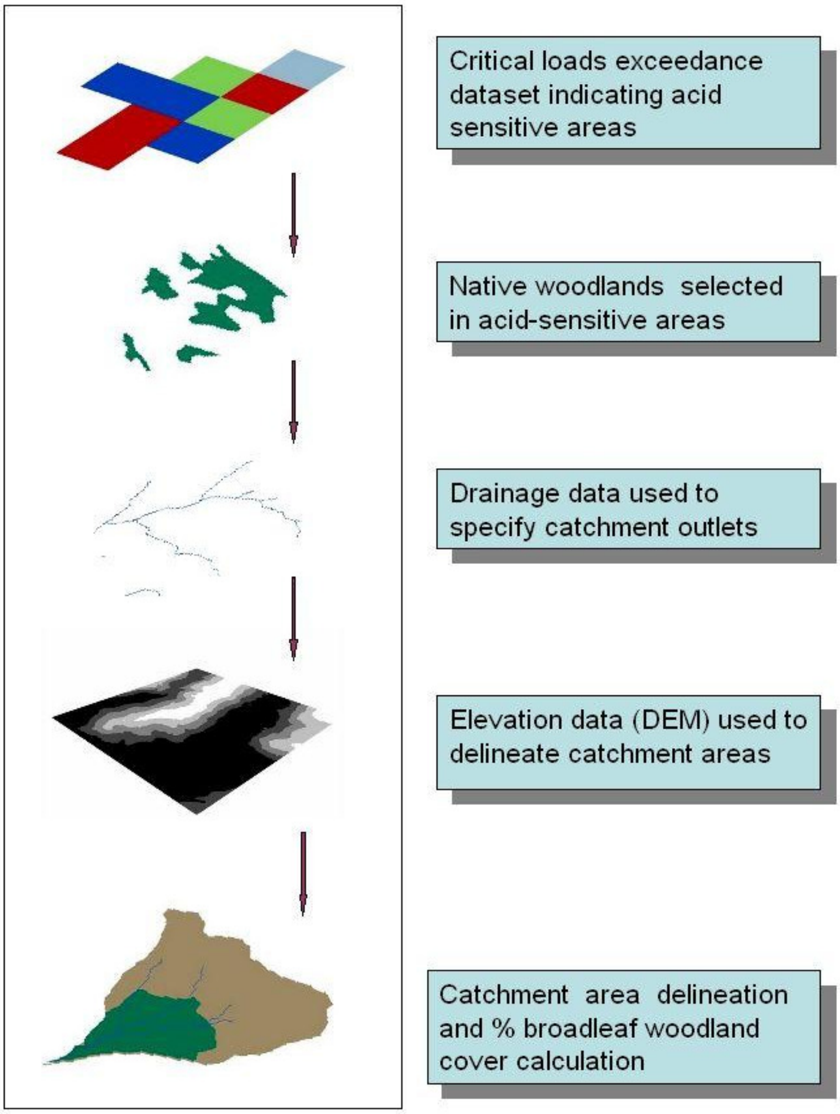

Figure 3.1 Diagram of catchment selection process

The SSWC CL exceedance dataset (see Figure 2.4) consisted of a single shapefile divided into 10 km x 10 km CL exceedance squares covering the whole of the UK. CL exceedance values were classified in four classes of 0.0-0.2, 0.2-0.5, 0.5-1 and >1 keq H ha^{-1} yr^{-1}. Due to the indicative nature of the 10 km x 10 km exceedance squares and also due to sampling and scaling factors, it was possible that freshwaters bordering exceedance squares could also be at risk of acidification. Therefore the squares adjacent to the ones where critical loads were exceeded, including those diagonally opposite, were also considered to be acid-sensitive.

The NIWT-IFT dataset included all areas of woodland (public or private) in the UK with an area greater than 2 ha and crown density $\geq$ 50%. It consisted of three shapefiles for Scotland, England and Wales respectively which were compiled from interpretation of 1:25 000 aerial photographs. The interpreted aerial images were plotted on top of Ordnance Survey (OS) 1:25 000 mapping for the Forestry Commission (FC) and the result was stored digitally. The NIWT-IFT woodland polygon data were updated by the Woodland Surveys section to include FC new planting and new Woodland Grant Schemes as at March 31st 2002. The dataset consisted of four broad woodland categories; conifer, broadleaf, mixed woodland and open areas. Broadleaf woodland was defined as an area where 80% or more of the present tree cover consisted of broadleaf trees. The NIWT-IFT did not provide any information on tree species composition for the recorded woodland areas.

3.1.2 GIS software

ArcGIS 8.3 developed by ESRI (CA, USA) was used for the storage and analysis of the spatial datasets. The ArcMap suite of applications was used during the project for processing vector data, visualisation and map production. Analysis of raster datasets, such as watershed delineation from digital elevation models was performed in the GRID module available in ARCINFO. All digital datasets were projected to the Ordnance Survey British Grid (OSGB).

3.1.3 Woodland selection

The first step of the analysis was to select broadleaf woodland polygons that lay within the CL exceedance squares or the adjacent (not-exceeded) squares. The selection was performed using the “select by location” operation in ArcMap and resulted in shapefiles containing all woodlands in acid-sensitive areas of Scotland, England and Wales. Separate shapefiles were created for each woodland type (broadleaf, conifer and mixed) using the “select by attribute” operation in ArcMap. Then in order to select catchments with no conifer or mixed woodland, which might confound the analysis, the “buffer” tool in ArcMap was used to create zones around broadleaf woodland polygons to ensure that only those woodland polygons that did not include conifer or mixed woodland within the buffers were selected. As a result many broadleaf woodland areas were excluded which lay next to conifer plantations and mixed woodlands in areas such south-west Scotland (Dumfries and Galloway region) and north Wales (Snowdonia). This meant that most areas in Galloway and Snowdonia were not included in the analysis although they were heavily impacted by acidification in the past and even today a great part of their area remains acid-sensitive.

From the set of broadleaf woodland polygons those at greatest risk of acidification were identified as solid blocks of broadleaf woodland, preferably at elevations above 200 m, since the canopy scavenging effect is more evident at high elevations and for rough and homogeneous woodland surfaces. Therefore linear strips of riparian woodlands in flat valley floors were identified from digital elevation models (DEMs) and removed from the analysis. Another method used to identify linear woodlands was calculation of the ratio of the woodland area to its perimeter and woodland areas with low ratio values were also removed from the analysis.

Knowledge of the spatial distribution of broadleaf woodlands in the UK enabled areas of substantial broadleaf woodland cover to be targeted, such as the Loch Lomond and the Trossachs National Park in central-west Scotland, the Lake District National Park in Cumbria, north-west England, and Exmoor and Dartmoor National Parks, in south-west England. The heavily acidified area of the Pennines was not included in the analysis due to the lack of broadleaf woodland cover.

After suitable broadleaf woodland polygons were identified as described above, the catchments in which these were located had to be delineated and proportions of woodland cover calculated. The delineation of drainage networks and catchment areas was done from PANORAMA® DEMs (1: 50 000, EDINA, Digimap). The drainage networks and the catchment areas were extracted from grid files using the overland flow simulation algorithm (Jenson & Domingue, 1988), available in the

GRID module in ARCINFO. The method comprises of three phases. First, topographic sinks (or depressions) present in the grid files due to data errors or resolution limitations were filled using the SINK and then the FILL functions. The "depressionless" grids were then processed to build flow direction grids using the FLOWDIRECTION function. Flow between cells was assumed to be unidirectional and occurred in the direction of the steepest descent, determined for each cell by its eight surrounding cells (known as the D-8 flow routing approach). The third stage was to assign a value to each cell equal to the number of cells flowing to it by using the FLOWACCUMULATION function. Any cells having a flow accumulation value of zero corresponded to ridges. All cells in the 'depressionless' grids had a path to the dataset edge so a fully connected drainage network could emerge by highlighting cells with flow accumulation values higher than a pre-selected threshold value. Testing of different flow accumulation values revealed that threshold values of 80-100 cells gave a satisfactory representation of the stream network. For quality control, the derived stream networks were compared to the OS Strategi® digital stream features (1: 250 000) downloaded from EDINA Digimap. In most cases the grid derived networks represented reality more accurately and avoided errors present in the Strategi dataset, such as streams crossing ridges.

In order to delineate the catchment boundaries, it was necessary to define the outlet (or pour point) of each catchment. The outlets were identified by looking at the drainage data in ArcMap and selecting a suitable point on the main stream draining the woodland above which a catchment area could be found and recording its coordinates. Catchment boundaries were then delineated with the WATERSHED function. The watershed grids were converted to shapefiles, also loaded on ArcMap, and catchment areas were calculated. Woodland polygons or parts of them included within the boundaries of the catchment areas were selected by intersecting the woodland polygons with the catchment area shapefiles. Catchment broadleaf woodland cover was calculated with a VBA script and was expressed as percentage of the total catchment area. The accessibility to the catchments for field sampling was investigated using road network digital data from Digimap.

3.1.4 Candidate catchments

Overall, 31 suitable acid-sensitive catchments were identified in Scotland, England and Wales with proportions of the catchment covered by broadleaf woodland ranging from 13% to 57%. These catchments were investigated further to identify the final ones for the research.

Due to the indicative nature of the 10 km x 10 km critical load exceedance mapping squares the British Geological Survey solid geology dataset at 1:625 000 (BGS, 1995), supplied in digital format (shapefiles) under licence by Forest Research, was used to investigate if the catchments were underlain by an acid geology. All catchments were confirmed to have an acidic substrate apart from two English catchments that were underlain by Carboniferous limestone. These catchments were considered well buffered to acidic inputs and were removed from the study. The list of the remaining candidate catchments was given to Forest Research to investigate if staff at their field stations in Talybont, south Wales, and in Exeter, southwest England could provide help with the collection of water samples at high flows, in particular in catchments located at great distance from Edinburgh in England and Wales. This meant that the candidate catchments in north Wales and two catchments in north Devon had to be removed from the study for logistical reasons. Since Forest Research could not offer any help with the catchments in northwest England it was decided to retain two catchments close to Penrith, because they were closer to Edinburgh and also had the highest percentages of broadleaf woodland cover.

3.1.5 Field visits

Field visits were made to the remaining 20 candidate catchments from November 2004 to January 2005 in order to further identify any confounding factors on site, get permission from landowners to access the sites, identify the most suitable access routes to the sites and select suitable streamwater sampling points. Field visits also had the purpose of identifying catchments lying adjacent to the forested ones that had no woodland cover. Streamwater was also sampled from these “control” catchments to help assess the effects of broadleaf woodland on streamwater chemistry.

To further ensure that catchments were acid-sensitive, streamwater pH was measured on site using a portable Hanna Instruments 9025 Microcomputer pH meter. Flow conditions during the visits were low to moderate and catchments with streamwater pH values greater than 6.5 were excluded from the study because these values indicated well-buffered conditions. After site investigations, all the Scottish catchments in Glen Arnisdale and the Loch Katrine area were included in the study. Of the potential five catchments in the Devon area two were excluded immediately due to confounding land uses and two because chemical analysis of streamwater samples showed excessive nitrate streamwater concentrations, up to 14 mg l^{-1} NO_3, due to runoff from nearby farms. Therefore, only one catchment (Yarner Wood) in Devon was included in the study. Both catchments in the Ullswater area were included while none of the five Welsh candidate sites were included because of high streamwater pH values. At each selected catchment, outlet points were identified and their coordinates recorded using an eTrex Garmin GPS receiver (2 to 10 metres horizontal accuracy).

In addition, non-wooded ("control") catchments were identified adjacent to the wooded catchments in Glen Arnisdale and the Loch Katrine and Ullswater areas and their outlet coordinates were also recorded. In the case of the Yarner Wood catchment, the presence of extensive conifer and mixed woodlands nearby made it difficult to identify a suitable control catchment. Therefore the Narrator Brook catchment was selected as the control site. Narrator Brook has almost no woodland (broadleaf woodland cover is only 2%) and lies 20 km west of Yarner Wood. The catchment is part of the UK Acid Waters Monitoring Network (AWMN) and the chemistry of its streamwater has been analysed on a monthly basis since 1988. Access to streamwater chemistry data from the Narrator Brook catchment was granted from the Environmental Change Research Centre (ECRC), University College London.

3.1.6 Study catchments

Overall, 14 catchments were included in the study; ten catchments with different proportions of broadleaf woodland cover and four control catchments with none or almost no woodland cover. Three wooded catchments were selected in Glen Arnisdale, four in the Loch Katrine area, two in the Ullswater area and one in Devon. The recorded catchment outlet coordinates were imported in ArcMap to re-calculate the catchment areas and percentages of catchment woodland cover. Catchment boundaries were delineated from the higher resolution PROFILE® DEMs (1: 10 000, EDINA Digimap) using the same methodology as described earlier. For improved accuracy, the final catchment areas were delineated using terrain analysis tools available in TauDEM, which has multiple methods for the delineation of channel networks (Tarboton, 1997). This enabled the delineation of the two forested catchments in the Ullswater area because their outlets were located in flat terrain and could not be well-defined with the D-8 algorithm available in ARCINFO. TauDEM also uses the D-8 algorithm in non-flat areas but in flat areas uses the method of Garbrecht and Martz (1997) to assign flow directions away from higher ground and towards lower ground. Catchment boundaries were delineated using a contributing area threshold of 80 cells for all study catchments. Catchment areas and percentage broadleaf woodland covers were calculated using the same methodology in ArcMap as described earlier. The solid geology data showed that all the four control catchments had acidic geological substrates.

The geographical location of the 14 study catchments is shown in Figure 3.2 and their characteristics are summarised in Table 3.1. Broadleaf woodland cover ranged from 0 to 78.7% in the study catchments. Critical loads exceedance ranged from 0.0 to 1 keq H ha^{-1} yr^{-1} in the Scottish catchments (Glen Arnisdale and Loch Katrine area) while the catchments near Ullswater lie in a not-exceeded/adjacent square. Catchments YAR and NAR had the same acid-sensitivity with critical loads exceeded by 0.2 to 0.5 keq H ha^{-1} yr^{-1}. Catchment areas ranged from 8.6 ha in UL1 to 255 ha in NAR.

Table 3.1 Characteristics of the study catchments in Glen Arnisdale (GA), Loch Katrine (LK), Ullswater (UL), Yarner Wood (YAR) and Narrator Brook (NAR). Control catchments are GACON, LKCON, ULCON and NAR (see text for explanation). Critical load exceedance is from the provisional map for UK freshwaters

Catchment code	Outlet coordinates		Catchment area (ha)	% Broadleaf woodland cover	Critical load exceedance class (keq H ha^{-1} yr^{-1})
	Latitude (° north)	Longitude (° west)			
GA1	57.123	5.506	66.0	27.3	0.0-0.2
GA2	57.124	5.516	16.9	24.9	0.0-0.2
GA3	57.123	5.516	53.5	20.3	0.0-0.2
GACON	57.123	5.528	35.6	0.00	0.0-0.2
LK1	56.272	4.597	103	29.0	0.5-1
LK2	56.289	4.626	132	16.3	0.5-1
LK3	56.277	4.604	20.9	19.7	0.5-1
LK4	56.292	4.644	39.6	10.3	0.5-1
LKCON	56.284	4.616	47.6	0.00	0.5-1
UL1	54.595	2.823	8.6	53.4	Not exceeded-adjacent square
UL2	54.595	2.831	17.0	78.7	Not exceeded-adjacent square
ULCON	54.589	2.834	9.0	0.00	Not exceeded-adjacent square
YAR	49.967	3.696	134	49.9	0.2-0.5
NAR	49.959	3.979	255	2.00	0.2-0.5

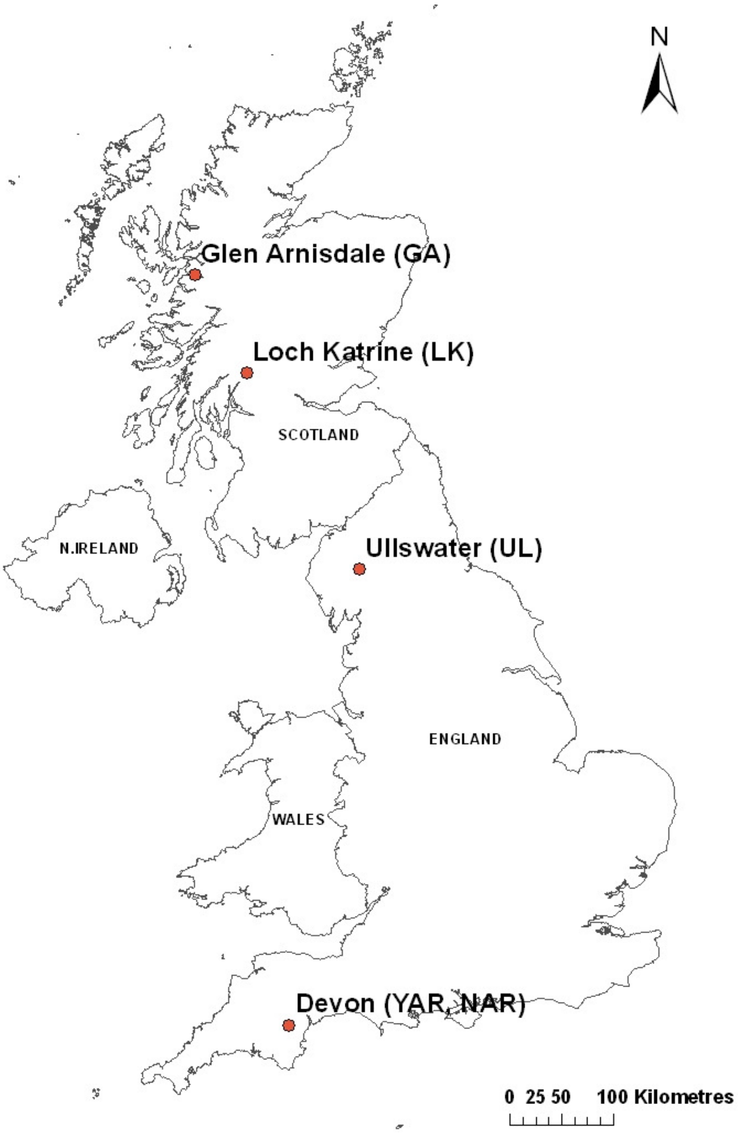

Figure 3.2 Location of the study catchments in Scotland and England

3.2 Catchment description

3.2.1 Methods for catchment characterisation

Section 3.2 gives the description of the study catchments. Topographical information (e.g. mean altitudes) was calculated from the catchment elevation grids. Mean catchment slope (in degrees) was calculated using the SLOPE command in Spatial Analyst in ArcMap. Catchment stream orders were determined using the flow accumulation grids and the STREAMORDER function in the GRID module in

ARCINFO which uses the Strahler classification method. Catchment perimeter was calculated to determine circularity indices (A/Ac). A/Ac is the ratio of catchment area, A, to area Ac (all in km^2), where Ac is the area of a circle with perimeter P (km) identical to the actual catchment perimeter (Kotoulas, 2001). Values close to 1 indicate round watersheds while values closer to 0 indicate more elongated catchment areas. More circular catchment areas are generally characterised by longer flow accumulation times producing more even flow patterns compared to elongated catchments. The proportions of different soil types within the catchments in Scotland were determined from the Soil Map for Scotland (1: 250 000) (MISR, 1981) and in the English catchments from the digital 1: 250 000 Soil Map of England and Wales (NSRI, 1984).

3.2.2 Glen Arnisdale (GA) catchments

3.2.2.1 Location and description

Glen Arnisdale is located in the north-west Highlands, Scotland, 340 km from Edinburgh (Figure 3.3). The catchments lie on land owned by the Arnisdale Estate and are adjacent to each other from west to east, from GACON, followed by GA3, GA2 and GA1 respectively (Figure 3.4). The distance between the outlets of GACON and GA1 was 1.5 km. The catchments were situated close to the sea at distances ranging from 1.9 to 2.9 km. The catchment outlets were located close to the valley floor and catchments had a wider range of altitudes between 489 and 640 m (Table 3.2). The terrain was quite steep with mean catchment slopes ranging from 26° to 29°. High slopes have resulted in steep rocky stream channels containing fast flowing water, with a large amount of rock debris deposited in the lower stream reaches.

Figure 3.3 Location of study catchments in Glen Arnisdale, NW Highlands and the Met Office station at Eilanreach

Table 3.2 shows the characteristics of the study catchments, including the value of circularity of each catchment. GA2 had the most elongated catchment area in the four catchments, indicating quicker peak flows. Broadleaf woodland cover, according to the NIWT-IFT dataset, ranged from 20.3% in GA3 to 27.3% in GA1, with no woodland cover in GACON (Table 3.2).

Daily rainfall data were available from 1969 until August 2004 through the British Atmospheric Data Centre (BADC) for the Met Office station at Eilanreach (Lat: 57.199 ºN, Long: 5.629 ºW) at 8 m elevation, located 14 km from the catchments (Figure 3.3). The mean annual rainfall (1969-2003) at this station was 2059 mm while total rainfall for 2003 was 1793 mm.

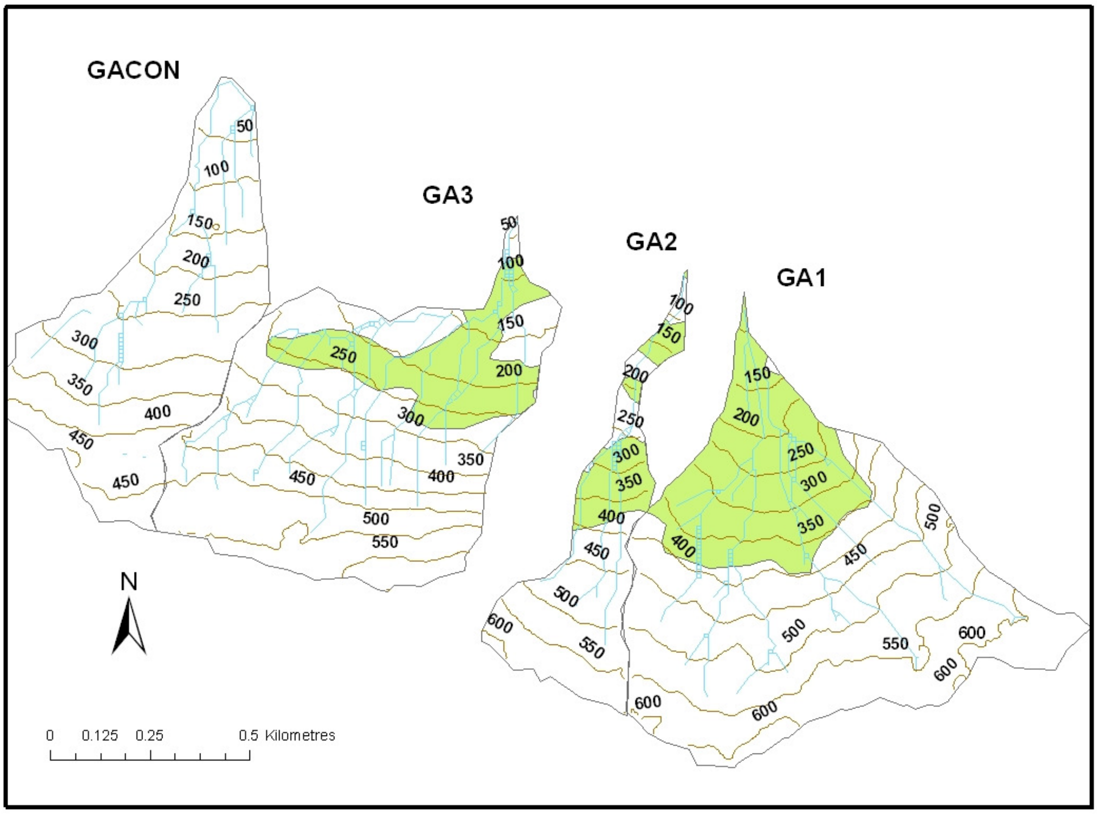

Figure 3.4 1: 10 000 contour maps of the study catchments in Glen Arnisdale (GA) (contours at 50 m intervals). Shaded areas show broadleaf woodland cover according to NIWT-IFT

Table 3.2 Characteristics of the study catchments in Glen Arnisdale (GA). Mean catchment altitude and slope is given with minimum and maximum altitudes in brackets

Catchments	Broadleaf woodland cover (%)	Area (ha)	Stream order	Altitude (m)	Mean slope (°)	Circularity
GA1	27.3	66.0	4th	444 (84-640)	29	0.6
GA2	24.9	16.9	3rd	428 (53-611)	28	0.3
GA3	20.3	53.5	3rd	338 (40-600)	29	0.6
GACON	0.0	35.6	3rd	272 (9-489)	26	0.5

3.2.2.2 Geology and soils

The geological substrate of the catchments was composed of quartz-feldspar-granulites belonging to the Moine group of metamorphic rocks (BGS, 1995). Catchment soils belonged to two main soil associations, Arkaig and Corby/Boundie/Dinnet (MISR, 1981). Arkaig soils include peaty gleys, peaty podzols and peaty rankers occurring on hillsides (0-500 m) with steep slopes. Brown forest soils, humus-iron podzols and some gleys and rankers occurred on hill and valley sides, usually below 400 m. Soils of the Corby/Boundie/Dinnet association are mainly peaty podzols, some humus-iron podzols and peat found at high altitude (500-700 m) in mounds, ridges and terraces with gentle to steep slopes. Non-rocky humus iron podzols, peaty podzols and some peaty gleys occurred at low altitudes towards the valley floor. The proportions of different soil types within each catchment are shown in Table 3.3. Also, mean soil pH in water for surface horizons (O and A) of the soil series present in the Glen Arnisdale catchments ranged from 4.72-4.79 and C/N values were around 21 (soil series chemistry data provided from the Macaulay Institute).

Table 3.3 Soil type composition (%) of the Glen Arnisdale catchments

Catchments	Peaty ranker	Mineral alluvial soil	Brown earth	Orohemi arctic podzol	Humus-iron podzol	Stagno podzol	Peaty gley	Raw peat soils
GA1	13.2	0.0	15.7	20.0	15.7	17.0	16.8	1.6
GA2	15.1	0.0	8.4	27.4	8.4	19.5	19.3	1.9
GA3	23.8	0.0	5.2	0.0	5.2	31.4	30.8	3.6
GACON	21.6	6.3	0.0	0.0	0.0	32.8	31.7	7.6

3.2.2.3 Vegetation

Downy birch (*Betula pubescens*) was the dominant tree species in the catchment woodlands with scattered oak trees (*Quercus petraea*). Alder (*Alnus glutinosa*) and hazel (*Corylus avellana*) were common in the wetter areas alongside stream banks. The woodland canopy was rather open. The Glen Arnisdale woodlands have not been surveyed for classification according to the National Vegetation Classification (NVC), but the woodland composition is typical of the upland birch woodland community (W17 *Quercus petraea-Betula pubescens-Dicranum majus* woodland) found in north-western Scotland where oak is scarce (Hall et al., 2004). The birch-dominated woodland covering the Glen Arnisdale catchments is shown in Figure 3.5.

Figure 3.5 Birch woodland covering the Glen Arnisdale catchments (June 2005)

The woodland areas have been affected in the past by deer grazing. A deer fence now encloses most of the woodland areas, including those inside the catchments, in order to protect the vegetation from deer grazing and encourage natural regeneration. There has not been any past management or disturbance, such as liming, in the area covered by the broadleaf woodland. Most of the woodland was present in the lower and middle sections of the catchments (Figure 3.4).

3.2.3 Loch Katrine area (LK) catchments

3.2.3.1 Location and description

The five catchments (LK1, LK2, LK3, LK4 and LKCON) lie within the Loch Lomond and Trossachs National Park and were situated 115 km from Edinburgh north-west of Loch Katrine (Figure 3.6), which has been used as a reservoir supplying water to Glasgow since 1859. The area around Loch Katrine belongs to Scottish Water and has been leased to the Forestry Commission since May 2005. Catchment LK1 was located by the north-west shore of Loch Katrine, LKCON 2 km north and catchments LK2, LK3 and LK4 after a further 0.8, 1.8 and 1.9 km to the north, respectively.

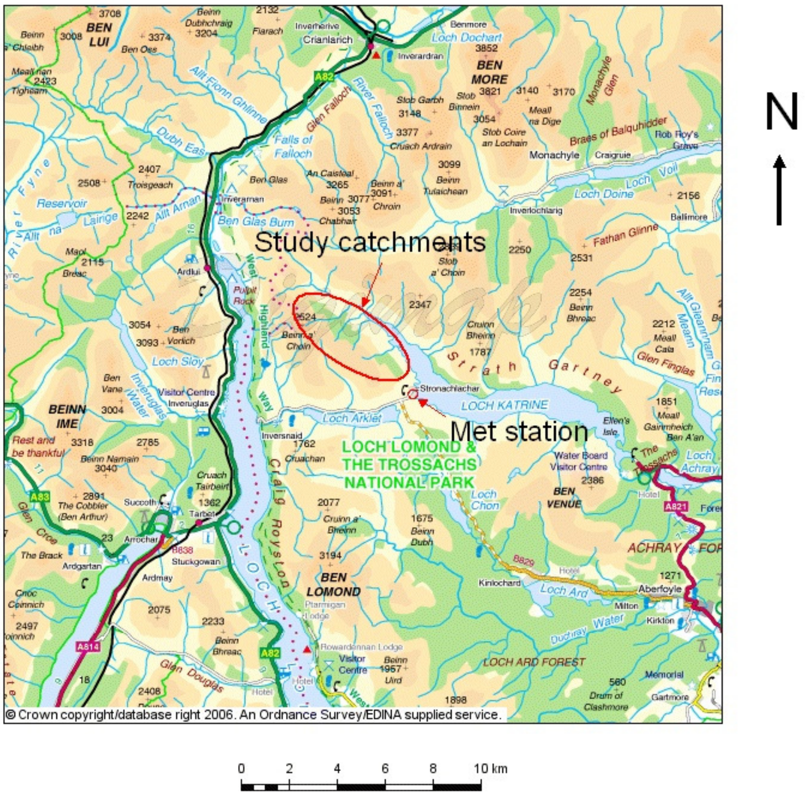

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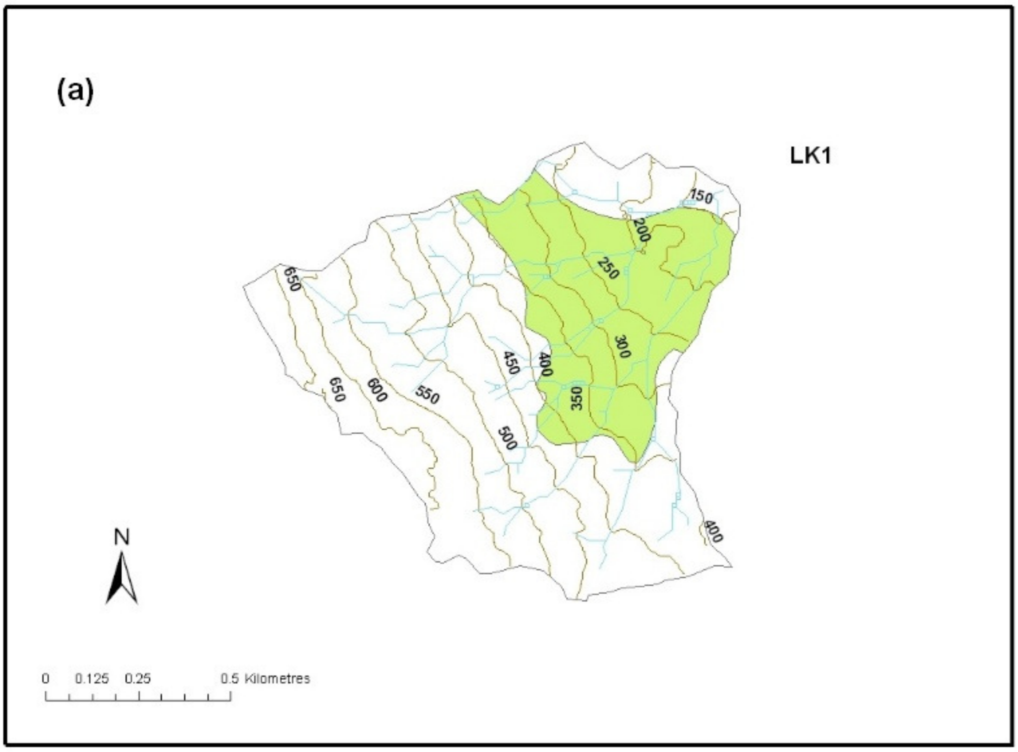
Figure 3.6 Location of the study catchments near Loch Katrine, Trossachs, Scotland, and the Met Office station at Stronachlachar

The topography of the west side of Loch Katrine is characterised by steep gradients (30° to 60°) at altitudes between 300 and 600 m, with lower gradients (< 15°) at lower altitudes below 300 m. Overall, mean catchment slopes were similar and steep, ranging from 23° in LK2 to 26° in LK1 and LK4 (Table 3.4). According to the NIWT-IFT dataset, broadleaf woodland covered 10.3% to 29.0% of the catchment areas (Table 3.4, Figures 3.7a-c).

Table 3.4 Characteristics of the study catchments in Loch Katrine (LK). Mean catchment altitude and slope is given and minimum and maximum altitudes in brackets

Catchments	Broadleaf woodland cover (%)	Area (ha)	Stream order	Altitude (m)	Mean slope (°)	Circularity
LK1	29.0	103.3	4th	412 (128-683)	26	0.6
LK2	16.3	132.3	3rd	461 (139-763)	23	0.5
LK3	19.7	20.9	2nd	367 (185-556)	24	0.5
LK4	10.3	39.6	3rd	502 (182-726)	26	0.4
LKCON	0.0	47.6	3rd	407 (134-681)	24	0.4



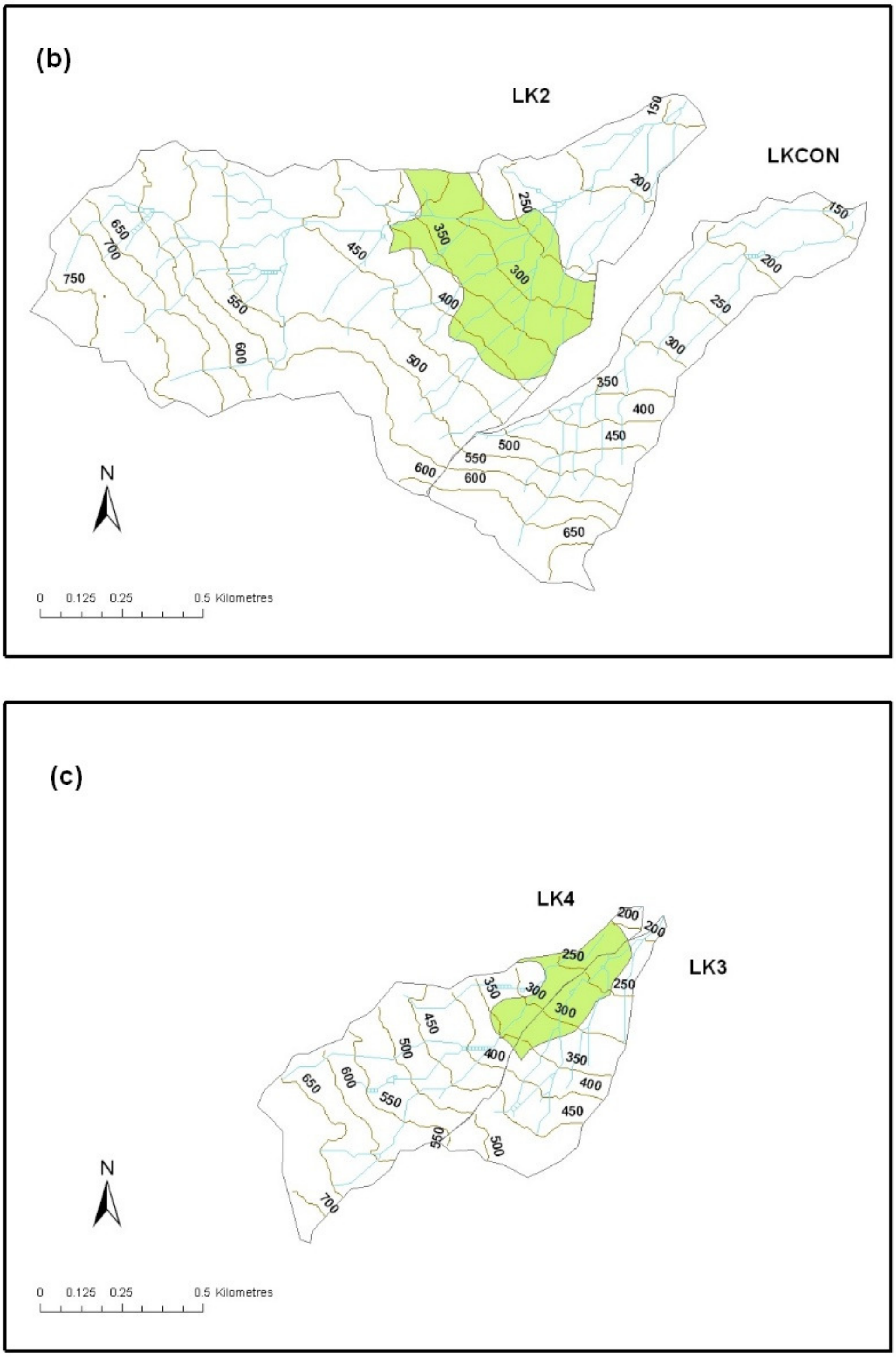


Figure 3.7 1: 10 000 contour map of study catchments (a) LK1, (b) LKCON and LK2 and (c) LK3 and LK4 in the Loch Katrine (LK) area (contours at 50 m intervals). Shaded areas show broadleaf woodland cover according to NIWT-IFT

Daily rainfall data were available through BADC from 1961 to 2005 for the Met Office station at Stronachlachar (Lat: 56.258 ºN, Long: 4.581 ºW) at 117 m elevation, located 4 km from LK1 and around 8 km from LK4 (Figure 3.6). The mean annual rainfall was 2275 mm (1961-2005) and total rainfall for 2005 was rather higher at 2778 mm.

3.2.3.2 Geology and soils

According to the BGS (1995) solid geology data the catchments lie on substrate composed of quartz-mica-schists, grits, shales and phyllites of the Upper Dalradian. Catchment soils belong to the Strichen association series and the main soil types present were humus-iron podzols, peaty podzols and some peaty gleys and rankers (MISR, 1981). Humus-iron podzols and stagnopodzols, dominated the catchment soil composition and covered the catchment areas at proportions ranging from 81% to 91%. Humus-iron podzols and some gleys occurred at low altitudes (<200 m) on valley moraines and close to the shore of Loch Katrine. Peaty podzols, humus-iron podzols and some gleys and rankers of rocky nature were found at higher altitudes (200-600 m) in hills with steep slopes. Rankers, peaty podzols and some humus-iron podzols and gleys of a very rocky nature were also found on hillsides with very steep slopes at altitudes above 600 m. The proportion of different soil types within the catchment areas is shown in Table 3.5.

Table 3.5 Soil type composition (%) of the Loch Katrine catchments

Catchments	Peaty Ranker (%)	Humus-iron podzol (%)	Stagnopodzol (%)	Peaty gley (%)
LK1	7.7	48.0	41.8	2.5
LK2	17.6	35.4	45.7	1.3
LK3	0.0	66.8	26.0	7.2
LK4	8.2	49.7	38.8	3.3
LKCON	3.7	57.9	33.5	4.9

Mean soil pH in water for surface horizons (O and A) of the soil series present in the Loch Katrine area catchments ranged from 4.13-4.24 and C/N values were around 21 (soil series chemistry data provided from the Macaulay Institute).

3.2.3.3 Vegetation

The woodlands in the catchment areas were dominated by downy birch (*Betula pubescens*) with a quite open canopy. Two woodland surveys were conducted of Glengyle birchwood (Lat: 57.519 °N, Long: 5.214 °W) in 1993 and 1997 (Thiel & Hannah, 1997) which covers the southern part of the LK1 catchment area and is typical of the woodlands covering the other Loch Katrine catchments. The woodland survey in 1993 classed Glengyle woodland as NVC W4a (*Betula pubescens*-*Molinia caerulea* woodland, *Sphagnum* sub-community). The 1997 survey reported that the woodland was almost exclusively dominated by an even-aged stand of downy birch with a very open canopy, which was interspersed in a mosaic-like fashion with areas of marshy grassland and a large area of acid grassland, which itself was interspersed with a network of acid flushes, as well as an area of fen. The woodland was ancient and natural regeneration was absent due to continuous sheep and deer grazing pressure. In terms of the distribution of the woodland, most of the woodland in the four forested catchments was present in the lower and middle reaches at elevations between 250 and 350 m, with no woodland cover above 400 m in catchments LK3 and LK4 (Figures 3.7a-c). Part of the birchwoods covering the Loch Katrine area catchments is shown in Figure 3.8.

Figure 3.8 View of the birchwoods covering the Loch Katrine area catchments (June 2005)

3.2.4 Ullswater area (UL) catchments

3.2.4.1 Location and description

The catchments were located on the south-eastern shore of Ullswater, in the eastern part of the Lake District National Park in Cumbria, north-west England, 196 km from Edinburgh (Figure 3.9). Catchments UL1 and UL2 are adjacent to each other and their outlets were located where the streams flowed out of the woodland into the fields. Catchment ULCON lay 0.7 km to the south.

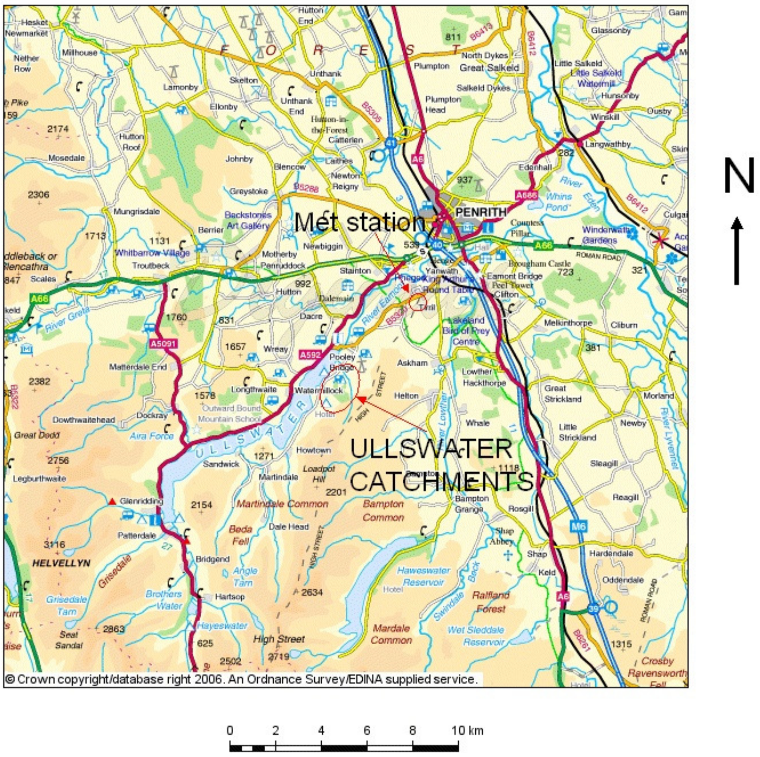


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Figure 3.9 Location of study catchments near Ullswater, Cumbria, NW England, and Met Office station at Penrith Tirill

Catchments UL1 and UL2 were characterised by gentle relief with mean catchment slopes of 9° and 10° respectively, while the mean catchment slope of ULCON was higher at 22° (Table 3.6). The Ullswater area catchments had smaller altitude range and gentler slopes than the Scottish catchments. All three catchments had long and narrow catchment areas. Broadleaf woodland cover was the highest of the study catchments in UL1 and UL2 and was 53.4% and 78.7%, respectively (Table 3.6, Figure 3.10).

Table 3.6 Characteristics of the study catchments near Ullswater (UL). Mean catchment altitude and slope is given with minimum and maximum altitudes in brackets

Catchments	Broadleaf woodland cover (%)	Area (ha)	Stream order	Altitude (m)	Mean slope (°)	Circularity
UL1	53.4	8.6	1st	306 (204-401)	9	0.2
UL2	78.7	17.0	3rd	265 (176-386)	10	0.3
ULCON	0.0	9.0	1st	313 (187-462)	22	0.2

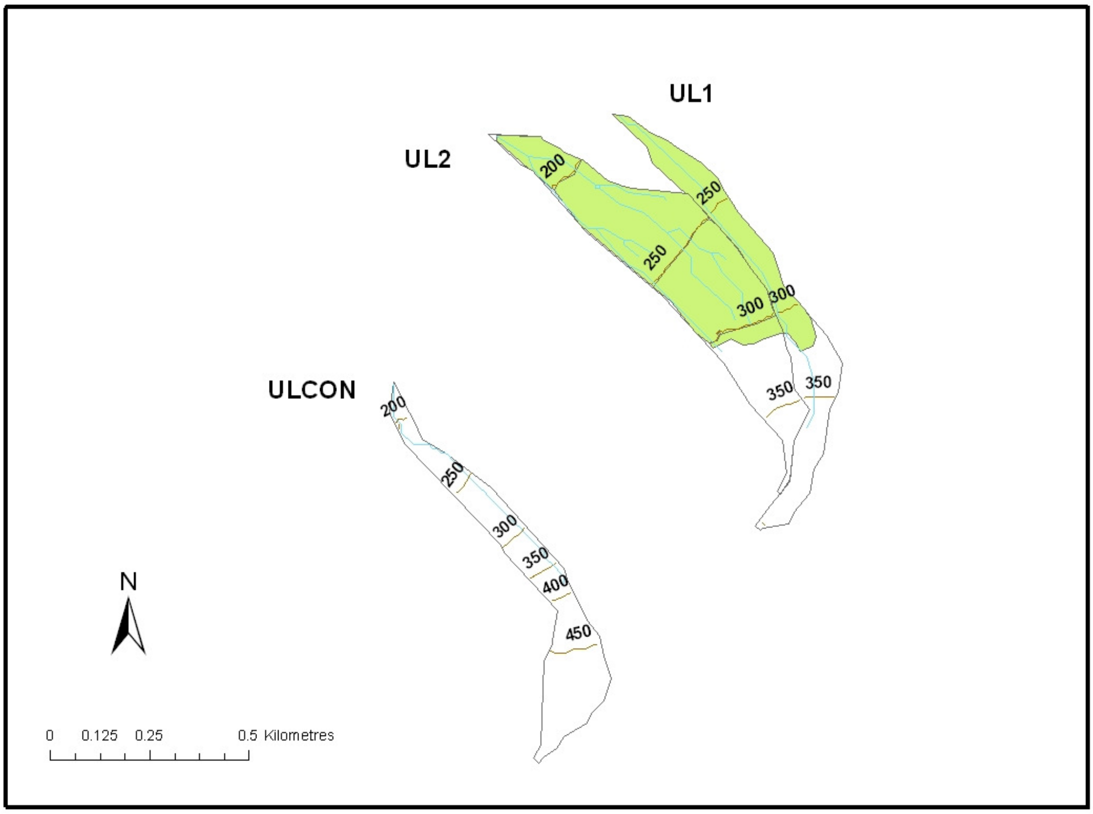

Figure 3.10 1: 10 000 contour maps of study catchments near Ullswater (UL) (contours at 50 m intervals). Shaded areas show broadleaf woodland cover according to NIWT-IFT.

Daily rainfall data were available through the BADC from 1969 to 2005 for the Met Office station at Penrith Tirill (Lat: 54.628 ºN, Long: 2.779 ºW) at 182 m elevation, located about 4 km to the east of the catchments (Figure 3.9). Mean annual rainfall for the period 1969-2005 was 1010 mm while in 2005 the annual rainfall was 912 mm.

3.2.4.2 Geology and soils

The geological substrate of the catchments belongs to the Llarvirn and Arenig group with small areas of undifferentiated tuff, mainly andesitic (BGS, 1995). These rocks belong to the Skiddaw Slates Group which is the oldest group of rocks in the Lake District (Jarvis et al., 1984) and was formed during the Ordovician period.

Soil types present in the two forested catchments are mainly peaty gley soils and stagnogley soils of the Wilcocks association, while ULCON is largely covered by podzolic rankers of the Bangor association, with smaller contributions from stagnopodzol, stagnogley and peaty gley soils of the Brickfield 2 association (NSRI, 1984) (Table 3.7). Almost 15% of the area of ULCON was covered by iron pan stagnopodzols of the Hexworthy association (651b) located at the highest catchment altitudes above 350 m.

Table 3.7 Soil type composition (%) of the Ullswater catchments

Catchments	Podzolic ranker (%)	Stagnopodzols (%)	Stagnogley (%)	Peaty gley (%)
UL1	0.0	0.0	9.0	91.0
UL2	3.3	0.0	19.0	77.7
ULCON	70.4	14.9	12.3	2.4

3.2.4.3 Vegetation

The woodland cover in the UL1 and UL2 catchments is part of the Barton Park woodland which is considered to be a relic of more extensive woodland in the past. The first edition Ordnance Survey map of 1863 shows the woodland cover to be similar to today. Despite the lack of historic information on how man's activities have affected the woodland, the past management of the woodland can be inferred from a knowledge of local agricultural practices, ground conditions and tree species tolerance to grazing pressure. Presently the remaining woodland is dominated by alder but it is quite possible that significant areas of drier oak woodland might have been cleared for agriculture. It is also likely that ash and other species would have been present in the past but they have been lost due to methods such as ring barking used for clearing woodlands for agriculture. Alder is less palatable to stock and deer and damaged trees regenerate well, so this is probably why the remaining woodland is dominated by alder. Part of the alder-dominated Barton Park woodland covering catchments UL1 and UL2 is shown in Figure 3.11.

Figure 3.11 View of the alder-dominated woodland covering the Ullswater area catchments (June 2005)

A survey of the Barton Park woodland was carried out in 1980 (Phil Taylor, Lake District Park Authority, personal communication) using Peterken stand types (Peterken, 1967, the method used at that time) rather than the National Vegetation Classification. The survey found that according to the Stand Type Classification (Peterken, 1967) most of the woodland is a mix of wet valley alderwoods, upland birch cherry alderwoods and slope alderwood. The rest of the woodland area is covered by open acid sessile oak-hazel-ashwoods, upland hazel-sessile oakwoods and western valley ash-wych elm woods. The different tree species formed a dense canopy of variable height with multi-stemmed alder trees being the dominant species. Most of the woodland area in UL1 and UL2 was concentrated in the lower and middle reaches of the catchments below 350 m elevation (Figure 3.10). The main present land-use of the woodland in Barton Park is grazing by cattle from the nearby farm during the spring months. The fields downhill of the woodland have been artificially improved in the past with lime so care was taken to ensure that the sampling points were located uphill before the streams entered the improved fields.

3.2.5 Devon catchments (YAR and NAR)

3.2.5.1 Location and description

The Yarner Wood (YAR) and Narrator Brook (NAR) catchments are in Devon, south-west England, and are both inside the boundary of the Dartmoor National Park (Figure 3.12). YAR is located within the Yarner Wood National Nature Reserve (NNR), owned and managed by English Nature. NAR is located upstream of the Burrator Reservoir, 20 km south-west of YAR.

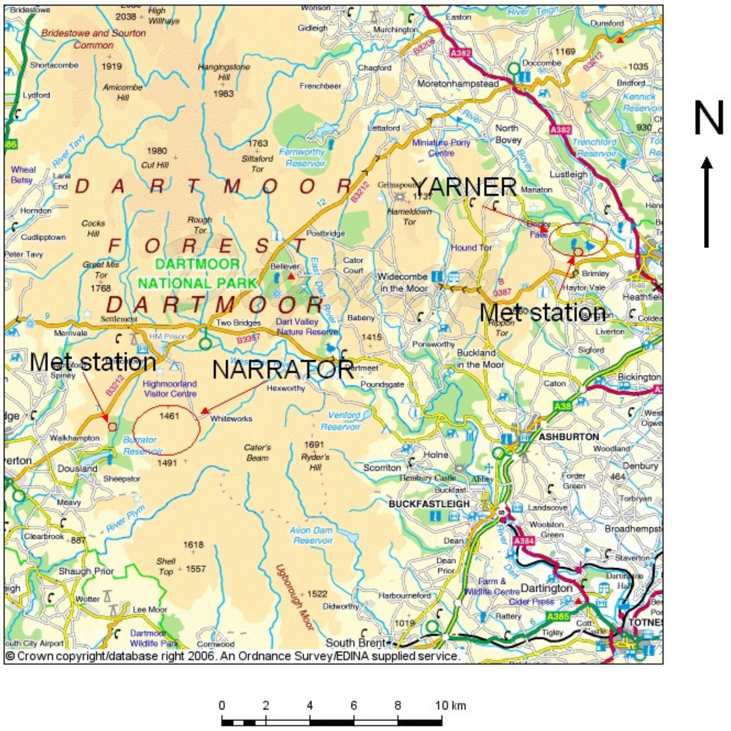

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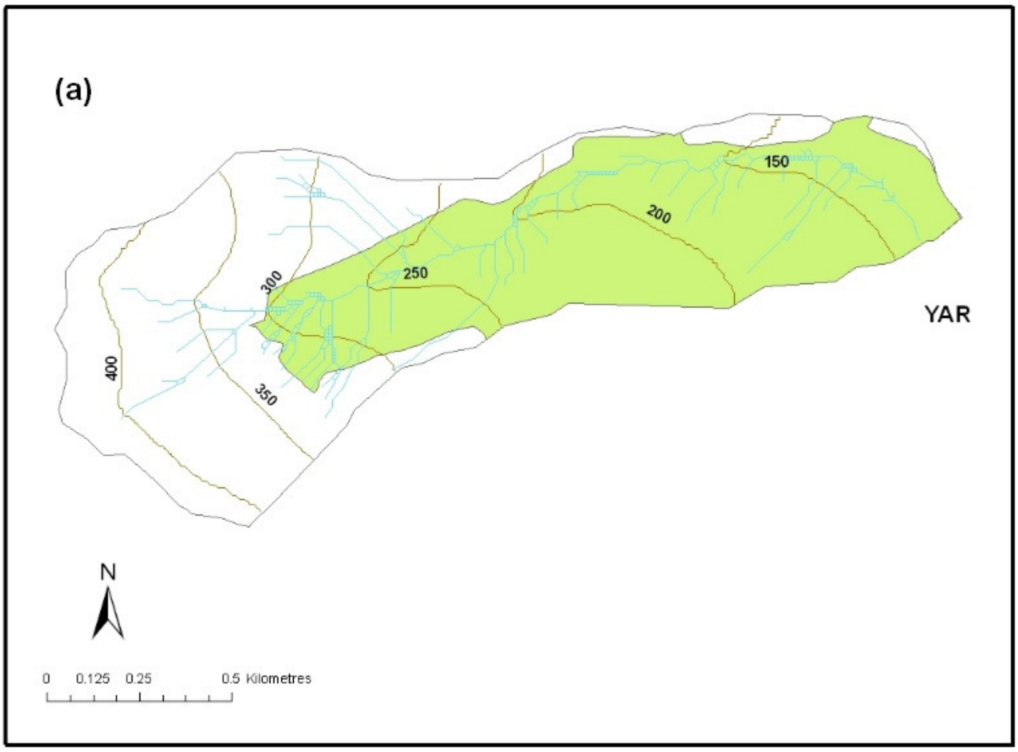
Figure 3.12 Location of study catchments Yarner Wood (YAR) and Narrator Brook (NAR), Devon, SW England, and the Met Office stations at Yarner Wood and Leather Tor Farm

Table 3.8 contains a summary of the catchment characteristics. The altitude of the catchment YAR outlet was 108 m and the maximum altitude was at 411 m (Table 3.8, Figure 3.13a). Most of the catchment area is characterised by gentle relief with a mean catchment slope at 11° and few slopes exceeding 20º. Broadleaf woodland cover in YAR was the third highest cover of all study catchments.

Table 3.8 Characteristics of the Yarner Wood (YAR) and Narrator Brook (NAR) catchments in Devon. Mean catchment altitude and slope is given with minimum and maximum altitudes in brackets

Catchments	Broadleaf woodland cover (%)	Area (ha)	Stream order	Altitude (m)	Mean slope (°)	Circularity
YAR	49.9	134	4th	272 (108-411)	11	0.5
NAR	2.0	255	5th	366 (255-456)	18	0.8

As mentioned earlier, NAR has been part of the Acid Waters Monitoring Network (AWMN) since 1988. The catchment area draining to the monitoring point since 1991 is 255 ha via a 5th order stream network (Table 3.8). The catchment is characterised by gentle relief with a mean slope of 18°. The terrain is steeper in the lower parts of the catchment with slopes between 20° and 30° but the terrain becomes flatter at the more extensive higher altitudes. Overall, 83% of the catchment area had slopes <10º. Altitude range was small compared to the other study catchments. A small proportion of the catchment (2%) near the outlet is covered by broadleaf woodland (Figure 3.13b).



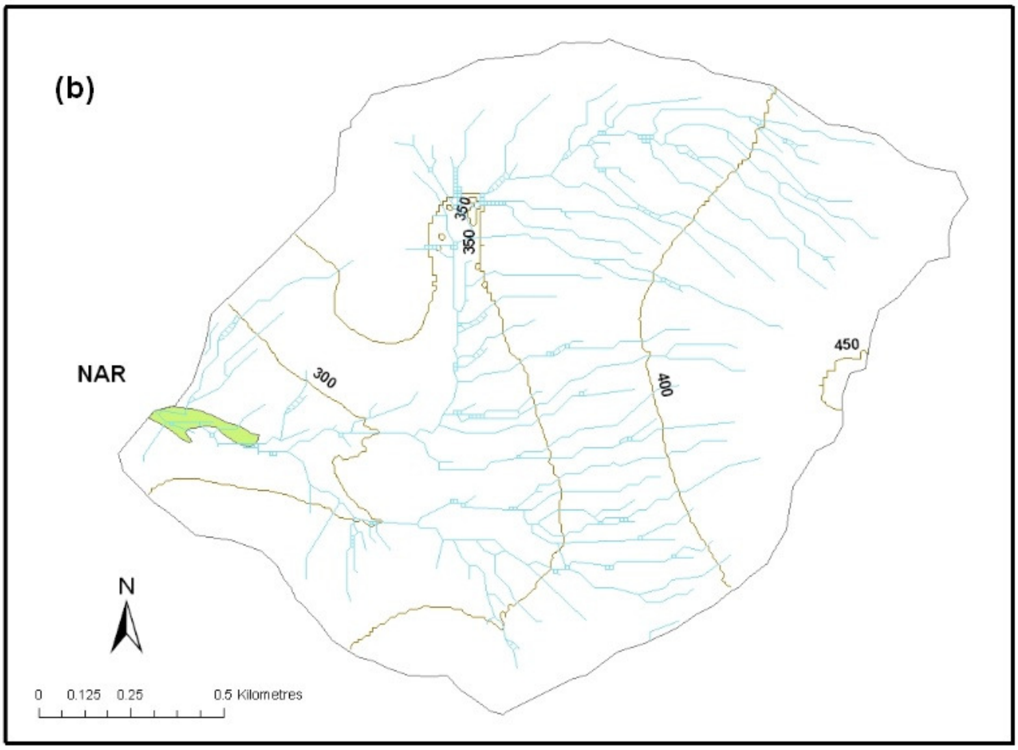


Figure 3.13 1: 10 000 contour map of study catchments (a) Yarner Wood and (b) Narrator Brook (NAR) (contours at 50 m intervals). Shaded areas show broadleaf woodland cover according to NIWT-IFT

Daily rainfall amounts for YAR were obtained from the Yarner Wood Met Office station (Lat: 50.599 ºN, Long: 3.715 ºW) at 198 m, located at the southern edge of the Reserve, around 300 m from the YAR outlet (Figure 3.12). Available meteorological data held in BADC were from 1961 up to present day. Mean annual rainfall for the period 1961-2005 was 1320 mm while the 2005 rainfall was 1251 mm in 2005. A station of the Acid Deposition Monitoring Network (ADMN) operated by English Nature is also located 200 m from the YAR catchment outlet (Lat: 50.585 °N, Long: 3.702 °W).

Daily rainfall amounts for NAR were obtained from the Leather Tor Farm Met Office station (Lat: 50.509 ºN, Long: 4.022 ºW) located close to the northern shore of the Burrator Reservoir (Figure 3.12). Available meteorological data held in BADC were from 1961 up to 2004. Mean annual rainfall for the period 1961-2004 was 1669 mm while 1451 mm of rainfall occurred in 2004.

3.2.5.2 Geology and soils

According to the BGS (1995) solid geology data, YAR is underlain by sandstones and slates of the Upper Carboniferous known as the Culm Measures in Devon and Cornwall (Clayden, 1971). NAR is underlain by Dartmoor granite along with syenite, granophyre and allied types.

The soils of the Yarner Wood were found to have extraordinarily hard and compact bluish grey Ea horizons and were classified as “indurated podzols” (Fenton, 1960). Soils within the YAR catchment were dominated by brown podzolic soils and stagnopodzols (NSRI, 1984) (Table 3.9). Brown podzolic soils covered 40.8% of the catchment area, 37.6% from the Manod association and the remaining 3.2% from the Moor Gate association. The rest of the catchment area (59.2%) is covered by stagnopodzols, mainly in the upper and lower parts, 45.6% by the Hafren association and 13.6% by iron pan stagnopodzols of the Hexworthy association.

Table 3.9 Soil type composition (%) of the YAR and NAR catchments

Catchments	Brown podzolic soils	Stagnopodzols	Peaty gley
YAR	40.8	59.2	0.0
NAR	28.9	37.9	33.2

The main soil types within the NAR catchment area were podzols and peaty gleys derived from granite (NSRI, 1984). Podzols covered 66.8% of the catchment area: 37.9% by iron pan stagnopodzols of the Hexworthy association, 18.1% by humic brown podzolic soils of the Moor Gate association and 10.8% by typical brown podzolic soils of the Moretonhampstead association (Table 3.9). The rest of the catchment area (33.2%) was covered by cambic stagnohumic gley soils of the Princetown association.

Although YAR and NAR are 20 km apart, NAR was considered as a suitable control for YAR as the two catchments have geologies of similar acid-sensitivity and also similar soil types.

3.2.5.3 Vegetation

The Yarner Wood NNR is managed by English Nature and is part of the East Dartmoor and Heaths NNR and also of the South Dartmoor Special Area of Conservation (SAC), due mainly to the rare habitat of western oakwood found in the Reserve. The site is characterised as ancient semi-natural woodland and is also a Site of Special Scientific Interest (SSSI). The latest woodland survey was conducted by English Nature in March 2005 (English Nature, 2005). The survey was of the whole woodland and not only the 67 ha of the northern part of the woodland covering the YAR catchment. The woodland supports mainly NVC W17b (*Quercus petraea-Betula pubescens-Dicranum majus*) with bilberry the dominant ground flora species. Sessile oak is the most common canopy species, with only occasional downy birch and an understorey of hazel with holly and rowan. The community grades into W16b (*Quercus* spp.-*Betula* spp.-*Deschampia flexuosa* woodland) on lower slopes with sessile oak dominating the canopy and birch and rowan being limited to gaps and margins. On some higher slopes the community grades into W11a (*Quercus petraea-Betula pubescens-Oxalis acetosella*) with the canopy usually dominated by oak rather than birch and the shrub layer dominated by hazel, downy birch and rowan. Riparian areas are variously identified as W4c (*Betula pubescens–Molinia caerulea* woodland), W5c (*Alnus glutinosa-Carex paniculata* woodland) and W7b (*Alnus glutinosa-Fraxinus excelsior* woodland). Most of the woodland within the YAR catchment area occurs in the lower and middle reaches below 350 m (Figure 3.13a). Part of the Yarner Wood covering catchment YAR is shown in Figure 3.14.

Figure 3.14 View of the Yarner Wood close to the outlet of catchment YAR in Devon (December 2004)

Almost all of the NAR catchment area (98%) is covered by blanket bog dominated by *Molinia caerulea* and acid grassland with a small area of valley bog. The remainder is covered by deciduous woodland consisting mainly of oak trees. The catchment is utilised for low-intensity grazing by sheep, cattle and ponies.

3.3 Streamwater sampling from the study catchments and chemical analysis

3.3.1 Streamwater sampling

This section describes the sampling strategy and briefly outlines the chemical analysis of the streamwater samples collected from the study catchments. The results of an inter-laboratory comparison of chemistry from selected streamwater samples are also presented, along with the description of streamflow monitoring in a selected study catchment.

3.3.1.1 Sampling strategy

Streamwater samples were collected from the catchment outlets in high flow conditions in January to April 2005 and November 2005 to April 2006. Streamwater samples from the nine catchments in Glen Arnisdale and the Loch Katrine area were collected from Edinburgh. Sampling was more frequent from the Loch Katrine catchments to assess how representative is the collection of few samples of overall streamwater chemistry. Samples from the Yarner Wood catchment (YAR) were collected by staff from the Forest Research field station in Exeter and from the Ullswater catchments by staff from Eden Rivers Trust based in Appleby-in-Westmorland, Cumbria. Overall, only two high flow samples were collected from the Glen Arnisdale catchments, ten to nine from the Loch Katrine area catchments, five from the Ullswater area catchments and eight from YAR. Additional low flow streamwater samples were collected during summer 2005 from the Scottish catchments and the catchments near Ullswater. Metre rules were placed at the catchment outlet points to determine relative flow conditions on each sampling occasion and streamwater depth was measured to the nearest 0.5 cm. Narrator Brook streamwater chemistry data for 2005 were obtained from the Environmental Change Research Centre (ECRC), University College London. Three monthly streamwater samples from NAR for January, February and March 2005 were included in the analysis to coincide with the samples collected from the Yarner Wood catchment. Dates and number of streamwater samples collected from the study catchments are shown in Tables A.1-A.5 (Appendix A).

Rainfall information from the UK Met Office website was used to schedule sample collection from the study catchments. Effort was made to collect streamwater samples during wet periods with more than three days antecedent rainfall when there was greater chance of high soil saturation producing more overland flow and higher flow conditions. Overall rainfall amounts in 2005 were close to average for Scotland but below average for England and Wales (Met Office). Also, rainfall was quite varied, both spatially and temporally, making it difficult to sample in high flow conditions. Additionally, January and February 2006 had below average rainfall for all parts of the UK, especially for England and Wales, while there was above average rainfall in March 2006. Thus, for 2006, most streamwater samples from the catchments near Ullswater and from Yarner Wood were collected during a wet period in early March.

3.3.1.2 Streamwater sampling protocols

Sampling protocols were given to Forest Research and Eden Rivers Trust staff prior to streamwater sample collection. Sample bottles used were 500 ml high density polyethylene (HDPE) bottles. When sample bottles had to be re-used they were acid washed to prevent sample contamination.

When collecting streamwater samples, the procedure listed below was followed, based on water quality monitoring guidelines published by the United Nations Environment Programme (UNEP) and the World Health Organisation (WHO) (Bartram and Ballance, 1996).

During sample collection it was necessary to:

- Check that there was limited presence of epiphytes or other aquatic vegetation in the actual stream section from which the streamwater sample was collected.

- Check that the sample bottles to be filled were correctly labelled. Sample bottles should not have been opened prior to the collection time.

- Collect the streamwater sample upstream to avoid including any sediment/leaves disturbed by the sampler.

- Rinse the sample bottles and the bottle caps three times with portions of water from the stream before filling it.

- Fill the bottle by holding the bottle near its bottom and submerging it to a depth of about 10-20 cm, with the mouth facing slightly downwards and towards the direction of water flow. Turn the bottle upright to fill and fill to the brim. Avoid collecting dead leaves or small pieces of wood debris in the sample.

- Keep the samples cool until returning to the laboratory/field station (e.g. in a coolbox, if available).

Samples from the Ullswater and Yarner Wood catchments were sent to Edinburgh by courier within 24 to 48 hours after collection. Icepacks were used during transportation to keep sample bottles cool at temperatures around 4 ºC. On arrival at Edinburgh, streamwater samples were taken immediately to the laboratory for analysis.

3.3.2 Streamwater chemical analysis

Streamwater was analysed for pH, Gran alkalinity, base cations (calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K)), chloride (Cl), sulphate (SO_4), nitrate (NO_3), ammonium (NH_4) and soluble trace metals (aluminium (Al), manganese (Mn), iron (Fe), lead (Pb) and zinc (Zn)). The streamwater parameters analysed were necessary for: a) investigating the effect of percentage woodland cover on streamwater chemistry, b) calculating streamwater critical loads and c) investigating internal solute relationships and processes controlling streamwater chemistry. Standard methods were used and a summary of the streamwater chemical analysis is shown in Figure 3.15. Sample handling, chemical analysis techniques and instrumentation used for the determination of the chemical species are described in Section A.2 (Appendix A).

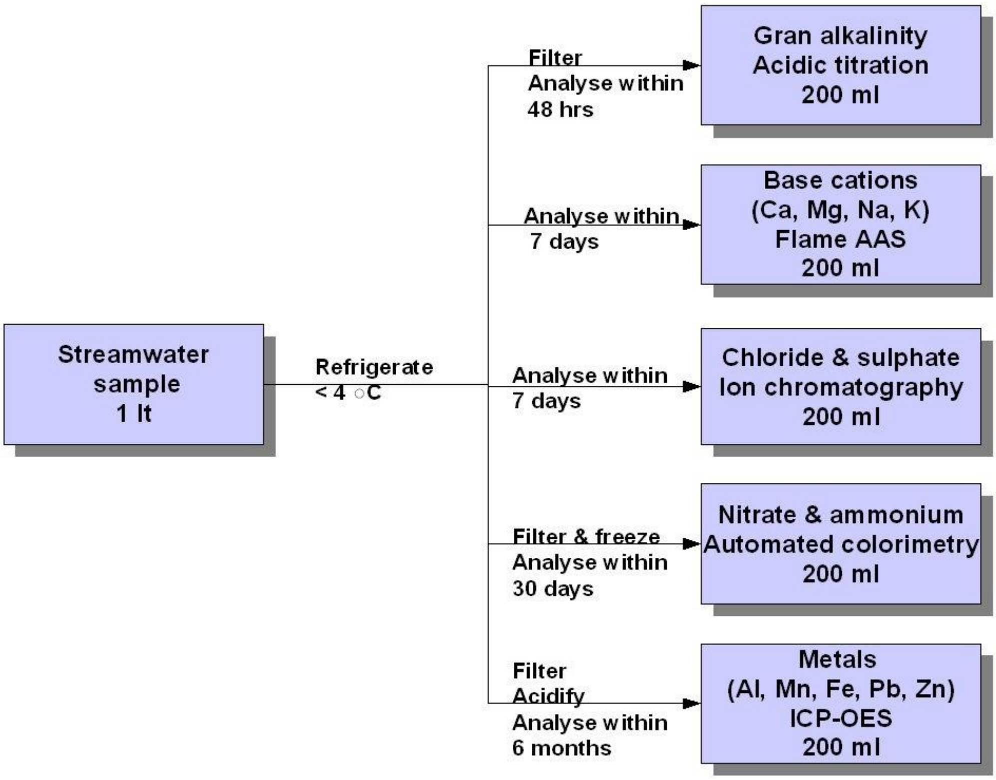


Figure 3.15 Summary flowchart of chemical analysis of streamwater samples

3.3.3 Inter-laboratory comparison of streamwater samples with Forest Research

For external quality assurance of the streamwater chemistry results, an inter-laboratory comparison of streamwater sample analysis was conducted on two occasions. Additional streamwater samples were collected from the Yarner Wood (YAR) catchment on March 30th 2005 and from the Loch Katrine (LK) area catchments on November 2nd 2005 and were sent for analysis at the Forest Research Station at Alice Holt, Surrey. Analytical techniques used by Forest Research were similar to the ones used in the laboratories at Edinburgh: Gran alkalinity was analysed using automated acidic titrations, ion chromatography was used for anion

(Cl, SO_4 and NO_3) determinations and ICP-OES for metal (Ca, Mg, Na, K, Al, Mn, Fe, Pb and Zn) determination. The results of the inter-laboratory comparison are given in Tables 3.10 and 3.11.

Table 3.10 Concentrations of Gran alkalinity (µeq l^{-1}), Ca, Mg, Na, K, Cl, SO_4, NO_3, NH_4 (mg l^{-1}) and Al, Mn, Fe, Pb and Zn, (µg l^{-1}) for sample from YAR analysed by Forest Research and the School of GeoSciences

	Forest Research	GeoSciences
Alkalinity	32.8	28.7
Ca	1.08	0.64
Mg	1.31	1.15
Na	7.20	6.02
K	0.63	0.61
Cl	11.7	10.9
SO_4	4.07	3.77
NO_3	2.38	2.59
NH_4	0.00	0.00
Al	49.0	48.0
Mn	5.00	6.00
Fe	18.0	16.0
Pb	1.00	6.00
Zn	11.0	4.00

Table 3.11 Concentrations of Gran alkalinity (μeq l^{-1}), Ca, Mg, Na, K, Cl, SO_4, NO_3, NH_4 (mg l^{-1}) and Al, Mn, Fe, Pb and Zn, (μg l^{-1}) for sample from the Loch Katrine area catchments analysed by Forest Research and the School of GeoSciences

	Forest Research					GeoSciences				
	LK1	LK2	LK3	LK4	LK CON	LK1	LK2	LK3	LK4	LKC ON
Alkalinity	45.6	11.6	24.4	65.2	62.0	42.0	7.50	26.2	64.0	72.8
Ca	1.49	0.82	1.07	1.61	1.52	1.50	0.84	0.99	1.59	1.52
Mg	0.49	0.40	0.40	0.55	0.57	0.50	0.42	0.41	0.56	0.58
Na	2.42	2.22	2.51	2.25	2.43	2.44	2.33	2.56	2.34	2.45
K	0.30	0.21	0.23	0.24	0.32	0.33	0.34	0.31	0.32	0.35
Cl	3.85	3.85	3.98	3.69	3.74	3.54	3.50	3.76	3.23	3.56
SO_4	1.89	1.52	1.70	2.04	1.93	1.76	1.48	1.70	2.02	1.95
NO_3	0.27	0.19	0.18	0.34	0.35	0.43	0.35	0.28	0.45	0.35
NH_4	0.05	0.04	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	56.0	55.0	46.0	31.0	26.0	68.0	60.0	46.0	33.0	26.0
Mn	1.00	2.00	3.00	1.00	1.00	3.00	8.0	11.0	2.00	6.00
Fe	58.0	143	67.0	43.0	48.0	95.0	159	75.0	59.0	89.0
Pb	3.00	2.00	4.00	2.00	0.00	1.00	0.00	0.00	0.00	0.00
Zn	5.00	9.00	444	3.00	3.00	7.00	7.00	7.00	6.00	7.00

Overall, the results from the inter-laboratory exercise show good agreement between solute concentrations measured by laboratories in the School of GeoSciences and Forest Research. Mean difference in concentrations between Forest Research and GeoSciences analyses was 0.4 to 8% for each determinant, apart from K, Fe, Mn and Zn, where samples concentrations were low. Analysis from GeoSciences of streamwater samples from the Loch Katrine area catchments for NO_3 gave mean concentration around 40% higher than Forest Research analysis. This is probably because NO_3 is unstable in water and concentrations depend on sample preservation, especially water temperature, and transportation time to the laboratories (Bartram and Ballance, 1996). Samples from the YAR catchment arrived in Edinburgh the day after collection and, due to the cold conditions present at that time, were adequately preserved during transportation. Samples from the Loch Katrine area were transported to Edinburgh inside a cool box with ice-packs and then were frozen immediately, whilst the additional samples were placed in the fridge overnight and sent the next day to Forest Research. This additional time meant that sample degradation was possible during transportation and could have caused the lower NO_3 concentrations measured by Forest Research. The differences in the measured Mn and Fe concentrations for all samples between Forest Research and GeoSciences were not significant overall for the study objectives.

3.3.4 Streamflow monitoring in catchment LK1

Streamflow monitoring was conducted in catchment LK1 (Loch Katrine area) to investigate how representative the “high flow” streamwater samples collected were of high flow conditions. Catchment LK1 was chosen for flow monitoring because: a) it is located close to Edinburgh and streamwater samples could be collected more frequently, b) it is easily accessed and c) it has the highest broadleaf woodland cover of the Loch Katrine area study catchments. Streamwater depth was monitored in a stable section of the channel using a pressure transducer and converted to a flow using a ratings curve constructed from manual measurements of flow using the flow velocity-area method. A Druck PDCR1830 pressure transducer was installed in the catchment outlet and was connected to a CR510 Campbell Scientific datalogger, in a waterproof container on the streambank adjacent to the measurement point. Depth measurement with the transducer is achieved by measuring the difference in pressure between the atmosphere and the pressure transducer. The pressure transducer converts the recorded pressure into an analogue electrical signal by the physical deformation of strain gauges which are bonded into the diaphragm of the pressure transducer and wired into a wheatstone bridge configuration. Pressure applied to the transducer produces a deflection of the diaphragm which introduces strain to the gauges and produces an electrical resistance change proportional to the pressure. The transducer also takes account of variations in atmospheric pressure. The transducer sensor and cable were placed in a stilling well (a 40 cm diameter, 1 metre length plastic tube with holes drilled in the side) by the streambank, both to protect the sensor from damage and to act as a firm reference point for depth measurement. The datalogger was programmed and records of the electrical output were recorded and data stored in SMC 256K byte RAM memory cards inserted in the data logger. The cards were loaded with a programme file recording electrical output every 10 minutes.

Streamflow at the monitoring point was measured on 11 occasions using a current meter and the velocity (V)-area (A) method. A Model 1205 Price Type “Mini” current meter with a top-setting wading rod and a CMD 9000 Digimeter (Scientific Instruments, Inc., WI, USA) were used to determine mean velocity. The channel cross-section was divided into three segments and the mean velocity at 0.6 of the water depth and the cross-sectional area of flow were measured in each segment. The flow was calculated at each of the three segments by multiplying V and A, and total flow was the sum of the flows of the three segments. The measured discharge values in LK1 ranged from 0.03 to 0.97 $m^3 s^{-1}$. During flow measurements, the data logger was programmed to record water depth every 5 seconds. A ratings curve was constructed by regressing the calculated discharge values against the mean of the recorded 5 s millivolt readings from the pressure transducer, to acquire a relationship enabling flow determination from all pressure transducer readings (Figure 3.16).

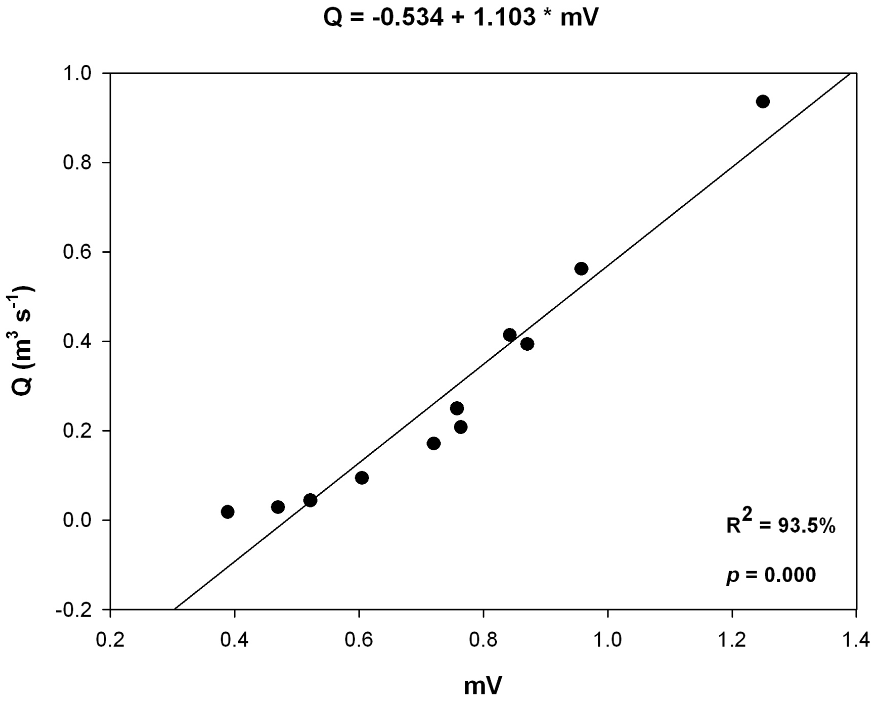


Figure 3.16 Discharge vs. millivolt readings from the pressure transducer for 11 flow measurements in catchment LK1. The regression equation is also given

The ratings curve showed a strong linear relationship, especially for measured discharge from 0.09 to 0.97 m^3 s^{-1}. Transforming both discharge values and millivolt readings to logarithm base 10 gave a slightly stronger relationship (R^2 = 97.5%), but this resulted in unfeasibly high estimated discharge values, up to 30 m^3 s^{-1}. Calculation of maximum discharge for LK1 using Manning's equation (Ward and Robinson, 2000) gave values between 2.64 to 3.35 m^3 s^{-1}, depending on different roughness coefficient values. Thus the ratings curve was constructed with unlogged data.

Transducer readings taken at 10 minute intervals were converted to discharge values and were used to construct a flow duration curve for catchment LK1 (Figure 3.17).

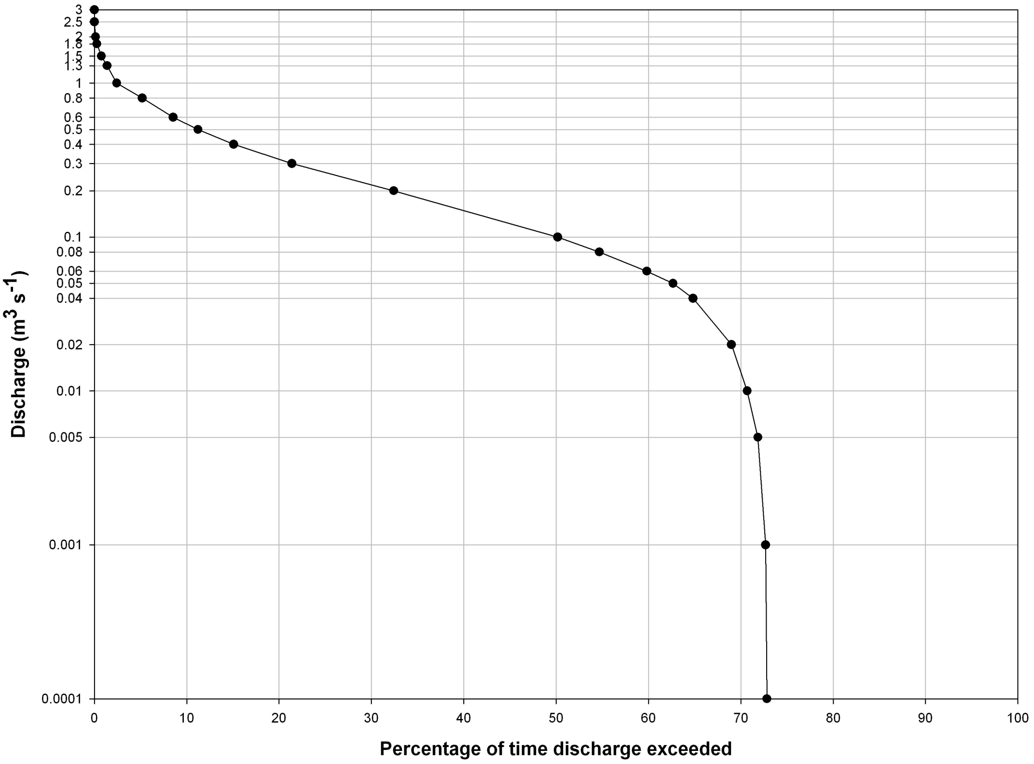


Figure 3.17 Flow duration curve for catchment LK1 using discharge measured every 10 minutes in the period March 2005-May 2006

The transducer operated from March 17th 2005 to May 7th 2006, but due to datalogger malfunctions there were no data from November 2nd 2005 to February 15th 2006. This indicated that there could be an underestimation of high flow conditions due to the lack of data from winter 2005 to 2006. Overall 37 days were missing from completing a full year of flow monitoring. The maximum flow recorded was 3.49 m^3 s^{-1}, which was within the range of maximum discharge values calculated with Manning's equation. Streamwater sampled at high flow in LK1 was within 3 to 50% of time discharge exceeded.

3.3.5 Stream macroinvertebrate sampling

Macroinvertebrates were sampled from the Glen Arnisdale, Loch Katrine area and Ullswater area catchments during June 2005 in order to assess the ecological status of streamwater in the study catchments. Macroinvertebrates have been used for biological monitoring of environmental quality in aquatic ecosystems impacted by acidification and are currently being used as indicators of freshwater recovery from acidification (Tipping et al., 2002). Streamwater was also sampled from the study catchments at the same time as macroinvertebrate sampling and analysed for the usual set of chemistry parameters. Macroinvertebrate sampling and identification was carried out by Kate Newman for her MSc dissertation at the University of Edinburgh (Newman, 2005). Macroinvertebrates were sampled using the kick sampling method and following the procedure described below:

- Shallow fast-moving areas (riffles) with a depth of 10-50 cm and stones 6-7 cm or larger, were selected within the catchment streams;

- The kick-sampling net (c. 500 µm mesh) was fitted tightly against the stream bed and placed downstream from the streamflow direction. The riffle was approached from downstream to avoid disturbing the macroinvertebrates;

- For sample collection, the stream bed was disturbed for a distance of one metre upstream of the sampling net, by kicking mud and stones on the stream bed for three minutes, in order that more macroinvertebrates were dislodged by the water current into the net;

- The net was lifted out of the water with a forward scooping motion to prevent insects from escaping;

- The net contents were emptied into a plastic bucket and 60% ethanol was added to kill and preserve the macroinvertebrates. The plastic bucket contents were emptied into labelled plastic bags which were placed into large black bags and kept in a cool and dark place until return to the laboratory in Edinburgh.

Macroinvertebrate samples collected were placed in individual labelled vials and were identified individually, to the species level, using microscopes and identification keys. Macroinvertebrate samples were collected at low flow conditions from the Loch Katrine and Ullswater areas catchments and from the Glen Arnisdale

GA2, GA3 and GACON catchments from June 18-28th 2005. Sampling from each Loch Katrine area catchment was repeated three times at approximately 20 m intervals. Due to the low flow levels in the catchments near Ullswater, only one sample was collected from UL1 and ULCON and sampling from UL2 was repeated twice at approximately 20 m intervals. Samples from the GA2, GA3 and GACON catchments were collected over a two day period. GA2 and GACON were sampled three times on each day, but only one sample was collected from GA3.

3.4 Data analysis

3.4.1 Frequency distributions

Visual inspection of frequency distributions of streamwater chemistry data showed positive skewness for all streamwater solute concentrations and Anderson-Darling tests also showed that streamwater chemical parameters did not come from a normal distribution. The application of logarithmic and square root transformations of streamwater concentrations were also used but failed to achieve normality. Data skewness was probably caused by the selective collection of high flow streamwater samples from all study catchments and the relative small size of the streamwater chemistry dataset. Hence, data analysis was conducted primarily using non-parametric methods.

3.4.2 Correlation analysis

Spearman's rank correlation was used to investigate relationships between percentage broadleaf woodland cover and indicators of streamwater acidification and also to identify relationships between different solutes within the study catchments. Correlation analysis was performed using SPSS 12.0 for Windows.

3.4.3 Differences in streamwater chemistry between study catchments

The Kruskal-Wallis test was used to investigate differences between streamwater solute concentrations in selected study catchments. Where these differences were significant ($P \leq 0.05$), a non-parametric method was used, developed by Dunn (1964, quoted in Zar, 1999), for multiple comparisons with unequal samples. The method was used for catchment pairwise comparisons of streamwater chemistry to investigate differences in median streamwater solute concentrations between forested and unforested catchments. Both tests used assumed that the distributions of the streamwater solute concentrations compared had the same shape (same skewness), which was valid for most chemistry parameters analysed. Mann-Whitney *U* tests were also used to compare high and low flow median solute concentrations in the Loch Katrine area catchments. Kruskal-Wallis and Mann-Whitney *U* tests were performed using Minitab v.14 for Windows, while multiple comparison tests were calculated manually using mean ranks for each catchment calculated from the Kruskal-Wallis tests.

3.4.4 Macroinvertebrate survey analysis

The macroinvertebrate species identified were used to calculate taxonomic diversity and population density of macroinvertebrate families and biological quality indices for each study catchment. The indices calculated by Kate Newman were the Biological Monitoring Working Party (BMWP) score and the Average Score Per Taxon (ASPT). The BMWP score uses taxonomic resolution to the family level and allocates each family a score between zero and ten, depending on the sensitivity of each family to pollution. ASPT is calculated by dividing BMWP scores by the total number of taxa (families) in each sample, in order to reduce the effect of sampling size.

In order to assess any difference in macroinvertebrate assemblages between study catchments, the macroinvertebrate data were analysed using Detrended Correspondence Analysis (DCA), which is a unimodal multivariate gradient analysis (ordination) method. DCA was performed in CANOCO 4.4 Windows package using segments and by downweighting rare macroinvertebrate species.

3.5 Calculation of critical loads and exceedance

3.5.1 Introduction to the critical loads concept

The aquatic chemical criterion used to indicate the threshold for damage, and thus determine the critical load for freshwaters, is Acid Neutralising Capacity (ANC). The most wide-ranging studies linking ANC to biological damage have been carried out in Norway, where surveys of fish population and water chemistry have been conducted in hundreds of lakes. These surveys provided the data for a widely used dose-response function linking ANC to probability of damage to brown trout (Salmo trutta) populations (Lien et al., 1996), where damage is defined as a reduction in fish populations. Since brown trout is a widespread and economically important species in UK freshwaters, it has been used as an indicator species for UK critical loads applications.

In Norway the threshold ANC selected for critical loads assessments is 20 μeq l^{-1}, which represents a 10% probability of damage to brown trout populations. In the UK, uncertainties regarding pre-industrial ANC values of freshwaters have meant that a lower threshold ANC of zero has also been used, providing less stringent critical loads (i.e. critical loads are exceeded less frequently) and a lower probability of protection to brown trout. The Forests and Water Guidelines (Forestry Commission, 2003) have adopted an ANC value of 0 μeq l^{-1} for assessment of streamwater critical loads, which, according to the Norwegian work, represents a 50% probability of brown trout populations being protected based on mean chemistry (UK National Focal Centre, 2004) but is thought to provide complete protection when applied to high flows.

Ideally, fish and water chemistry survey data from the UK would be used to derive a dose-response function that is appropriate to UK waters, but these data are currently lacking at the national scale. Therefore, there has been ongoing debate over the applicability of the Norwegian dose-response function for UK waters. A workshop organised by DEFRA in 2003 (UK National Focal Centre, 2003) concluded that for assessing critical loads in the UK, a critical ANC value (ANC_{crit}) of 20 μeq l^{-1} should be applied to all sites, except where site-specific data suggested that the pre-industrial value was lower, in which case an ANC_{crit} value of 0 μeq l^{-1} should be used.

3.5.2 Acid neutralising capacity (ANC)

ANC is defined as the sum of base cations (BC) minus the sum of acid anions (AA) in a water sample (Henriksen et al., 1992):

$$ANC = \sum BC - \sum AA = [Ca^{2+}] + [Mg^{2+}] + [Na^{+}] + [K^{+}] - [SO_4^{-2}] - [NO_3^{-}] - [Cl^{-}]$$

(Equation 3.1)

which is, when expressed in equivalents (μeq l^{-1}), equivalent to:

$$ANC = [HCO_3^{-}] + [OA^{-}] - [H^{+}] - [Al^{n+}] \qquad \text{(Equation 3.2)}$$

where:

$[HCO_3^-]$ = bicarbonate ion

$[OA^-]$ = organic anions

$[H^+]$ = hydrogen ion

$[Al^{n+}]$ = sum of positively charged Al species

This definition excludes ions which are generally present in relatively small concentrations (e.g. NH_4^+, Fe^{n+} and F^-), but, in waters where these other ions are thought to be important, they should be included in the calculation of ANC to avoid a charge balance error. Since critical loads relate to acid deposition inputs only, the proportion of ions deriving from neutral sea-spray inputs needs to be quantified and removed, so that the definition of ANC becomes:

$$ANC = [BC]_t^* - [AA]_t^* \qquad \text{(Equation 3.3)}$$

where * denotes the non-marine component and $[BC]_t^*$ is the calculated sum of non-marine base cations (= Ca* + Mg*+ Na* + K*) and $[AA]_t^*$ is the sum of non-marine acid anions (= SO_4^*+ NO_3). It is assumed that all Cl is derived from marine sources, so the marine contribution of each ion may be subtracted as a proportion of measured Cl concentration derived from the known ratios of these ions in seawater, using "seasalt correction factors" for each ion. The seasalt correction factors given in the UN/ECE Mapping Manual (UBA, 1996) for calculating the non-marine ion concentrations are:

[Ca*] = [Ca] – (0.037 × [Cl])

[Mg*] = [Mg] – (0.198 × [Cl])

[Na*] = [Na] – (0.858 × [Cl])

[K*] = [K] – (0.018 × [Cl])

$[SO_4^*] = [SO_4] - (0.103 \times [Cl])$ (all concentrations in μeq l^{-1})

The concentration of NO_3 in sea spray is assumed to be negligible. In western Britain, contribution from HCl deposition is also considered negligible.

3.5.3 The SSWC model

The equation defining ANC (Equation 3.3) forms the basis of modelling freshwater critical loads of acidity using the Steady-State Water Chemistry (SSWC) model. Critical loads of acidity for surface waters are based on the principle that that the acid load to water should not exceed the non-marine base cation input (BC_{dep}^*) and average supply of base cations from weathering (BC_w) in the catchment minus a buffer (ANC_{crit}) to protect selected biota from being damaged (Henriksen et al., 1992):

$$Critical\ Load = \left(BC_w + BC_{dep}^* - ANC_{crit}\right) \cdot Q \qquad \text{(Equation 3.4)}$$

Concentrations are multiplied by catchment runoff Q (in mm) to convert them into annual fluxes (in equivalents per unit area and time). The critical load is therefore a critical flux of acid anions. In the Forests and Water Guidelines, Q is assumed to be 85% of catchment rainfall where Q has not been measured. The average amount of base cations weathered in a catchment and reaching freshwaters is difficult to compute from available soil mineralogy data, thus critical loads are calculated using water chemistry alone. The SSWC model employs certain assumptions and empirical relationships in order to determine the "permanent" buffering provided by the pre-industrial base cation concentration ($[BC]_0^*$), which is the sum of the weathering supply and base cation deposition, assuming that base cation deposition has not significantly changed since pre-industrial times:

$$BC_0^* = BC_w + BC_{dep}^* \qquad \text{(Equation 3.5)}$$

Thus the critical load from Equation 3.4 becomes:

$$Critical\ Load = \left([BC]_0^* - [ANC_{crit}]\right) \cdot Q \qquad \text{(Equation 3.6)}$$

The non-marine flux of base cations ($[BC]_t^*$), which is taken to be the non-marine measured base cation concentration in water, is equivalent to the supply of base cations from weathering, deposition and the release of base cations due to ion-exchange processes (BC_{ex}):

$$BC_t^* = BC_w + BC_{dep}^* + BC_{ex} \qquad \text{(Equation 3.7)}$$

BC_{ex} is related to the long term changes in inputs of non-marine acid anions and is calculated using the term "F" (Henriksen and Posch, 2001):

$$BC_{ex} = F \cdot \left([AA]_t^* - [AA]_0^*\right) \qquad \text{(Equation 3.8)}$$

where $[\mathrm{AA}]_0^*$ is the pre-industrial concentration of non-marine acid anions from weathering and natural atmospheric sources. The term “F” is given by (Brakke et al., 1990, quoted in UK National Focal Centre, 2004):

$$F = \sin\left(\frac{\pi}{2} \cdot \frac{[\mathrm{BC}]_\mathrm{t}^*}{\mathrm{S}}\right) \qquad \text{(Equation 3.9)}$$

where S is a constant representing the current non-marine base cation concentration of a catchment likely to be unaffected by acid deposition and which varies regionally according to geology, but from empirical studies is taken as 400 μeq l^{-1} for the UK (Harriman and Christie, 1995). F can be interpreted as an index of the “exchangeability” of base cations in the soil exchange complex of a catchment and takes values from 0 to 1 for $[\mathrm{BC}]_\mathrm{t}^*= 0$ and 400 μeq l^{-1}, respectively. For values of $[\mathrm{BC}]_\mathrm{t}^*$ greater than 400, F is set to 1, since it would otherwise decrease again with $[\mathrm{BC}]_\mathrm{t}^*$ according to the sine function. When F=1, the base cation flux is increased by exactly the value of the acid anion load, resulting in no change in ANC in runoff.

$[\mathrm{AA}]_0^*$ is estimated from data from near-pristine lakes in northern Scotland which indicate that “background” concentrations of NO_3 are close to zero, and that “background” concentrations of SO_4 are empirically related to base cations. Hence, for UK freshwater critical loads $[\mathrm{AA}]_0^*$ is given by (Tom Nisbet, personal communication):

$$[AA]_0^* = \left(15 + \left(0.16 \cdot [BC_t^*]\right)\right) \qquad \text{(Equation 3.10)}$$

Therefore by using Equations 3.7 and 3.8, Equation 3.5 takes the form:

$$[BC]_0^* = [BC]_t^* - F \cdot \left([AA]_t^* - [AA]_0^*\right) \qquad \text{(Equation 3.11)}$$

All parameters in Equation 3.11 are calculated from measured water chemistry. After calculating $[\mathrm{BC}]_0^*$, the SSWC critical load can be calculated with Equation 3.6. If the critical load of acid deposition is exceeded, the leaching of base cations to water will decline from its current value $[BC]_t^*$, as the base cation pool in the soil-exchange complex is depleted, until it reaches the concentration $[BC]_0^*$ when the ANC of the water body will fall below the threshold concentration of ANC_{crit}. Critical load exceedance in the SSWC model is calculated using Equation 3.12, which takes into account both S deposition (modelled estimates) and NO_3^- leaching:

$$Exceedance = \left(S_{dep} + \left([NO_3^-] \cdot Q\right)\right) - Critical\,Load \qquad \text{(Equation 3.12)}$$

Critical loads exceedance in the Forests and Water Guidelines is calculated using modelled non-marine S deposition for 1995-97 (ECRC, 2001). Deposition of non-marine S is expected to continue to decline up to 2010 and beyond (NEGTAP, 2001), thus the use of the 1995-97 deposition data overestimates the risk of freshwater acidification. On the other hand, the Forests and Water Guidelines underestimate acid-sensitivity because they use an ANC_{crit} value of 0 μeq l^{-1}, instead of a value 20 μeq l^{-1} currently used for the calculation of the critical loads mapping dataset in the UK. Lower ANC_{crit} values lead to higher critical load values, consequently providing a lower level of protection to brown trout.

The critical load calculated using the SSWC model (Equation 3.6) forms a key input to the First-order Acidity Balance (FAB) model. The major difference between the two models lies in their treatment of nitrogen retention and leaching processes.

3.5.4 Treatment of nitrogen processes in critical loads models

The SSWC model assumes that the SO_4 anion is mobile in catchments, and therefore S leaching into surface waters would quickly reach a steady state with S deposition (S_{leach}=S_{dep}^*) (Henriksen and Posch, 2001). However, the situation is much more complex for NO_3. Terrestrial processes, including vegetation uptake, can remove or immobilise N deposition over very long timescales or even permanently. For example, denitrification returns N to the atmosphere as N_2O, NO or N_2 and permanently neutralises the associated acid inputs. Microbial cycling of N can lead to immobilisation in refractory organic matter, again retaining the associated protons. Catchment input-output budgets generally indicate that only a small proportion of N deposition leaches to surface waters with its associated protons (Curtis et al., 1998). If the retention of a known proportion of N deposition represented a steady-state situation then modelling the effects of N deposition and setting a critical load for N would be straightforward. For example, if the current retention rate for N was 90%, it might be assumed that as the N deposition load changes, 10% of the new load would still be leached into surface waters. However, studies of terrestrial N dynamics indicate that under conditions of enhanced N deposition N saturation can occur, whereby N accumulates in the soil-vegetation system until it is present in excess of biological demand and leaching increases, until potentially almost all N deposition is leached (Chapman and Edwards, 1999). It cannot therefore be assumed that N leaching under a fixed deposition load will remain constant nor that, if the N deposition load changes, the proportion of N leaching will remain constant. The process of N saturation takes place over a timescale that is largely independent of the processes which affect S leaching and its associated cation-exchange processes.

N processes make it difficult to define a steady-state situation for surface water chemistry. Therefore, the quantification of N retention processes over the long term is necessary for a steady-state model of freshwater critical loads for total acidity that can be used for scenario testing. The SSWC model has a very simplistic treatment of NO_3 leaching. This model takes account of NO_3 leaching by using measured water NO_3 concentrations, converted into a flux using runoff, as a measure of the contribution of N deposition to critical load exceedance (Henriksen and Posch, 2001). Since N deposition data are not used to calculate critical load exceedance the calculated exceedance only refers to present rates of N retention in the catchment and hence cannot take account of possible changes in NO_3 leaching under a different N deposition scenario. In contrast, process-oriented models such as FAB, use best available knowledge (in terms of published data) to derive a steady-state mass balance for N. The FAB formulation identifies several key N retention processes: denitrification, N immobilisation, N removal in vegetation (grazing, forestry, burning) and in-lake retention. The long-term, steady-state rates at which all these processes operate for a given deposition load of N (and the equivalent terms for S) must be quantified in order to define a critical load of total acidity.

3.5.5 General description of the FAB Model

The FAB model uses a charge balance to determine the leaching rate of acid anions from the catchment, incorporating the major processes affecting the acid anion budget for the lake and catchment (Posch et al., 1997):

$$N_{dep} + S_{dep} = \{fN_{upt} + (1-r)(N_{imm} + N_{den}) + r(N_{ret} + S_{ret})\} + AA_{leach} \quad \text{(Equation 3.13)}$$

where:

N_{dep} = total N deposition

S_{dep} = total S deposition

N_{upt} = net growth uptake of N by forest vegetation (removed by harvesting)

N_{imm} = long term immobilisation of N in catchment soils

N_{den} = N lost through denitrification in catchment soils

N_{ret} = in-lake retention of N

S_{ret} = in-lake retention of S

AA_{leach} = acid anion leaching from catchment

f = fraction of forested area in the catchment

r = lake: catchment area ratio

All units are expressed in equivalents per unit area and time. Some notations in Equation 3.13 and other FAB equations have been changed slightly from the ones used in relevant publications (i.e. Posch et al., 1997) to make them consistent with notations used by the SSWC model for parameters common to both models. Estimates of N (oxidised and reduced) and non-marine S deposition are obtained from atmospheric pollutant deposition models. Braces enclose "internal" catchment processes, i.e. those terrestrial and in-lake processes which operate on acid anion inputs to control the net export in catchment runoff. Several major assumptions are made in this charge balance (Posch et al., 1997):

1. long term sinks of S in the terrestrial part of the catchment (soils and vegetation) are negligible;

2. there are no significant N inputs from sources other than atmospheric deposition, i.e. no fertiliser application in the catchment;

3. NH_4^+ leaching is negligible because any inputs are taken up by the biota, adsorbed by soil, or nitrified to NO_3.

Equation 3.13 has been formulated for lakes and thus requires modification for application to stream catchments. For river catchments, the lake:catchment area ratio, *r*, is zero and net S and N retention in streams is assumed to be zero. Therefore, for streams Equation 3.13 takes the following form:

$$N_{dep} + S_{dep} = \{fN_{upt} + (N_{imm} + N_{den})\} + AA_{leach} \qquad \text{(Equation 3.14)}$$

If there is no harvesting of forest in the catchment, Equation 3.13 is further modified to:

$$N_{dep} + S_{dep} = (N_{imm} + N_{den}) + AA_{leach} \qquad \text{(Equation 3.15)}$$

Given a pre-selected ANC_{crit} value for the protection of selected biota, the leaching rate of acid anions (AA_{leach}) in the charge balance equates to the critical acid load to water which will depress ANC below the ANC_{crit} value and thus in this case AA_{leach} is equivalent to the critical load value (CL) calculated with the SSWC model (Equation 3.6) using water chemistry data. Thus, Equation 3.15 takes the form:

$$N_{dep} + S_{dep} = (N_{imm} + N_{den}) + CL \qquad \text{(Equation 3.16)}$$

The internal catchment processes in the FAB model affecting acid anion budgets are linked to vegetation cover, soil type and catchment morphology, and are quantified as described in the sections below. The parameters described refer to the FAB charge balance as in Equation 3.16 since this FAB formulation was used in the project because there has not been any forest harvesting in the study catchments.

3.5.5.1 N_{imm}: long term immobilisation of N in catchment soils

Estimates of the long term immobilisation of N in different soil types have been derived from the total N content of soil profiles, which is divided by the age of the profile (often assumed to be approximately 10 000 years since the end of the last glaciation) to determine the annual immobilisation rate. A suggested long-term range of net immobilisation rates (including N-fixation) is 2-5 kg N ha^{-1} yr^{-1} (UBA, 1996). However, under present conditions in which plant growth has been stimulated due to elevated N deposition this figure may be higher. Since N immobilisation rate varies with soil type, the relative proportion of the catchment covered by each soil type is required to determine the mean N_{imm} value for soils in the whole catchment.

3.5.5.2 N_{den}: N lost through denitrification in catchment soils

A first order denitrification term (f_{de}) has been recommended (UBA, 1996) for quantifying N denitrification with FAB. The denitrification term is based on the percentage cover of peat soils which are assumed to have $f_{de} = 0.8$, which implies that 80% of net N inputs (after N uptake and N immobilisation) are denitrified in peat soils. The problem with this method for determining denitrification is that, due to the high N deposition rates in parts of the UK, the estimated denitrification rate may be far higher in UK soils (Curtis et al., 2000). With total N deposition exceeding 30 kg N ha^{-1} yr^{-1} across some parts of the UK uplands (RGAR, 1997), the denitrification rates for un-afforested peat catchments estimated using f_{de}, after subtracting the component immobilised in catchment soils (a figure of 2-5 kg N ha^{-1} yr^{-1} is used for the UK), equate to 80% of at least 25 kg N ha^{-1} yr^{-1}, i.e. 20 kg N ha^{-1} yr^{-1}. This value is an order of magnitude higher than observed denitrification values for peat soils in the UK (Emmett and Reynolds, 1996) and five times greater than the recommended maximum value for UK soils (Hall et al., 1998).

For the UK the FAB model is therefore modified to include the denitrification component as a fixed value for certain soil types, independent of N deposition (Curtis et al., 2000). Each soil type is allocated a fixed denitrification value (Hall et al., 1998) and its proportional cover within the catchment is quantified in order to determine a mean value of N_{den}, in an identical way to the calculation of mean N immobilisation for the catchment.

3.5.5.3 The Critical load function (CLF)

With the FAB model it is not possible to define a single value to represent the critical load of total acidity because the acid anions SO_4 and NO_3 behave differently in the way they are transported with hydrogen ions, and one unit of deposition of S will not have the same net effect on surface water ANC as an equivalent unit of N deposition. However, critical deposition loads for S and N can be defined individually, based on the following equations (for streams):

$$CL_{\max}(S) = CL \quad \text{(Equation 3.17)}$$

$$CL_{\min}(N) = fN_{upt} - (N_{imm} + N_{den}) \quad \text{(Equation 3.18)}$$

$$CL_{\max}(N) = fN_{upt} - (N_{imm} + N_{den}) + CL \quad \text{(Equation 3.19)}$$

Critical deposition loads for S and N refer to a pre-selected ANC_{crit} value as in Equation 3.16. If there is no forest harvesting in the catchment area, fN_{up} is zero and Equations 3.18 and 3.19 become:

$$CL_{\min}(N) = N_{imm} + N_{den} \quad \text{(Equation 3.20)}$$

$$CL_{\max}(N) = N_{imm} + N_{den} + CL \qquad \text{(Equation 3.21)}$$

$CL_{max}(S)$ defines the critical load for S when total N deposition is less than $CL_{min}(N)$ and equates to the CL value calculated in the SSWC model. When S deposition exceeds $CL_{max}(S)$, the critical load is exceeded by S alone, regardless of the level of N deposition. The contribution of N deposition to an increase in exceedance over that resulting from S alone is determined by the FAB charge balance. $CL_{min}(N)$ defines the deposition of total N (NH_x + NO_y) at which terrestrial catchment processes effectively remove all N, so that deposition loads lower than $CL_{min}(N)$ result in no net leaching of NO_3. $CL_{max}(N)$ defines the critical load for total N deposition when S deposition is zero. When total N deposition exceeds $CL_{max}(N)$ the critical load is exceeded by N deposition alone, although critical load exceedance may be further increased by S deposition.

The nature of critical load exceedance for any given pair of S and N deposition values is determined by the Critical Load Function (CLF), shown in Figure 3.18. In practice, neither S nor N deposition will ever be zero, so the critical load for the deposition of one species is influenced by the deposition of the other (Posch et al., 1997). For pairs of S and N deposition values that are located in the unshaded (white) area of the CLF, the site is protected. If the deposition values fall outside the white area of the CLF, the critical load is exceeded. The options for protecting the site, in terms of deposition reductions, are then determined by the location of the given deposition values in a particular sector of the CLF. However, the CLF can only provide qualitative information, in terms of whether reductions in either N or S deposition or both are optional or compulsory to achieve non-exceedance. There is no quantitative indication of the amount by which the deposition of either species must be reduced, and indeed this is not possible because of the inter-dependence of the two species in jointly causing critical load exceedance.

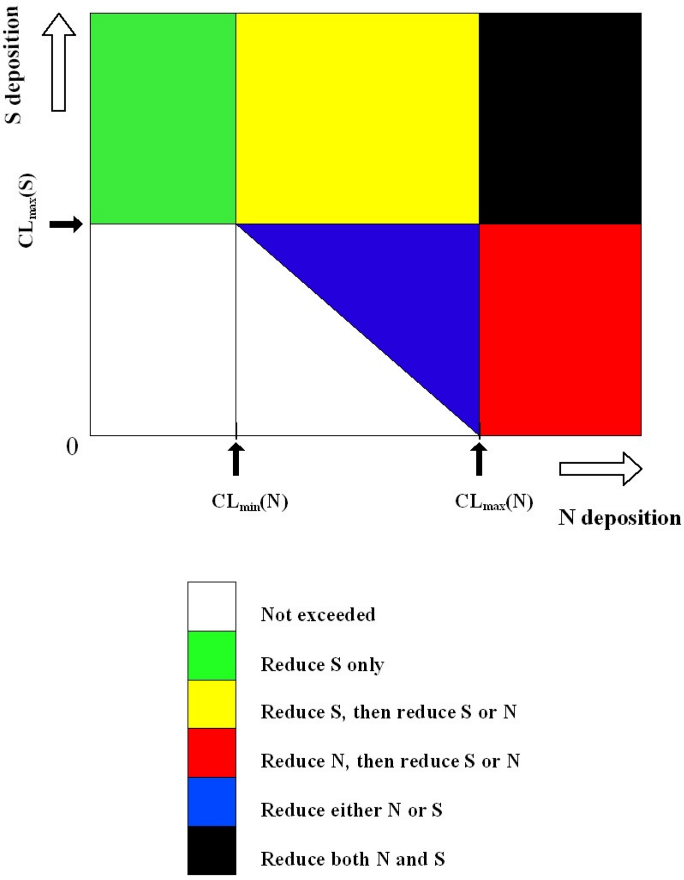


Figure 3.18 Schematic interpretation of exceedance on the CLF (UK National Focal Centre, 2004)

There are only two specific cases where the deposition reduction requirement for a species can be quantified (UK National Focal Centre, 2004). If the deposition of S is zero, the critical load exceedance and reduction requirement for N can be quantified. Such a situation is, however, extremely unlikely to occur because of the ubiquitous nature of atmospheric S pollution. A more feasible situation in this formulation of the FAB model is that N deposition may be less than $CL_{min}(N)$, suggesting that all deposited N is retained within the catchment, and in this case, the FAB model would be able to provide a critical load exceedance value for S. However, this particular case is only valid if it is assumed that N deposition directly onto a lake surface is negligible. Furthermore, in stream catchments some N leaching is inevitable and both S and N contribute to exceedance.

Despite the impossibility of quantifying a deposition reduction requirement for either N or S independently, except in the special circumstances mentioned above, the FAB model can provide a numerical value for critical load exceedance (see Equation 3.22). This value can only be interpreted as the amount by which the total acid flux (from both S and N) exceeds the critical load, and provides no indication of how site protection (non-exceedance) can be achieved.

3.5.5.4 FAB model predictions and quantifying critical load exceedance

Total critical load exceedance is calculated in the FAB model as the difference between the predicted leaching fluxes of S and N and the critical leaching flux of acid anions and can be calculated as:

$$Total\ Exceedance = S_{dep} + \left(N_{dep} - \left(N_{imm} + N_{den}\right)\right) - CL \qquad \text{(Equation 3.22)}$$

The critical load exceedance calculated indicates the amount by which the leaching flux of acid anions must be reduced, which could potentially be achieved by many different combinations of reductions in S and N deposition.

The FAB model assumes that S and N deposition is uniform over the whole catchment. However, Henriksen and Posch (2001) argue that because deposition, mainly dry, is larger over forest than open land, enhanced dry deposition should be taken account of in the formulation of the FAB model by replacing N_{dep} by $\varphi_f N_{dep}$, where $\varphi_f > 1$ is the factor describing enhanced deposition onto forests. In the European application of critical loads (including the UK), N_{dep} is not the deposition onto a particular catchment, but a spatial average over a grid square including several land cover classes (and forests) and thus a proper choice of φ_f is difficult. Dry S and N deposition inputs to forest covering the Loch Katrine catchments were modelled and their effect on the calculation of FAB streamwater critical loads was investigated and is reported in Chapter 6.

3.6 Summary

This chapter has reviewed the approach and methods used to select the study catchments for detailed field sampling. The final catchment selection required some compromise between accessibility and the geographical coverage of the most extensive areas of broadleaf woodland in the UK. The study focused on broadleaf woodlands in the most acid-sensitive areas in the UK, as identified by the SSWC Exceedance map for 1995-97. Using digital woodland and elevation datasets in a GIS, 31 candidate catchments were initially selected. Following extensive field visits, the presence of various confounding factors was identified and resulted in the removal of candidate catchments from the study. The final 14 study catchments selected comprised 10 catchments with percentage broadleaf woodland cover ranging from 10.3 to 78.7%, plus four control catchments close to the forested catchments and with similar characteristics but with little or none broadleaf woodland cover. The study catchments characteristics (topography, geology and soil composition and land-use) were presented in this chapter. Chapter 3 also described the streamwater sampling strategy and the macroinvertebrate survey methodology, along with the statistical methods used for the analysis of the chemical analysis results and macroinvertebrate data. The chapter concluded by describing the critical load concept and the critical loads models used to estimate acid-sensitivity in the study catchments.

Chapter 4 Streamwater chemistry and macroinvertebrate survey results

Chapter 4 presents the streamwater chemistry and macroinvertebrate results and the statistical analysis of these results. Section 4.1 presents the chemistry analysis results of the high flow streamwater samples collected from the study catchments. Section 4.2 gives the results of the multivariate analyses performed to interpret streamwater chemistry variability and identify catchment groupings. Section 4.3 presents the relationships between streamwater solute concentrations and catchment characteristics, including percentage broadleaf woodland cover and inter-solute relationships. Section 4.4 presents the faunal composition and taxon richness of the macroinvertebrate samples, the values of calculated biological indices and the results from multivariate analyses using macroinvertebrate data to assess catchment groupings. The chapter concludes by discussing the factors influencing the associations between streamwater chemistry and broadleaf woodland cover and catchment characteristics.

4.1 Streamwater chemistry results

4.1.1 General description of high flow streamwater chemistry results

Mean concentrations of species in high flow samples from the catchments in Glen Arnisdale, Loch Katrine and Ullswater areas and Devon are presented in Tables 4.1 to 4.4. Non-marine SO_4 concentrations were calculated using seasalt correction factors based on the known ratio of SO_4 in seawater (UBA, 1996).

Table 4.1 Mean concentrations of pH, Gran alkalinity (µeq l^{-1}), Ca, Mg, Na, K, Cl, marine SO_4 and non-marine SO_4 (xSO_4), NO_3 and NH_4 (all mg l^{-1}) and soluble Al, Mn, Fe, Pb and Zn (µg l^{-1}) in streamwater sampled at high flow from the Glen Arnisdale catchments. Minimum and maximum values are given in brackets

	GA1	GA2	GA3	GACON
No. samples	2	2	2	2
pH	6.0	5.9	4.9	5.9
	(5.9-6.1)	(5.8-6.0)	(4.7-5.0)	(5.8-6.0)
Gran	33.9	8.80	-13.4	24.4
alkalinity	(19.5-48.2)	(4.10-13.5)	(-20.5- - 6.20)	(17.5-31.2)
Ca	2.33	1.84	1.37	2.42
	(1.25-3.41)	(0.88-2.79)	(0.59-2.14)	(1.14-3.69)
Mg	1.30	1.54	1.91	1.86
	(0.59-2.01)	(0.63-2.45)	(0.75-3.07)	(0.73-2.99)
Na	7.76	9.13	9.87	10.7
	(4.41-11.1)	(5.05-13.2)	(5.66-14.1)	(5.49-15.9)
K	0.70	0.78	1.14	0.92
	(0.49-0.90)	(0.54-1.01)	(0.82-1.45)	(0.62-1.21)
Cl	18.9	20.0	23.0	24.9
	(7.75-30.1)	(9.03-30.9)	(10.9-35.0)	(10.2-39.6)
SO_4	2.76	2.82	3.10	3.40
	(1.31-4.20)	(1.36-4.28)	(1.51-4.69)	(1.86-4.93)
xSO_4	0.81	0.92	0.60	0.66
	(0.22-1.39)	(0.90-0.95)	(0.07-1.13)	(0.43-0.90)
NO_3	0.23	0.21	0.22	0.21
	(0.21-0.25)	(0.19-0.23)	(0.21-0.22)	(0.20-0.22)
NH_4	0.02	<0.02	<0.02	<0.02
	(0.02-0.03)			
Al	48	51	53	46
	(30-65)	(31-71)	(40-66)	(28-64)
Mn	<1	2	18	4
		(1-3)	(5-31)	(1-7)
Fe	6	19	34	18
	(<1-12)	(8-30)	(15-53)	(7-29)
Pb	1	1	<1	<1
	(<1-1)	(<1-1)		
Zn	1	2	3	3
	(1-2)	(1-3)	(1-5)	(2-4)

Table 4.2 Mean concentrations of pH, Gran alkalinity (μeq l^{-1}), Ca, Mg, Na, K, Cl, marine SO_4 and non-marine SO_4 (xSO_4), NO_3 and NH_4 (all mg l^{-1}) and soluble Al, Mn, Fe, Pb and Zn (μg l^{-1}) in streamwater sampled at high flow from the Loch Katrine area catchments. Minimum and maximum values are given in brackets

	LK1	LK2	LK3	LK4	LKCON
No. samples	10	10	10	10	9
pH	6.2	5.6	6.1	6.3	6.4
	(5.7-6.6)	(5.2-5.8)	(5.9-6.5)	(5.7-6.7)	(6.1-6.6)
Gran alkalinity	41.6	-11.0	2.51	36.7	31.7
	(15.2-97.5)	(-45.3-10.0)	(-28.9-26.2)	(17.4-61.0)	(-12.2-72.8)
Ca	1.55	0.89	1.09	1.58	1.42
	(1.04-1.87)	(0.59-1.11)	(0.74-1.39)	(1.14-1.90)	(1.01-1.66)
Mg	0.51	0.45	0.45	0.54	0.55
	(0.39-0.58)	(0.35-0.50)	(0.36-0.51)	(0.43-0.62)	(0.44-0.60)
Na	2.68	2.51	2.76	3.00	2.63
	(2.29-3.29)	(2.21-3.07)	(2.33-3.47)	(2.18-3.13)	(2.24-3.17)
K	0.31	0.26	0.27	0.27	0.32
	(0.24-0.43)	(0.18-0.40)	(0.18-0.42)	(0.20-0.35)	(0.24-0.48)
Cl	4.80	4.27	4.76	4.44	4.18
	(3.37-7.28)	(3.19-6.57)	(3.24-7.14)	(3.23-6.63)	(3.30-5.27)
SO_4	1.97	1.65	1.86	1.99	1.90
	(1.50-2.48)	(1.44-2.04)	(1.45-2.22)	(1.60-2.39)	(1.63-2.17)
xSO_4	1.30	1.06	1.19	1.37	1.31
	(0.59-1.48)	(0.53-1.51)	(0.58-1.59)	(0.73-1.79)	(0.90-1.62)
NO_3	0.53	0.41	0.33	0.71	0.43
	(0.26-0.85)	(<0.02-0.75)	(<0.02-0.76)	(0.34-1.04)	(0.13-0.83)
NH_4	0.02	0.03	0.02	0.02	0.02
	(<0.02-0.05)	(<0.02-0.12)	(<0.02-0.05)	(<0.02-0.08)	(<0.02-0.04)
Al	61	49	38	29	21
	(33-100)	(21-67)	(21-55)	(15-49)	(6-40)
Mn	7	12	7	4	6
	(3-15)	(8-19)	(4-11)	(2-7)	(5-10)
Fe	85	136	71	53	97
	(55-137)	(82-169)	(51-86)	(24-74)	(52-151)
Pb	1	1	1	1	1
	(<1-2)	(<1-2)	(<1-2)	(<1-1)	(<1-2)
Zn	4	3	3	3	3
	(<1-8)	(<1-7)	(<1-8)	(<1-6)	(<1-7)

Table 4.3 Mean concentrations of Gran alkalinity (μeq l^{-1}), Ca, Mg, Na, K, Cl, marine SO_4 and non-marine SO_4 (xSO_4), NO_3 and NH_4 (all mg l^{-1}) and soluble Al, Mn, Fe, Pb and Zn (μg l^{-1}) in streamwater sampled at high flow from the Ullswater area catchments. Minimum and maximum values are given in brackets

	UL1	UL2	ULCON
No. samples	5	5	5
Gran alkalinity	-35.5	278	141
	(-64.7- -1.44)	(171-385)	(120-162)
Ca	1.68	4.97	2.86
	(1.15-2.39)	(2.71-6.95)	(2.50-3.31)
Mg	1.18	2.34	1.34
	(0.93-1.68)	(1.51-3.60)	(0.84-1.68)
Na	5.32	6.79	4.02
	(4.43-6.17)	(5.11-8.20)	(3.03-4.88)
K	0.65	0.52	0.24
	(0.40-0.75)	(0.44-0.59)	(0.02-0.42)
Cl	9.96	9.86	5.52
	(6.76-11.9)	(8.34-11.1)	(1.99-8.27)
SO_4	4.70	4.85	4.03
	(3.65-5.91)	(4.40-5.56)	(1.90-5.90)
xSO_4	3.31	3.48	3.26
	(2.28-4.26)	(2.92-4.00)	(1.63-4.74)
NO_3	6.66	6.57	0.31
	(0.76-11.09)	(1.88-10.5)	(0.02-0.52)
NH_4	0.02	0.07	0.02
	(<0.02-0.05)	(<0.02-0.23)	(<0.02-0.04)
Al	88	39	15
	(56-109)	(19-64)	(13-17)
Mn	42	16	10
	(16-56)	(2-32)	(2-24)
Fe	24	20	25
	(6-40)	(4-45)	(11-43)
Pb	<1	2	1
		(<1-5)	(1-3)
Zn	3	1	<1
	(2-5)	(<1-2)	

Table 4.4 Mean concentrations of Gran alkalinity (μeq l^{-1}), Ca, Mg, Na, K, Cl, marine SO_4 and non-marine SO_4 (xSO_4), NO_3 and NH_4 (all mg l^{-1}) and soluble Al, Mn, Fe, Pb and Zn (μg l^{-1}) in streamwater sampled at high flow from the Devon catchments. Minimum and maximum values are given in brackets. Chemistry data for NAR are from ECRC, UCL.

	YAR	NAR
No. samples	8	3
Gran alkalinity	15.7	15.1
	(-33.7-37.9)	(11.4-22.0)
Ca	0.85	0.62
	(0.52-1.18)	(0.61-0.65)
Mg	1.03	0.77
	(0.71-1.39)	(0.75-0.80)
Na	6.41	4.83
	(5.82-7.23)	(4.80-4.90)
K	0.67	0.69
	(0.57-0.84)	(0.67-0.72)
Cl	11.9	8.87
	(9.87-16.0)	(8.60-9.20)
SO_4	3.84	4.00
	(3.46-4.42)	(3.70-4.50)
xSO_4	2.19	2.76
	(2.02-2.40)	(2.47-3.30)
NO_3	2.57	0.49
	(2.00-2.94)	(0.22-0.80)
NH_4	0.02	-
	(<0.02-0.04)	
Al	66	50
	(23-127)	(40-61)
Mn	6	6
	(3-11)	(5-6)
Fe	22	11
	(6-31)	(8-16)
Pb	1	-
	(1-2)	
Zn	6	-
	(2-10)	

Mean streamwater Gran alkalinity ranged from -64.7 to 41.6 μeq l^{-1} in the Glen Arnisdale, Loch Katrine area and Devon catchments and in UL1 and was well below the acid sensitivity threshold value of 200 μeq l^{-1} (Neal, 2001). UL2 and ULCON had mean streamwater alkalinity of 278 and 141 μeq l^{-1} respectively. Streamwater alkalinity values indicated that the catchments had similar acid-sensitivities apart from catchment UL2, and to a smaller extent ULCON, which appeared to be well buffered to acidic inputs. Negative mean streamwater alkalinity in catchments GA3, LK2 and UL1 indicated that the entire bicarbonate component was probably consumed by acidic inputs and natural organic acidity. Catchments in Glen Arnisdale, Loch Katrine and Ullswater areas had similar mean streamwater Ca concentrations ranging from 0.89 to 2.42 mg l^{-1}, apart from UL2 with the highest mean Ca concentration of 4.97 mg l^{-1}. YAR and NAR had the lowest mean Ca concentrations within the study catchments of 0.85 and 0.62 mg l^{-1}, respectively.

Streamwater chemistry showed a strong maritime influence which depended on catchment distance from the nearest coast. Thus a maritime influence was greatest in the catchments in Glen Arnisdale with mean streamwater Cl concentrations ranging from 18.9 to 24.9 mg l^{-1} and lowest in the most inland catchments in the Loch Katrine area which had Cl concentrations ranging from 4.18 to 4.80 mg l^{-1}. Streamwater Na contributed from 40% (UL2 and ULCON) to 66% (GA3) of the sum of base cations with a mean value of 55% for all sites (Figure 4.1). The mean ratio of Na to Cl for the 14 study catchments was 0.551 and therefore very close to that for seawater of 0.553, indicating that in winter high flow conditions seasalt inputs can account for almost 100% of Na presence in streamwater. The low Na:Cl ratios in the Glen Arnisdale catchments (0.41-0.46) were caused by a major seasalt event that resulted in Na retention in the catchments (see 4.1.3). Higher ratios (>0.60) indicated a weathering source of Na in some catchments, mainly in LKCON, UL2 and ULCON.

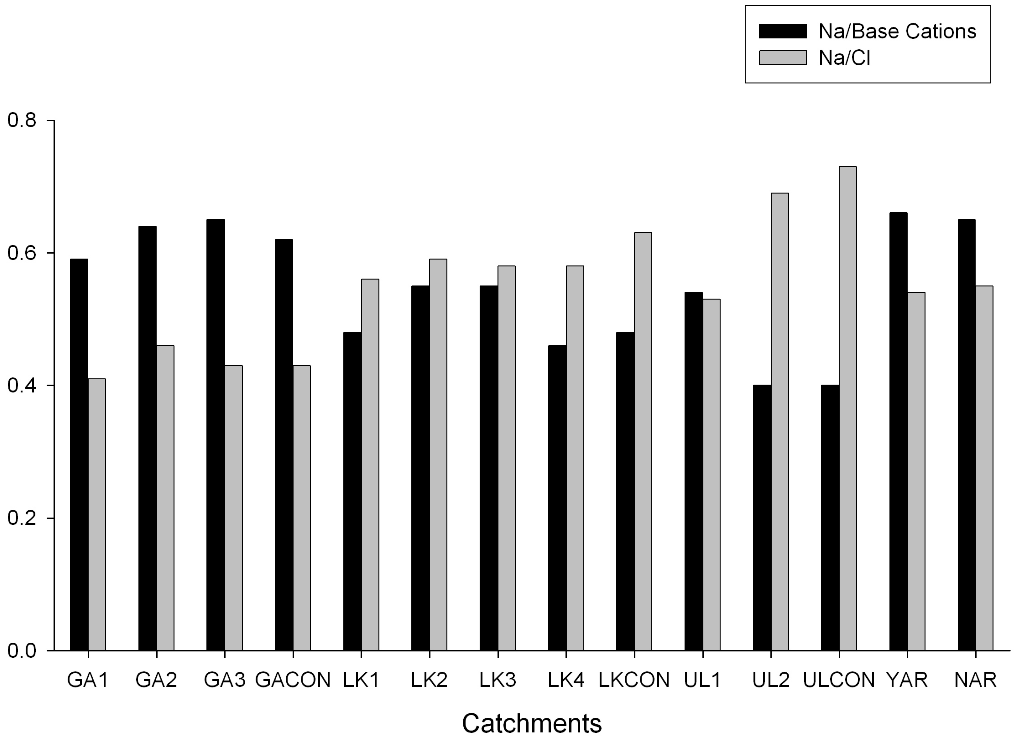


Figure 4.1 Values of the ratios of streamwater Na to the sum of base cations and Na to Cl for the 14 study catchments. Ratios are mass ratios

The influence of maritime inputs on streamwater chemistry was also demonstrated by the Na base cation dominance index (Na_{dom}) values calculated for the study catchments. Na_{dom} has been used as a quantitative index of weathering rates in catchments subject to strong maritime influence and with low base status in western Britain and is defined as (Stutter et al., 2002):

$$Na_{dom} = \frac{[Na^+]}{\left(\sum[Na^+]+[Ca^{2+}]+[Mg^{2+}]\right)} \qquad \text{(Equation 4.1)}$$

High values of Na_{dom} indicate a dominance of Na from marine inputs in streamwater and smaller base contributions from weathering within the catchment, especially for Ca. Na_{dom} values (expressed as percentages) ranged from 41% to 69% and, as expected, were highest in the Glen Arnisdale and Devon catchments (61% to 69%) and lowest in the Loch Katrine and Ullswater area catchments (41% to 57%).

Mean streamwater concentrations of marine SO_4 and non-marine SO_4 (xSO_4) ranged from 1.65 to 4.85 mg l^{-1} and 0.60 to 3.48 mg l^{-1}, respectively, with low xSO_4 concentrations in the more remote Scottish catchments and higher concentrations in the catchments in Devon and near Ullswater (Figure 4.2). Mean streamwater NO_3 concentrations were also lower in the Scottish catchments and highest in the catchments near Ullswater and ranged from 0.21 mg l^{-1} in GA2 and GACON to 6.66 mg l^{-1} in UL1 (Figure 4.2). Mean streamwater NH_4 concentrations were low in all catchments ranging from below detection limit (<0.02 mg l^{-1}) to 0.07 mg l^{-1}. Mean streamwater concentrations of soluble Al were highest in UL1 (88 µg l^{-1}) while the lowest concentrations occurred in streamwater from the non forested Loch Katrine area and Ullswater catchments (LKCON and ULCON). Mean streamwater Mn concentrations were again low, ranging from below detection limit (<1 µg l^{-1}) to 18 µg l^{-1}, apart from UL1 which had the highest Mn concentration of 42 µg l^{-1}. Mean streamwater Fe concentrations were highest in the Loch Katrine catchments, with mean concentration for the five catchments of 88 µg l^{-1}, while the remaining study catchments had mean Fe concentrations below 34 µg l^{-1}. Mean streamwater Pb and Zn concentrations were very low for all study catchments.

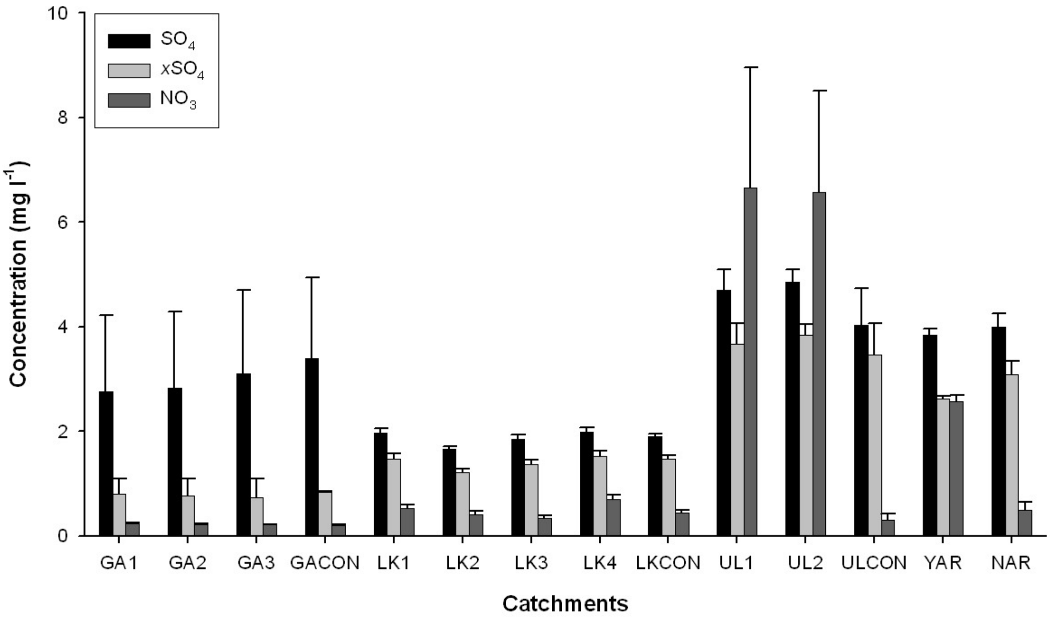


Figure 4.2 Mean streamwater SO_4, xSO_4 and NO_3 concentrations at high flow from the study catchments. Error bars represent standard error

4.1.2 Description of streamwater chemistry results by catchment area

Mean streamwater chemistry was very similar for the four Glen Arnisdale catchments and was influenced to a great extent by seasalt inputs due to the proximity of the catchments to the west coast. High flow samples were collected from each Glen Arnisdale catchment on two consecutive days, November 7th and 8th 2005. The streamwater sampling on November 8th coincided with high marine inputs to streamwater from a seasalt event, resulting in large increases in Ca, Mg, Na, K, Cl and SO_4 streamwater concentrations compared to the previous day. The effect of the seasalt event on streamwater chemistry is discussed in 4.1.3. Mean streamwater SO_4 concentrations in the Glen Arnisdale catchments were relatively high but mean $x$$SO_4$ concentrations were much lower (Figure 4.2), indicating that most SO_4 in streamwater was derived from maritime sources. Mean streamwater NO_3 concentrations were the lowest amongst the study catchments (Figure 4.2).

Overall, streamwater chemistry was similar in all the five Loch Katrine area catchments. Mean Cl concentrations were the lowest of the study catchments (Table 4.2). Streamwater from LK1 had the highest mean soluble Al concentrations of all the Loch Katrine area catchments (Table 4.2). Fe concentrations were the highest amongst the study catchments with the highest concentration (169 $\mu g\ l^{-1}$) measured in streamwater from LK2 (Table 4.2).

Streamwater chemistry was quite variable for the three catchments near Ullswater. Mean streamwater Gran alkalinity was the lowest and highest in UL1 and UL2, respectively, within the study catchments, while the highest mean Ca concentration also occurred in UL2 (Tables 4.1-4.4). Ratios of Na:BC and Na:Cl were lowest and highest in UL2 and ULCON, respectively, indicating in both cases large contributions of streamwater base cations from mineral weathering. Mean Cl concentrations were similar for catchments UL1 and UL2 while values for ULCON were almost 50% lower (Table 4.3). However, mean SO_4 and $x$$SO_4$ streamwater concentrations were similar for the three catchments and were the highest measured amongst the study catchments (Table 4.3). Similarly, streamwater NO_3 concentrations in UL1 and UL2 were the highest for all study catchments

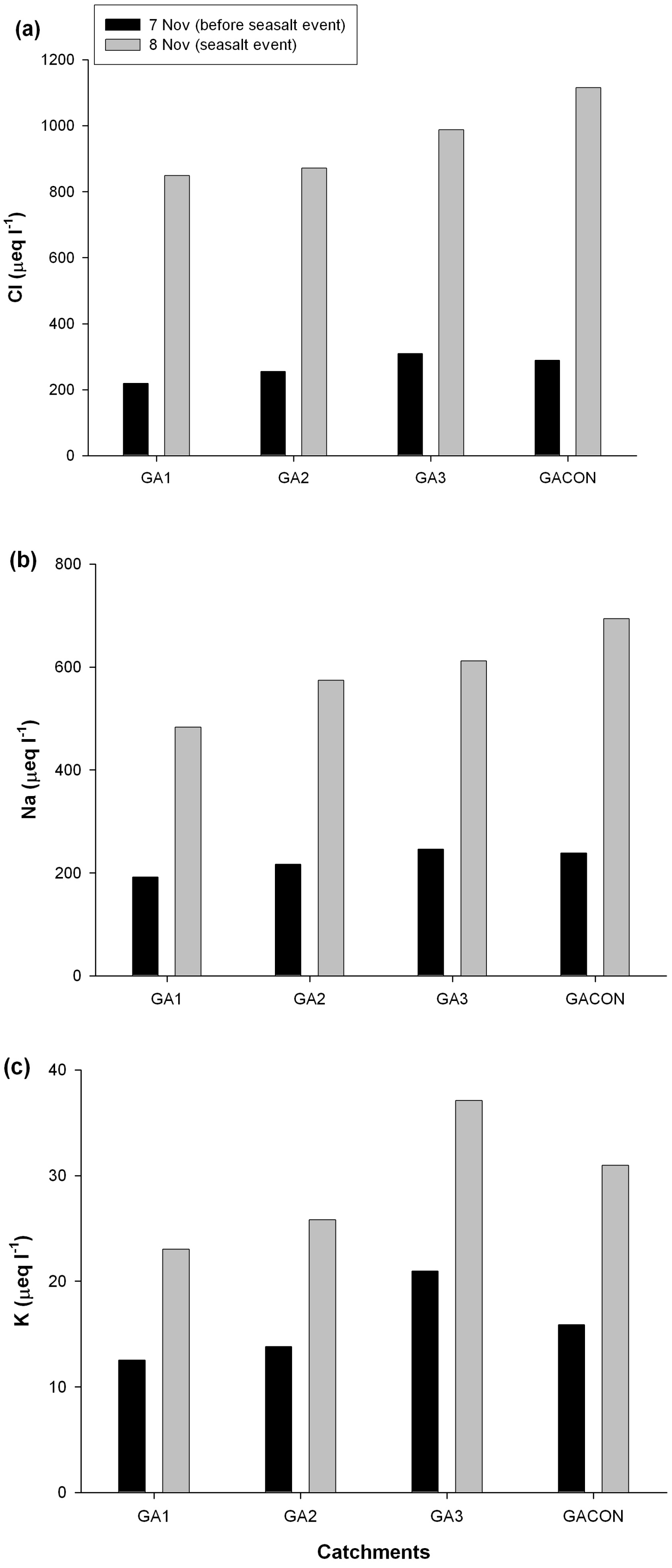
(Figure 4.2). UL1 and UL2 had mean streamwater NO_3 concentrations higher than mean streamwater SO_4 and xSO_4 concentrations and thus NO_3 was the dominant excess anion in these catchments. The highest mean soluble Al and Mn concentrations within the study catchments occurred in UL1 (88 and 42 µg l^{-1}, respectively). Mean Mn concentrations were lower for UL2 (16 µg l^{-1}) and ULCON (10 µg l^{-1}) (Table 4.3) and mean Fe concentrations were low in the three catchments, ranging from 20 to 25 µg l^{-1}.

Streamwater chemistry was generally similar in YAR and NAR. The two catchments were the only study catchments in which mean streamwater Mg concentrations exceeded Ca concentrations (Table 4.4). Na:Cl ratios for YAR and NAR (0.54 and 0.55, respectively) (Figure 4.1), indicated that almost all Na at high flow came from seasalt inputs. Mean soluble Al concentration was 66 µg l^{-1} for YAR and 50 µg l^{-1} for NAR, while the highest Al concentration measured in all the high flow samples collected from the study catchments was in streamwater from YAR (127 µg l^{-1}) (Tables 4.1-4.4). Mean Mn and Fe concentrations were low for both YAR and NAR (Table 4.4).

4.1.3 Seasalt event in Glen Arnisdale

Streamwater from the four Glen Arnisdale catchments was sampled on two consecutive days (November 7th and 8th 2005) at similar high flow conditions but a seasalt event influenced streamwater sampled on the second day. The seasalt event was caused by a deep depression (968 mbar) affecting north-west Scotland, and was accompanied by strong gales with gusts reaching 145 km $hour^{-1}$ according to the UK Met Office. Figure 4.3 shows streamwater chemistry concentrations, Figure 4.4 calculated non-marine concentrations and Figure 4.5 soluble metal concentrations in the Glen Arnisdale catchments before and after the seasalt event. Units of concentrations presented here are in µeq l^{-1} (instead of mg l^{-1} as previously) to help explain charge influences and cation-exchange mechanisms. Streamwater at the four Glen Arnisdale catchments responded rapidly to the seasalt inputs. Streamwater Cl concentrations were 3 to 5 times higher than the ones measured on the previous day ranging from 849 to 1116 µeq l^{-1} (Figure 4.3a). Streamwater Cl concentrations corresponded to catchment distance from the west coast with the highest concentrations occurring in GACON and the lowest in GA1, the most inland catchment.

Streamwater SO_4 almost tripled in the four catchments during the seasalt event, from 27-39 μeq l^{-1} to 87-103 μeq l^{-1} (Figure 4.3f). However, calculated $x$$SO_4$ concentrations decreased in streamwater sampled after the seasalt event from -0.5 to 8.9 μeq l^{-1} to -12 to -0.1 μeq l^{-1} (Figure 4.4e). Negative values probably indicate adsorption of SO_4 in catchment soils during the seasalt event (Larssen and Holme, 2006). Inputs of SO_4 to streamwater were small compared to Cl (expressed as the ratio of SO_4 to Cl) sampled before (10-13% of the Cl charge) and after (9-10% of the Cl charge) indicating that Cl was acting as the major “mobile anion” in the soil complex.


(a)
7 Nov (before seasalt event)
8 Nov (seasalt event)
Cl (μeq l^{-1})
0
200
400
600
800
1000
1200
GA1
GA2
GA3
GACON
(b)
Na (μeq l^{-1})
0
200
400
600
800
GA1
GA2
GA3
GACON
(c)
K (μeq l^{-1})
0
10
20
30
40
GA1
GA2
GA3
GACON
Catchments

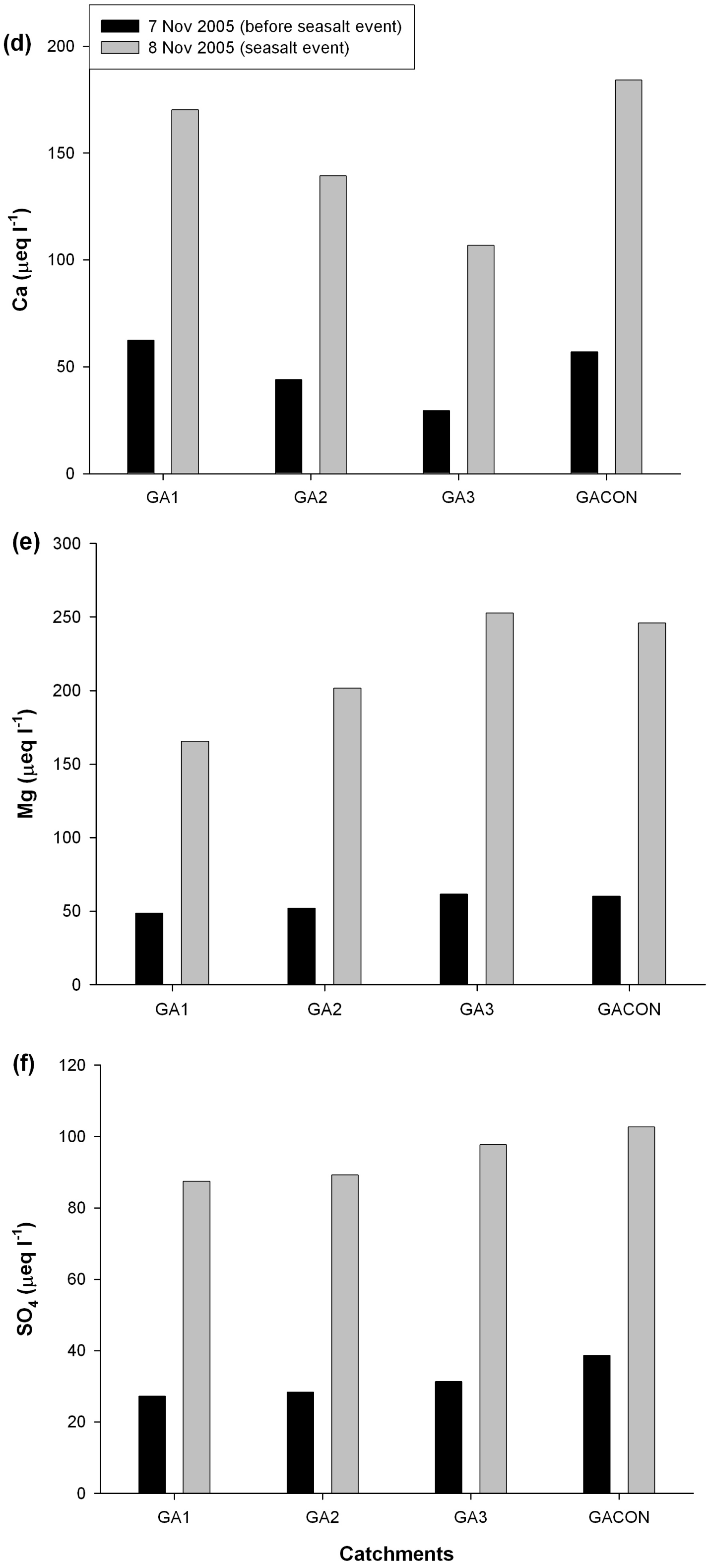


Figure 4.3 Streamwater concentrations of (a) Cl, (b) Na, (c) K, (d) Ca, (e) Mg and (f) SO_4 before and after the seasalt event in the Glen Arnisdale catchments

During seasalt episodes, a portion of the dominant cations in seasalt, mainly Na and Mg, can be retained in the catchment due to ion-exchange, whereas most of the more mobile Cl enters streamwater, leading to negative calculated non-marine concentrations (Larssen and Holme, 2006). This was observed in the four catchments in the calculated non-marine Na concentrations (Na*) which were negative (Figure 4.4a) and ranged from -173 to -264 μeq l^{-1} after the seasalt event, compared to -20 to 4 μeq l^{-1} before. The mean value of Na:Cl ratios for the four catchments also decreased from 0.84 to 0.62 after the seasalt event and, along with the negative Na* observed, indicated large retention of Na in the catchment, even at moderate levels of Cl deposition, probably due to ion-exchange processes. There were large increases in streamwater non-marine Mg (Mg*) during the seasalt event from concentrations of 1 to 5 μeq l^{-1} to -3 to 57 μeq l^{-1}, with Mg retention occurring only in catchment GA1 (Figure 4.4d).

The retention of Na in the soils should have led, due to ion-exchange, to the mobilisation of other cations, mainly Ca, H^+ and Al (Larssen and Holme, 2006). Most of the cation mobilisation in the four Glen Arnisdale catchments occurred as Ca, with concentrations of calculated non-marine Ca (Ca*) increasing 3 to 4 times after the seasalt event from 18 to 54 μeq l^{-1}, to 70 and 143 μeq l^{-1} (Figure 4.4c). Concentrations of H^+ in streamwater increased slightly in three catchments; the highest increase in streamwater H^+ concentration was observed in GA3, from 10 to 20 μeq l^{-1} and corresponded to pH depression from 5.0 to 4.7. There was a small unexpected decrease in H^+ concentration in GACON, from 1.6 to 1 μeq l^{-1} (pH increase from 5.8 to 6), which could have been caused by Ca* mobilisation, since GACON had the greatest increase in streamwater Ca concentrations of the Glen Arnisdale catchments after the seasalt event (Figure 4.4c). However, these changes in H^+ concentrations were very small, apart from in GA3, and are probably difficult to distinguish from error in pH measurements.

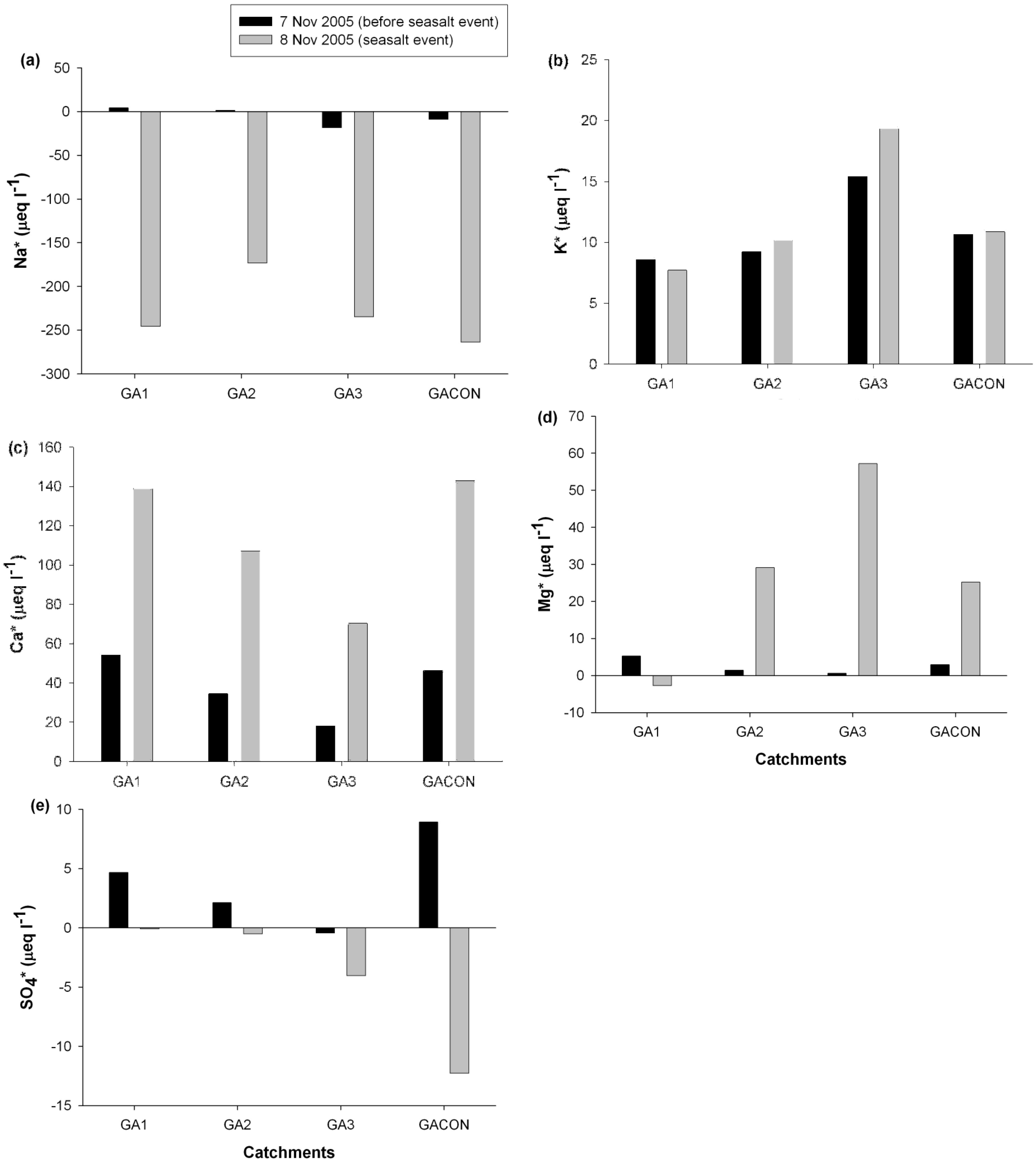


Figure 4.4 Streamwater concentrations of calculated non-marine (a) Na*, (b) K*, (c) Ca*, (d) Mg* and (e) SO_4* before and after the seasalt event in the Glen Arnisdale catchments

Streamwater Al concentrations were expected to increase after the seasalt event due to the increase in streamwater acidity in most catchments (Larssen and Holme, 2006). However, the seasalt event did not appear to trigger mobilisation of metals. Streamwater soluble Al concentrations were around half those measured before the seasalt episode in all four catchments, with concentrations before and after the seasalt event ranging from 64 to 71 µg l^{-1} and 28 to 40 µg l^{-1}, respectively

(Figure 4.5a). There was an indication of Mn mobilisation in GA2, GA3 and GACON, with the greatest Mn concentration increase from 5 to 31 µg l^{-1} in GA3, which was also the catchment with the greatest increase in H^{+} concentration (Figure 4.5b). Streamwater Fe concentrations were approximately four times lower in all catchments after the seasalt event and ranged from 0 to 15 µg l^{-1} (Figure 4.5c).

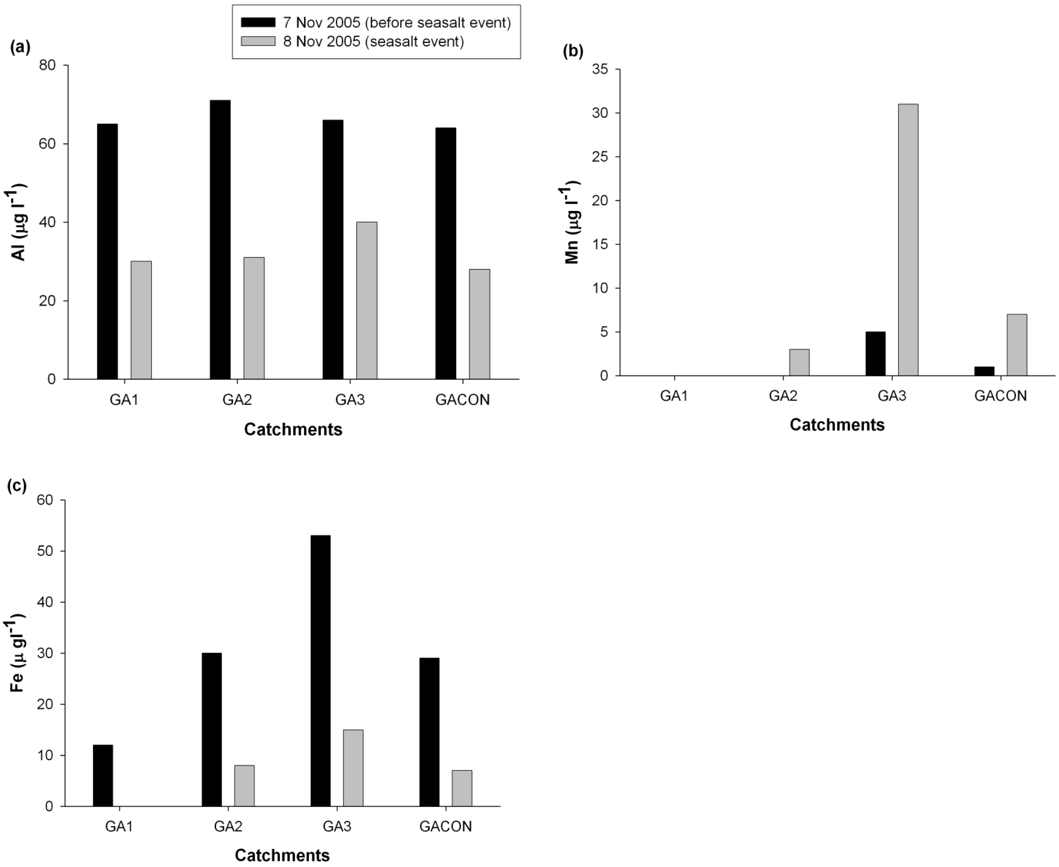


Figure 4.5 Streamwater concentrations of soluble (a) Al, (b) Mn and (c) Fe before and after the seasalt event in the Glen Arnisdale catchments

The lack of increased Al leaching to streamwater could indicate that catchment soils are not acidified enough for Al to dominate the soil cation-exchange sites, but the pHs of the soil types that occur in the catchments are low, ranging from 4.72 to 4.77 according to Macaulay Institute soil series data. Nevertheless, streamwater pH values before and after the seasalt event were relatively high, apart from GA3, indicating high soil buffering capacity. The increase in soluble Mn in GA3, which seems to have the lowest soil buffering capacity of the Glen Arnisdale catchments, could suggest displacement of Mn^{2+} instead of Al^{3+} by Ca^{2+}/Mg^{2+} in the soil complex.

4.2 Multivariate analyses of streamwater chemistry results

Multivariate methods were used to analyse the streamwater chemistry dataset from the study catchments. The aim of the analyses was to identify sources of variability in streamwater chemistry and groupings of study catchments based on their similarity in mean streamwater chemistry. The methods used were Cluster Analysis and Principal Components Analysis (PCA). Both analyses were performed using mean streamwater chemistry for Gran alkalinity, base cations (Ca, Mg, Na and K), acid anions (Cl, SO_4 and NO_3) and soluble Al, Mn and Fe from the 14 study catchments.

4.2.1 Cluster Analysis

As recommended by Townend (2002), the analysis was conducted using different linkage methods (single, complete and centroid) and Euclidean and Manhattan measures of distance. All variables (streamwater chemistry data) were standardised in order to have equal importance when calculating similarity between catchments. Figure 4.6 shows typical output of cluster analysis using complete linkage and Euclidean distance. Similar patterns emerged using all different linkage and distance measure methods and only the percentage of similarity between catchments differed. The analysis results revealed clear catchment groupings according to their geographical location (Figure 4.6). The catchments in Glen Arnisdale and the Loch Katrine area formed two clear groups, while YAR and NAR and UL1 and UL2 also formed their own respective groups. However ULCON was more similar to the Devon catchments than to UL1 and UL2. UL1 and UL2 were more similar to each other than to any other catchments but to a relatively small degree, probably due to the high streamwater alkalinity and Ca concentrations measured in UL2. The Loch Katrine area catchments were similar to the Devon catchments plus catchment ULCON and together formed a group with similar streamwater chemistry characteristics. The Glen Arnisdale catchments group was quite distinct due to the maritime influence on streamwater chemistry. There was little similarity between catchments UL1 and UL2 and other study catchments, probably due to the high SO_4, xSO_4 and especially NO_3 concentrations measured in UL1 and UL2. Overall, the catchment groups emerging from the cluster analysis highlighted the importance of local conditions, mainly topography, rainfall patterns, soil chemistry, pollution climate, and maritime influence, rather than woodland cover, in determining catchment streamwater chemistry.

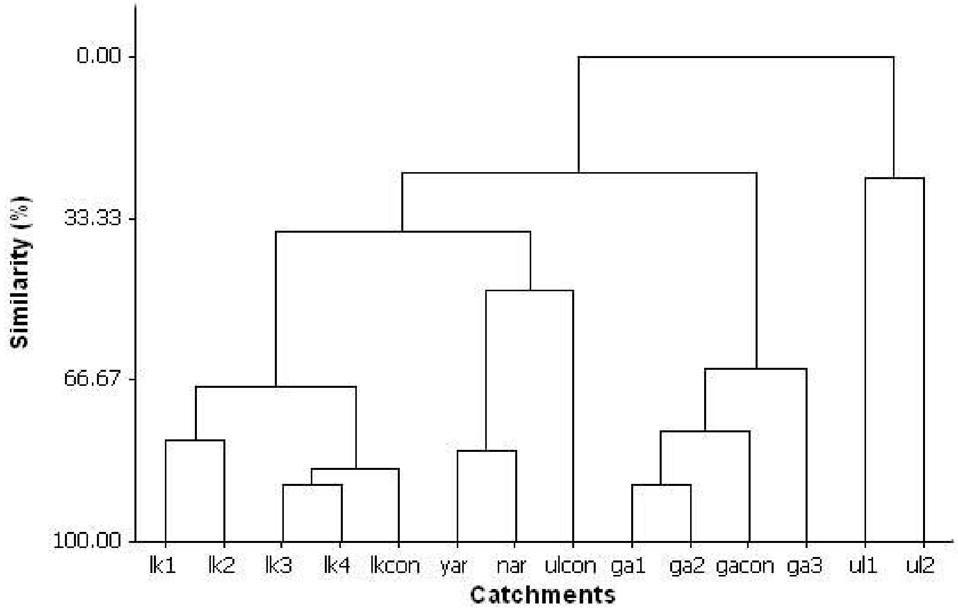


Figure 4.6 Dendrogram produced by cluster analysis of the study catchments using complete linkage and Euclidean distance

4.2.2 Principal Components Analysis (PCA)

The first three principal components (PC1, PC2 and PC3) accounted for 89% of the total variation in streamwater chemistry in the study catchments. Little additional cumulative variance was explained by PC4 (95%) and therefore the analysis focused on the interpretation of the first three principal components. Loadings for the principal components were calculated that related to each of the streamwater chemistry variables (Table 4.5). Variables with loadings close to zero were ignored and inspection of calculated loadings indicated that loadings (positive or negative) above 0.34 were adequate for the interpretation of the three principal components.

Table 4.5 Loadings of streamwater chemistry variables calculated for the first three principal components. Loadings highlighted in bold were used for the interpretation of the first three principal components

Variables	PC1	PC2	PC3
Gran alkalinity	-0.20	**-0.35**	**-0.39**
Ca	-0.27	-0.23	**-0.39**
Mg	**-0.41**	0.07	-0.20
Na	**-0.34**	0.33	-0.07
K	-0.31	**0.36**	0.13
Cl	-0.29	**0.41**	-0.04
SO_4	**-0.39**	-0.18	0.10
$x$$SO_4$	-0.18	**-0.45**	0.12
NO_3	-0.26	**-0.34**	0.24
Al	-0.15	0.08	**0.58**
Mn	-0.17	-0.23	**0.46**
Fe	**0.36**	-0.09	0.06

The loadings on streamwater chemistry variables in each principal component can be used to help investigate influences on streamwater chemistry. PC1 contained negative loadings for Mg, Na and SO_4 and therefore it seemed to reflect terrestrial sources of streamwater. Most streamwater Na and Mg in the majority of the catchments is derived from marine sources, while marine inputs of SO_4 are important in areas of low acid deposition (e.g. Glen Arnisdale). Streamwater Fe was negatively highly correlated with marine derived ions (see Table 4.7) but for reasons unrelated to the atmospheric deposition of these ions, since Fe has a terrestrial source in catchment soils.

PC2 was dominated by alkalinity and acid anions and had negative loadings for Gran alkalinity, SO_4 and NO_3 and positive loadings for K and Cl. It therefore seemed to reflect streamwater with low buffering capacity and acid anion concentrations but also with high marine inputs, represented by inputs of K and Cl, which are auto-correlated (see Table 4.7).

PC3 had negative loadings for Gran alkalinity and Ca and positive loadings for Al and Mn and could be regarded as an index of acid-sensitivity for catchments with low streamwater buffering capacity and enhanced Al and Mn leaching.

The score of each study catchment for the first three principal components was calculated to investigate the influence of the three principal components on streamwater chemistry (Table 4.6). The Loch Katrine area catchments had particularly high positive scores for PC1 reflecting the high streamwater Fe concentrations and also the low levels of marine inputs to streamwater due to the distance from the nearest coast. All other study catchments had negative scores for PC1, with high values for GACON, due to high Mg, Na and SO_4 from marine inputs, and for UL1 and UL2, due to high SO_4 from acid deposition and high Mg concentrations in UL2 possibly from weathering. The Glen Arnisdale and Devon catchments had positive scores for PC2, reflecting the low catchment buffering capacity and low streamwater NO_3 concentrations combined with high Cl inputs, especially in the Glen Arnisdale catchments. The catchments near Ullswater had high negative values for PC2, reflecting mainly the high SO_4 and NO_3 concentrations in UL1 and UL2 and the high alkalinity values in UL2 and ULCON. Positive scores for PC3 were found for GA3, LK1, LK2, UL1, YAR and NAR, with the highest scores for UL1 and YAR. The positive scores suggest a higher degree of acid-sensitivity for these catchments due to the low soil buffering capacity, indicated by low alkalinity and Ca concentrations, and the high soluble Al concentrations. The suggestion that PC3 is an indicator of acid-sensitivity was further supported by the highly significant negative (Spearman's rank) correlations between PC3 scores for each catchment and mean high flow streamwater alkalinity (r_s= -0.83, P= 0.000), Ca (r_s= -0.78, P= 0.000) and ANC (r_s= -0.72, P= 0.002) concentrations and the highly significant positive correlation with streamwater high flow soluble Al (r_s= 0.77, P= 0.001). The remaining catchments had negative scores for PC3 with the most negative values for UL2 and ULCON indicating that these catchments are less sensitive to streamwater acidification.

Table 4.6 Scores of the study catchments for the first three principal components

Catchments	PC1 scores	PC2 scores	PC3 scores
GA1	-0.71	1.79	-0.95
GA2	-0.91	2.30	-0.52
GA3	-1.86	2.76	0.52
GACON	-2.06	2.58	-0.91
LK1	2.20	-0.43	0.47
LK2	3.24	-0.35	0.75
LK3	2.60	-0.23	0.00
LK4	2.23	-0.54	-0.71
LKCON	2.71	-0.55	-0.69
UL1	-2.40	-1.93	3.85
UL2	-4.02	-3.49	-1.87
ULCON	-0.29	-2.18	-1.90
YAR	-0.70	0.23	1.20
NAR	-0.03	0.03	0.77

In order to identify catchment groupings, PC2 scores were plotted against PC1 scores for all study catchments (Figure 4.7). Clear catchment groupings emerged according to the geographical location of the study catchments which were similar to the ones resulting from cluster analysis. The analysis identified the groupings in Glen Arnisdale, the Loch Katrine and Ullswater areas and assigned the Devon catchments closest to the Glen Arnisdale catchments, probably due to the proximity of YAR and NAR to the coast and the low streamwater alkalinity. The PCA results generally agree with the cluster analysis results and illustrate again the important influence of local conditions, with distance from coast being the most obvious, on streamwater chemistry in the study catchments.

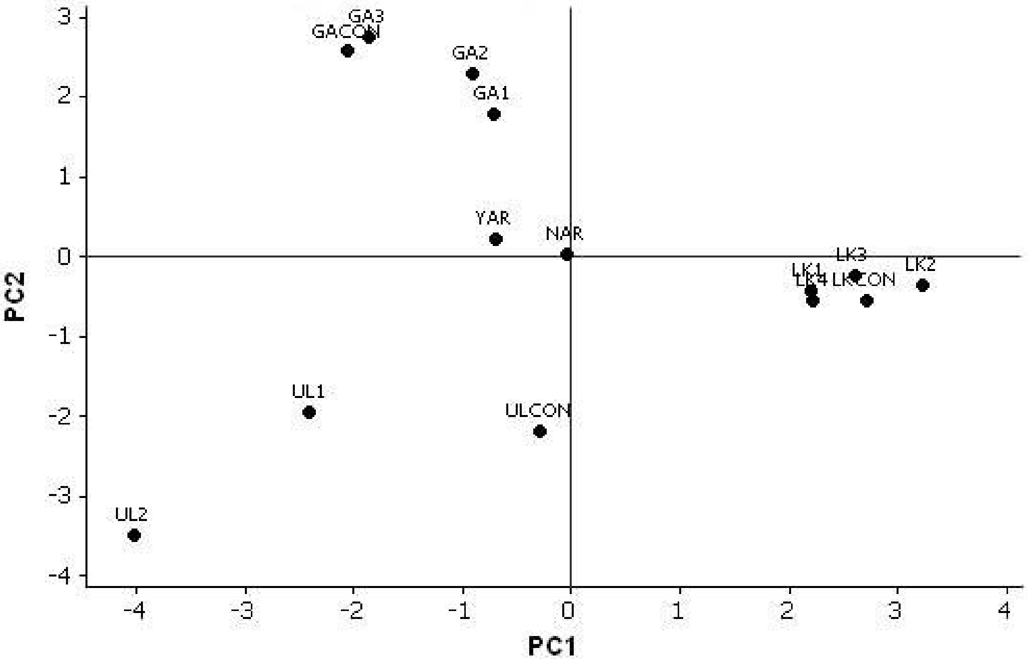


Figure 4.7 Scatter plot of scores for principal components 1 and 2 for the study catchments

4.3 Correlation analysis

Correlation analysis (Spearman's rank) was used to investigate inter-solute relationships in mean streamwater chemistry at high flow to help understand the processes controlling streamwater chemistry in the study catchments. Correlation analysis was also used to investigate relationships between mean high flow streamwater chemistry and percentage woodland cover in the study catchments and catchment characteristics, including topography and soil type.

4.3.1 Inter-solute relationships

The results of the correlation analysis for mean high flow streamwater chemistry, percentage broadleaf woodland cover and distance from coast for the study catchments are shown in Table 4.7. As expected mean streamwater Gran alkalinity and Ca were significantly positively correlated. Gran alkalinity was also significantly positively correlated with calculated ANC and streamwater critical load values (for critical load values see Table 5.3) (r_s= 0.80, P<0.001) and negatively correlated with

Na_{dom} values, suggesting that alkalinity was a good indicator of catchment buffering capacity. Streamwater Ca was significantly positively correlated with Mg and significantly negatively correlated with Na_{dom} values, probably because they are all influenced by weathering processes within catchment soils.

The predominantly marine-derived ions Na and Cl were highly significantly positively correlated and other mainly atmospherically-derived ions Mg and SO_4 were also significantly positively correlated with Na and Cl. All predominantly marine-derived ions (Mg, Na, K, Cl and SO_4) were significantly negatively correlated with distance from the nearest coast. On the other hand, mean streamwater NO_3 was significantly positively correlated with distance from the nearest coast, possibly reflecting the higher NO_3 concentrations in streamwater from the catchments near Ullswater and in Devon due to the proximity to pollution sources. Mean soluble Al was significantly negatively correlated with Gran alkalinity and critical load values (r_s= -0.69, P<0.01) and significantly positively correlated with Na_{dom} values, indicating the occurrence of high concentrations of soluble Al in more poorly buffered catchments. Some significant associations between apparently unrelated species emerged, such as between soluble Al and K and Cl and between streamwater Fe concentrations and all marine-derived ions (Table 4.7). A possible explanation for the relationships between Al and K and Cl could be Al immobilisation as a result of seasalt inputs. Significant negative streamwater Fe correlations with marine-derived ions were a result of the significant positive correlation between streamwater Fe and distance from coast and, since mean concentrations of marine-derived ions were negatively correlated with distance from coast, they were also autocorrelated to streamwater Fe. Mobilisation of Fe to streamwater is probably not related to seasalt inputs, but rather to soil type, especially podzols, which have a high organic matter content. This mechanism is supported by the high mean streamwater Fe concentrations in the Loch Katrine area catchments (Table 4.2), which are predominantly covered by podzolic soils (see Table 3.5). Furthermore, these catchments also had the highest dissolved organic carbon concentrations (DOC, analysed from one high flow sample by Forest Research) within the study catchments, ranging from 7.99 to 9.01 mg l^{-1}, compared to 1.25 to 2.13 mg l^{-1} in the Glen Arnisdale and Devon catchments (DOC not determined in the Ullswater area catchments).

The percentage of gley soils was significantly positively correlated with mean streamwater Ca, Mg, Na and Cl but the relationships did not stand for seasalt corrected concentrations for both Mg and Na. Negative relationships were found between the percentage of podzolic soils and Ca, Mg (non-marine Mg: $r_s = -0.51$, $P<0.05$) and SO_4, indicating that SO_4 may be retained by podzolic soils. Catchments with high percentage cover of gley soils appeared to be able to buffer acid inputs through release of Ca from weathering even at high flow, whereas catchments with a high percentage cover of podzolic soils had lower release of Ca at high flow.

Table 4.7 Correlation (Spearman's rank) matrix showing r_s-values of mean streamwater chemistry at high flow, percentage broadleaf woodland cover, percentage gleys and podzols and distance from coast for 14 study catchments. * $P<0.05$; **$P<0.01$ and ***$P<0.001$. ANC values were calculated as the difference between the sum of base cations and acid anions, and Na_{dom} values according to Equation 4.1

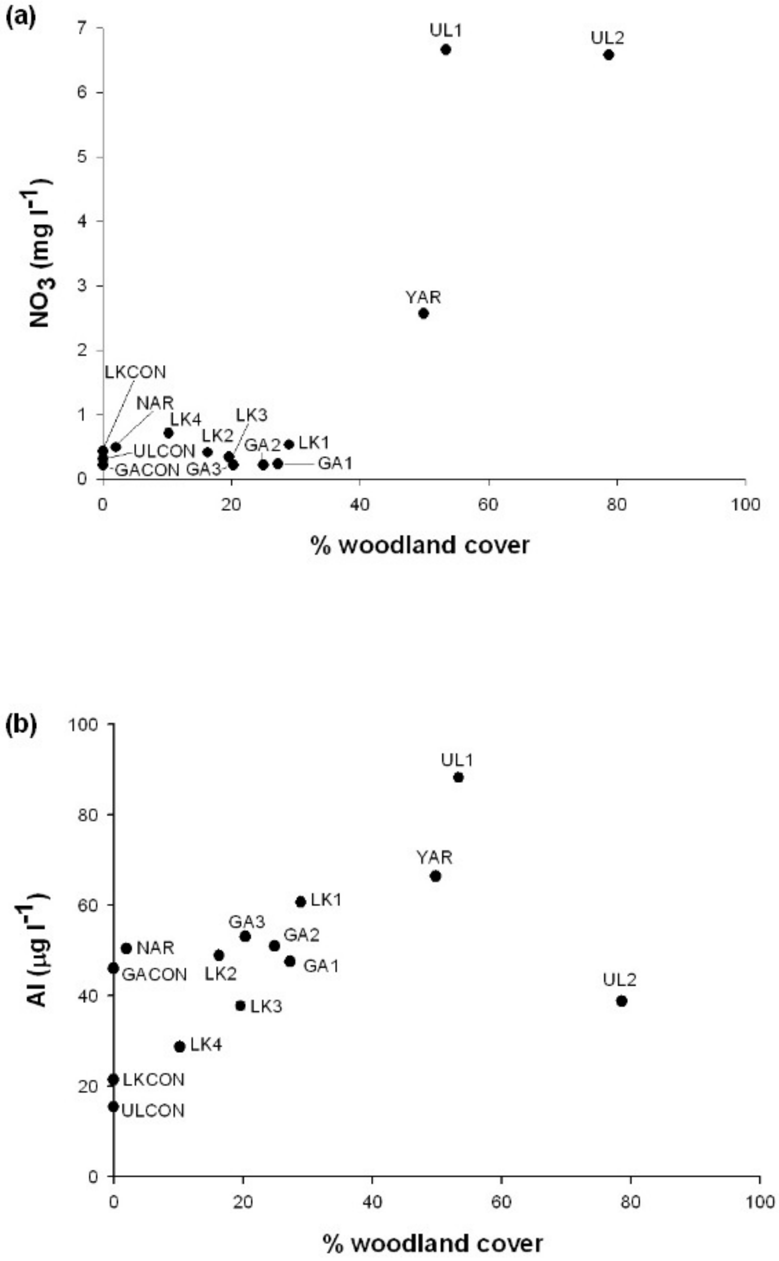
	Gran Alk.	Ca	Mg	Na	K	Cl	SO_4	NO_3	ANC	Na_{dom}	Al	Mn	Fe	Cover (%)	% gleys	% podzol
Ca	0.54*	1.00														
Mg	0.15	0.63**	1.00													
Na	-0.13	0.38	0.86***	1.00												
K	-0.33	0.03	0.63**	0.86**	1.00											
Cl	-0.20	0.31	0.79**	0.97***	0.86**	1.00										
SO_4	0.17	0.41	0.72**	-0.53*	0.30	0.52*	1.00									
NO_3	0.15	-0.17	-0.28	-0.44	-0.39	-0.42	0.28	1.00								
ANC	0.72**	0.42	-0.10	-0.45	-0.64**	-0.58*	-0.20	0.04	1.00							
Na_{dom}	-0.61*	-0.59*	0.06	0.55*	0.72*	0.62*	0.02	-0.28	-0.85**	1.00						
Al	-0.53*	-0.35	0.05	0.32	0.48*	0.46*	0.20	0.23	-0.78**	0.52*	1.00					
Mn	-0.25	-0.04	0.06	-0.14	-0.26	-0.16	0.23	0.38	0.02	-0.09	0.20	1.00				
Fe	-0.10	-0.34	-0.64**	-0.75**	-0.66**	-0.75**	-0.63**	0.20	0.39	-0.28	-0.18	-0.46*	1.00			
Cover (%)	-0.07	0.08	0.18	0.25	0.19	0.28	0.29	0.51*	-0.28	-0.13	0.64**	0.29	-0.17	1.00		
% gleys	-0.07	0.74**	0.72**	0.61*	0.38	0.53*	0.44	-0.19	0.02	-0.23	-0.11	0.28	-0.31	0.25	1.00	
% podzol	-0.10	-0.81**	-0.67**	-0.43	-0.12	-0.40	-0.51*	0.10	-0.11	0.41	0.06	-0.40	0.22	-0.20	-0.87**	1.00
Distance coast	-0.19	-0.23	-0.76**	-0.80**	-0.90***	-0.90***	-0.48*	-0.57*	0.49*	-0.62	-0.19	0.31	0.79**	-0.05	-0.39	0.29

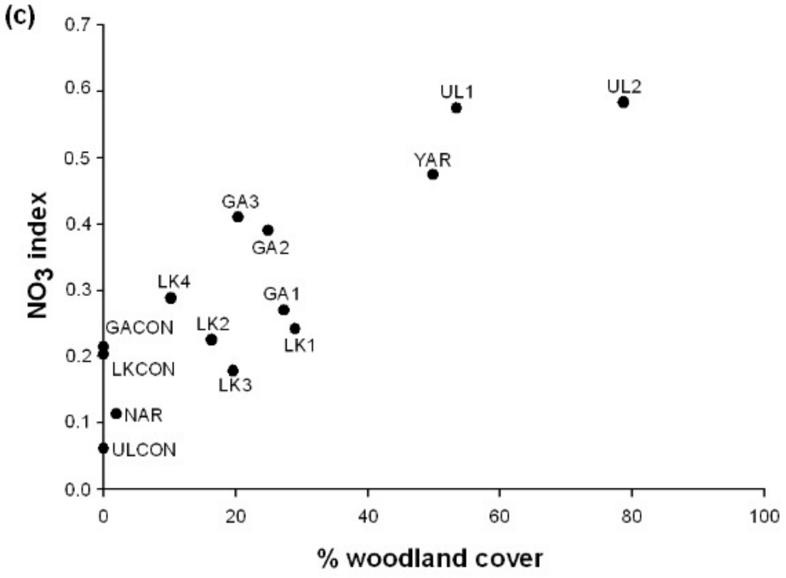
4.3.2 Relationships with percentage broadleaf woodland cover

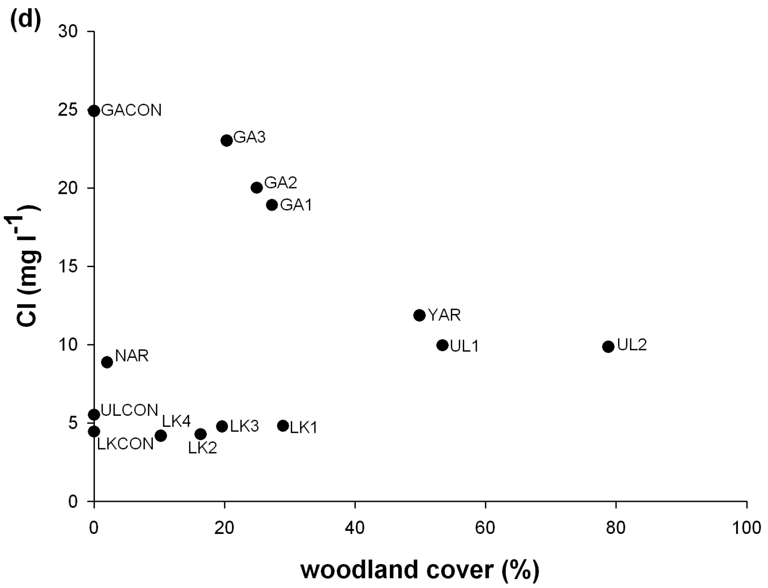
Percentage broadleaf woodland cover was significantly positively correlated with mean streamwater NO_3 (Figure 4.8a) and soluble Al concentrations (Figure 4.8b), indicating an effect of woodland cover on streamwater acidification. Catchments with percentage broadleaf woodland cover less than 30% had mean NO_3 concentrations below 0.71 mg l^{-1} while the more highly forested catchments YAR, UL1 and UL2 had the highest streamwater NO_3 concentrations. Soluble Al concentrations were lowest in the control catchments in the Loch Katrine and Ullswater (LKCON and ULCON) areas and highest in the more forested catchments, YAR and UL1. However, catchment UL2 with the highest woodland cover had a lower mean streamwater Al (38.8 μg l^{-1}).

The percentage broadleaf woodland cover was also highly significantly positively correlated with the nitrate index, the ratio of NO_3:($x SO_4$ + NO_3) (calculated in μeq l^{-1}) (Figure 4.8c). The ratio provides an index of the influence of NO_3 on acidification status, assuming that both anions are derived from anthropogenic acid deposition (Curtis et al., 2005). Values above 0.5 indicate that NO_3 has a greater influence than $x SO_4$ on surface water acidification. Catchments with the highest percentage broadleaf woodland cover, YAR, UL1 and UL2, had the highest ratio values (0.47, 0.56 and 0.57 respectively).

The expected positive associations between percentage broadleaf woodland cover and mean streamwater Cl (Figure 4.8d) and SO_4 (Figure 4.8e) were not found, due to the confounding effect of seasalt inputs which resulted in high Cl concentrations in the Glen Arnisdale catchments and also the acid deposition climate which resulted in high streamwater SO_4 concentrations in catchments ULCON and NAR (Tables 4.1-4.4). The results of the correlation analysis indicate that the significant positive association between mean high flow streamwater soluble Al and percentage woodland cover seems to be caused by atmospheric N rather S scavenging by forest canopies in the study canopies, which could increase streamwater NO_3 concentrations in the highly forested catchments and cause Al displacement from the soil complex.


(a)
NO$_3$ (mg l^{-1})
% woodland cover
0
1
2
3
4
5
6
7
0
20
40
60
80
100
UL1
UL2
YAR
LKCON
NAR
LK4
LK3
LK2
GA2
LK1
ULCON
GACON
GA3
GA1
(b)
Al (μg l^{-1})
% woodland cover
0
20
40
60
80
100
0
20
40
60
80
100
UL1
YAR
LK1
GA3
GA2
NAR
GACON
LK2
GA1
UL2
LK3
LK4
LKCON
ULCON


(c)
NO3 index
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
20
40
60
80
100
% woodland cover
UL1
UL2
YAR
GA3
GA2
LK4
GA1
GACON
LK2
LK1
LKCON
LK3
NAR
ULCON


(d)
Cl (mg l-1)
0
5
10
15
20
25
30
0
20
40
60
80
100
woodland cover (%)
GACON
GA3
GA2
GA1
YAR
UL1
UL2
NAR
ULCON
LK4
LK3
LK1
LKCON
LK2

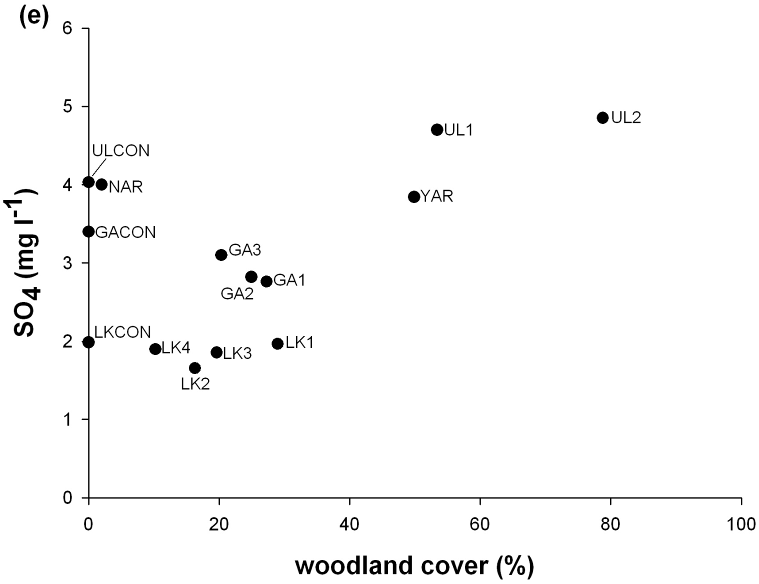


Figure 4.8 Association between percentage broadleaf woodland cover in the study catchments and mean high flow streamwater (a) NO_3 and (b) Al concentrations, (c) nitrate index values, (d) Cl and (e) SO_4 concentrations

4.4 Ecological quality of streams in the study catchments

4.4.1 Macroinvertebrate sampling

As part of a Masters project by Kate Newman macroinvertebrate samples were collected at low flow conditions from the Loch Katrine and Ullswater areas catchments and GA2, GA3 and GACON between June 18th and 28th 2005. The aim of the macroinvertebrate sampling was to assess the water quality in the study catchments and investigate whether macroinvertebrate communities were influenced by streamwater chemistry, percentage of broadleaf woodland cover and catchment soil type composition and topography. Macroinvertebrate assemblages were used to assess similarity of catchments using ordination techniques and also to classify them according to their degree of acid-sensitivity and to compare these classifications with acid-sensitivity determined with the critical loads approach.

Conditions in the streams were low flow during sampling. Sampling from the channel of each Loch Katrine area catchment was conducted at three locations, approximately 20 m apart. Due to the low flow levels in the catchments near

Ullswater, only one sample was collected from UL1 and ULCON, while sampling in UL2 was conducted at two locations approximately 20 m apart. Samples from the Glen Arnisdale catchments were collected during a two day period: GA2 and GACON were sampled three times on each day at same location and one sample was collected from GA3 at same location on both days. Full details of the sampling procedure are given in Section 3.3.5.

4.4.2 Results of taxonomical identification of macroinvertebrate samples

Most macroinvertebrates were identified by Kate Newman to the species level and the results are shown in Table 4.8. LK1 had low to moderate diversity and species density. From the Ephemeroptera order only the acid-sensitive *Baetis rhodani* was present, while several Plecopteran species were found, including the acid-tolerant *Isoperla grammatica*. There were also several Dipteran species, including *Chironomus* species which are indicative of polluted waters. LK2 had slightly higher species diversity than LK1 and the abundance of Ephemeropteran and Coleopteran species and the diversity within the orders was greater than LK1. The acid-sensitive *Baetis rhodani* was present in LK2, along with other *Baetidae* species. There was also a large diversity of Plecopteran species, which was divided into several family groups. Most Ephemeroptera species in LK3 belonged to the Baetidae family, while the Trichoptera order was quite diverse with *Polycentropus* species present, which are considered acid-tolerant. There was a large diversity of Ephemeropteran and Plecopteran species in LK4, while all individuals from the Trichoptera order belonged to the acid-tolerant *Polycentropus* species. LKCON had the highest numbers of individuals of Ephemeropteran species, most of which were the acid-sensitive *Baetis rhodani* species, while 13 individuals from seven Plecopteran species were also found. Overall, species diversity was similar in the Loch Katrine area catchments, apart from in LK1.

Table 4.8 Taxonomic penetration achieved in the identification of macroinvertebrate taxa and abundance of individual taxa in the 11 catchments sampled

Family	Order/species	LK1	LK2	LK3	LK4	LKCON	UL1	UL2	ULCON	GA2	GA3	GACON
	No. of samples	3	3	3	3	3	1	2	3	6	2	6
	Coleoptera											
Elmidae	Elmidae spp	2		5	9	4		9	4	1	4	4
Emnithidae	Emninthidae spp							1				
Dytiscidae	*Dytiscus marginalis*				2				1			1
Hygrobiidae	*Hygrobia hermanni*										1	1
	Diptera											
Chironomidae	*Chironomus* spp	3	3	18	18	3	10	2	25	35	1	24
Simullidae	*Simullium* spp		1	1	1			1		4		14
Tipulidae	*Tipula maxima & Tipula* spp	1	1	1	1	2					1	
Pediciidae	*Pedicia* spp	3		1					1			2
Tanyponidae	*Tanyponidae* spp		1	1	1							
Dixidae	*Dixa* spp									3	1	2
	Other Diptera spp	1			1	1				5		1
	Ephemeroptera											
Baetidae	*Baetis rhodani*	3	12	15	7	41		3		13		14
	Baetis spp		3	14	8	7				5		4
	Cloeon dipterum		2	3		5				2		2
Heptagenidae	*Ecdyonurus* spp		3	1	2	5				2		1
	Heptagenia spp				3	3						4
	Rhithrogena semicolorata				1	3				2		2
Ephemerellidae	*Ephemerella ignita*			3								

Siphlonuridae	*Siphlonurus* spp		1	2								2
	Hemiptera											
Vellida	*Velia caprai*		1				1		1		1	
Microvelia	*Microvelia* spp			1	3		1	11	3	11		4
Aphididae	*Hyalopterus pruni*		1		2		3					
	Plecoptera											
Perlodidae	*Isoperla grammatica* & *Isoperla* spp	3	15	1	4	2	1			16	4	20
	Perla bipunctata		5		1	2				4	2	1
	Perlodes spp		6	1	9	1						1
Chloroperlidae	*Chloroperla torrentium*		3		1	1				12		1
Leuctridae	*Leuctra* spp & *Leuctra geniculata*	2	10	1	3	5		1		9		11
Nemouridae	*Nemoura* spp & *Nemurella picteti*	2	2	1	2	1				8		5
Taeniopteraea	*Taeniopteryx* spp		3			1						
	Trichoptera											
Polycentropodidae	*Polycentropus* spp		2	4	6	2		3	2	1		7
Glossosomatidae	*Agapetus fusicipes*					3				1	15	10
Limnephilidae	*Limnephilus* spp							2	1			2
Leptoceridae	*Leptoceridae*			1							1	1
Brachycentridae	*Brachycentrus* spp			1							1	1
Ecnonomidae	*Ecnomus tenellus*			3							1	
Hydropsychidae	*Hydropsyche* spp	7						1		1	6	1
Sericostomatidae	*Sericostoma personatum*						1			1		1
Psychomyiidae	*Psychomyia pussila*			9								1
Phillopotamidae	*Philopotamus* spp						1		2			

	Odonata											
Aeschnidae	*Aeshna* spp				1							1
	Lepidoptera											
Pyralidae	*Nymphula stagnata*							1				1
	Hydracarina											
	Hydrachna spp	1				1						1
	Araneae											
Agelenidae	*Argyroneta aquatica*				1				1			2
	Pulmonata											
Lymnaeidae	*Lymnaea pereger*								3			3
Planorbidae	*Planorbis leucostoma*								1			1
	Planorbis albus	1										1
	Cyrenadonta											
Sphaeridae	*Pisidium* spp				1							1
	Lumbricus											
Lumbridae	*Eiseniella tetraedra*	2	1	1							1	6
	Clitellata											
Tubifidae	*Tubifex tubifex*							1	4	8		21
	Tricladida											
Seriata	*Dugesia lugubris*				1							1
	Amphipoda											
Gammaridae	*Gammarus* spp						55	293	19			
	Total No. of species	13	20	24	25	20	8	12	13	21	14	41
	Total No. individuals	31	76	87	89	93	73	328	68	145	40	184

UL1 was quite poor in species diversity and density, with only five major orders present in small numbers, expect for *Gammarus* species. The Ullswater area catchments had large numbers of the acid-sensitive *Gammarus pulex*, probably due to the low flow levels during sampling. *Gammarus* species are very common in shallow waters among plants and under stones and at the time of sampling they were clustered in the muddy bottom of the stream beds. No Ephemeropteran and Coleopteran species were found in UL1 while only *Isoperla grammatica* was found from the Plecopteran order. UL2 had the highest population of *Gammarus pulex* (293 individuals) but limited taxonomic diversity. Ephemeropteran and Plecopteran species were absent in ULCON, but there was high abundance of *Gammarus* and *Chironomus* species. Three individuals of *Lymnaea peregra* were found, which is common in large numbers in polluted streamwaters, and its presence was unexpected due to the high streamwater Ca and relatively low SO_4 and NO_3 concentrations in ULCON.

GA2 showed moderate species diversity with the Ephemeroptera and Plecoptera orders being represented by four and five species, respectively, while Dipteran and *Tubificidae* species were also present in considerable numbers. GA3 was taxonomically poor with no Ephemeropteran species present and only two species for each of Coleoptera and Plecoptera. However, GA3 had a relatively high number of individuals of Trichopteran species, especially the acid-sensitive *Agapetus fucipes*. Species diversity was highest in GACON of all the 11 catchments sampled, with every order being represented by at least one species.

Overall, the principal macroinvertebrate groups present were Ephemeroptera and Plecoptera, comprising 23% and 17% of all individuals, respectively, followed by Trichoptera which comprised 9% of individuals. EPT (Ephemeroptera, Plecoptera and Trichoptera) taxa comprised 49% of total individuals, while Gammarus species comprised 30% of all macroinvertebrates found, due to the high numbers sampled in the Ullswater area catchments. EPT taxa are considered particularly sensitive to several pollutants (especially to organic pollution) and their richness and abundance has been used as an indicator of streamwater quality. Based on mean EPT taxa abundance streamwater quality seems to be good in the study catchments, apart from in catchment LK1 and the Ullswater area catchments where mean EPT numbers are low.

4.4.3 Biological indices

Kate Newman used the macroinvertebrates results to calculate the Biological Monitoring Working Party (BMWP) score and Average Score Per Taxon (ASPT) for each of the 11 catchments sampled (Newman, 2005) (Table 4.9). A BMWP score greater than 100 and an ASPT score greater than four generally indicates good water quality. All catchments had ASPT scores greater than four. LK3, GA2 and GACON had BMWP scores greater than 100 and were thus classified as having good water quality. BMWP scores for LK1, GA3 and the Ullswater area catchments ranged from 57 to 76, indicating that the catchments had poor water quality, while LK2, LK4 and LKCON had BMWP scores from 82 to 89 and were considered to have moderate water quality (Table 4.9). These results did not correspond well with acid-sensitivity assessed from streamwater ANC for seven of the 11 catchments sampled, because scores for catchments LK1, UL2 and ULCON, which had positive streamwater ANC values, indicated poor streamwater quality while, conversely, scores for GA2 with negative streamwater ANC suggested good streamwater quality.

Table 4.9 Biological Monitoring Working Party (BMWP) score and Average Score Per Taxon (ASPT) values for the 11 catchments sampled

Catchments	BMWP	ASPT
LK1	57	5
LK2	89	7
LK3	134	7
LK4	92	6
LKCON	82	8
UL1	46	7
UL2	67	5
ULCON	62	5
GA2	103	16
GA3	76	6
GACON	182	6

4.4.4 Streamwater chemistry

Streamwater samples were collected at the same time as macroinvertebrate sampling to assess streamwater chemistry and its effect on macroinvertebrate populations in the 11 catchments sampled. Streamwater samples from the Ullswater area catchments included high quantities of suspended solids due to the very low flow conditions which made it difficult to collect water without disturbing stream sediments. Streamwater samples were analysed for pH, Gran alkalinity, base cations (Ca, Mg, Na and K), Cl, SO_4, NO_3 and NH_4 and soluble Al, Mn and Fe using the same methods as the high flow samples. The results were included in the calculation of mean streamwater chemistry for all samples (high and low flow) collected from the 11 catchments from February to late June 2005, when macroinvertebrate sampling occurred. It was considered more appropriate to use mean streamwater chemistry for the five months prior to macroinvertebrate sampling to assess its effect on macroinvertebrate populations instead of streamwater chemistry determined from single samples at the time of macroinvertebrate sampling because the presence and abundance of macroinvertebrates depends on streamwater chemistry conditions over longer periods, due to the relatively long life span of macroinvertebrates.

For the mean streamwater chemistry calculated from February to June 2005, streamwater base cation concentrations in the 11 catchments sampled were higher and acid anions and soluble metal concentrations lower than mean high flow streamwater chemistry, due to the inclusion of the low flow sample. The most notable differences were streamwater Gran alkalinity and Ca concentrations in the Ullswater area catchments which were much higher than mean high flow concentrations, due to the high Ca and alkalinity concentrations measured in the low flow samples collected during macroinvertebrate sampling from these catchments.

4.4.5 Associations between streamwater chemistry and macroinvertebrate populations

Correlation (Spearman's rank) analysis was used to investigate relationships between mean streamwater solute concentrations and catchment attributes and a) mean abundance of total macroinvertebrate taxa and of the principal macroinvertebrate orders, b) numbers of principal and total macroinvertebrate orders (taxonomical richness) and c) mean abundance of selected indicator species (the acid-sensitive *Baetis rhodani* and *Heptagenia lateralis* and the acid-tolerant *Isoperla grammatica* and *Chloroperla torrentum*) (Tables 4.10 and 4.11). Relationships were also investigated for mean total taxa abundance and streamwater chemistry excluding *Gammarus* species because their high abundance was greatly influenced by low flow levels in the Ullswater area catchments. Mean instead of total abundance was used in the analysis because several samples were collected in some streams and the three Glen Arnisdale catchments were sampled over two days.

Ephemeropteran abundance was significantly positively correlated with percentage podzols cover, while Trichopteran taxa abundance was significantly positively correlated with streamwater Na concentrations, and negatively correlated with streamwater soluble Mn concentrations. Plecopteran taxa abundance was significantly negatively correlated with mean Ca, SO_4 and NO_3. Negative correlations with Ca were unexpected, but emerged from the highly significant positive correlations between Ca and SO_4, which could be due to the mobile anion effect in the catchment soils. Coleopteran taxa abundance was significantly negatively correlated with streamwater Al concentrations. EPT taxa abundance was significantly negatively correlated with streamwater Gran alkalinity, Ca, Mg, SO_4 and NO_3 and percentage broadleaf woodland cover and percentage podzols cover. Total taxa abundance was significantly positively correlated with streamwater alkalinity and base cation concentrations (apart of Ca) and was negatively correlated with streamwater NH_4 and Fe. Total taxa abundance was significantly positively correlated with percentage gleysols but significantly negatively correlated with percentage podzols and catchment area. Total taxa abundance excluding *Gammarus* species was significantly negatively correlated with streamwater Ca, Al, Mn and percentage broadleaf woodland cover, but significantly positively correlated with mean catchment slope.

Table 4.10 Summary of correlation (Spearman's rank) coefficients (r_s) for mean solute concentrations, percentage broadleaf woodland cover and main catchment attributes with mean taxon abundance for principal macroinvertebrate orders and total taxon abundance. * $P<0.05$ and **$P<0.01$

	Mean Taxon Abundance						
	Ephemeroptera	Trichoptera	Plecoptera	Coleoptera	EPT	Total	Total (no *Gammarus* spp)
pH	-0.17	0.15	-0.38	0.52	-0.04	0.48	0.14
Gran Alk	-0.41	-0.34	-0.42	-0.07	-0.54*	0.61*	-0.40
Ca	-0.31	-0.19	-0.70**	0.24	-0.60*	0.37	-0.53*
Mg	-0.48	0.11	-0.47	0.36	-0.57*	0.75**	-0.24
Na	-0.27	0.57*	-0.23	0.32	-0.25	0.64*	0.06
K	0.13	-0.23	-0.02	-0.21	-0.09	0.63*	-0.12
Cl	-0.12	0.35	0.19	-0.06	-0.03	0.31	0.05
SO_4	-0.29	-0.11	-0.74**	0.33	-0.61*	0.37	-0.49
NO_3	-0.32	-0.25	-0.61*	0.25	-0.59*	0.37	-0.52
NH_4	0.25	-0.42	0.02	-0.07	0.08	-0.54*	-0.23
Al	-0.48	-0.26	0.05	-0.53*	-0.41	-0.28	-0.62*
Mn	-0.31	-0.55*	-0.47	-0.34	-0.44	0.21	-0.57*
Fe	0.24	-0.36	0.24	-0.35	0.33	-0.82**	-0.08
% woodland	-0.45	-0.12	-0.29	-0.19	-0.57*	0.11	-0.65*
% gleysols	-0.33	0.34	0.42	0.14	-0.37	0.78**	-0.14
% podzols	0.68*	-0.01	0.37	-0.12	0.66*	-0.61*	0.40
Min altitude	-0.36	-0.24	-0.63*	0.09	-0.50	0.16	-0.38
Catchment area	0.22	-0.05	0.54*	-0.18	0.46	-0.77**	-0.03
Mean catchment slope	0.28	0.38	0.61*	0.13	0.46	-0.33	0.53*

Relationships between species richness for principal orders and total species richness and mean streamwater chemistry, percentage woodland cover and catchment attributes are given in Table 4.11.

Table 4.11 Summary of correlation analysis (Spearman's rank) for mean solute concentrations, percentage broadleaf woodland cover and main catchment attributes with species richness for principal macroinvertebrate orders and total species richness. Only significant (*P*<0.05) relationships are listed. Correlation coefficients (r_s) are given in brackets.

Taxonomical order	Solutes
Ephemeroptera	-
Trichoptera	Ca (-0.61)
	SO_4 (-0.58)
	NO_3 (-0.59)
	NH_4 (-0.65)
Plecoptera	Ca (-0.56)
	Mg (-0.62)
	SO_4 (-0.58)
	Area (0.60)
	% gleys (-0.54)
	% podzols (0.56)
Coleoptera	Na (0.58)
	Al (-0.54)
	Mn (-0.62)
	Fe (-0.54)
EPT	Ca (-0.65)
	SO_4 (-0.68)
	NO_3 (-0.60)
Total	Al (-0.58)
	% woodland cover (-0.59)

Numbers of Ephemeropteran species were not significantly correlated with any of the streamwater chemistry parameters or catchment attributes. The richness of the acid-sensitive orders Trichoptera, Plecoptera and Coleoptera was significantly negatively correlated with one or more of streamwater Ca, Mg, SO_4, NO_3, NH_4, Al, Mn and Fe. Richness of EPT species was significantly negatively correlated with Ca, SO_4 and NO_3. Total species richness for the 11 catchments sampled decreased with increasing streamwater Al concentrations and increasing percentage broadleaf woodland cover (Figure 4.9).

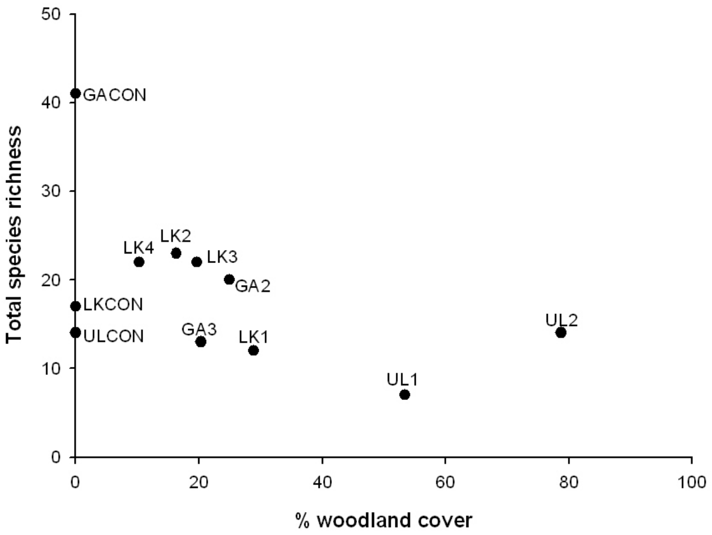


Figure 4.9 Association between total species richness and percentage broadleaf woodland cover for the 11 catchments sampled

Overall the results for species mean abundance and richness, especially for EPT and total number of species, suggest that both abundance and richness decline in catchments with higher streamwater concentrations of the acidifying anions SO_4 and NO_3 and of potentially toxic soluble Al. Percentage woodland cover also seems to be an important control on species abundance and richness, mainly due to the significant positive relationship between percentage woodland cover and streamwater soluble Al ($r_s = 0.81$, $P<0.01$). The significant negative correlations between species abundance and richness and streamwater Ca and Mg concentrations were unexpected, but probably emerged due to the significant positive associations between streamwater Ca and SO_4 and NO_3 ($r_s = 0.96$ and $r_s = 0.98$, both $P<0.001$), and streamwater Mg with NO_3 ($r_s = 0.55$, $P<0.05$). These relationships between Ca and Mg and the acid anions could be due the mobile anion effect in the catchment soils.

Correlation analysis, conducted using the mean abundance of selected macroinvertebrate species, showed that abundance of the acid-sensitive *Baetis rhodani* was significantly negatively correlated with mean streamwater Mg (r_s= -0.58, P<0.05) and positively correlated with percentage podzols cover (r_s= 0.73, P<0.01), probably because streamwater Mg was also significantly negatively correlated with percentage podzol cover (r_s= 0.90, P= 0.000). Numbers of the acid-sensitive *Heptagenia lateralis* were significantly negatively correlated with mean soluble Al and percentage broadleaf woodland cover (r_s= -0.56, P<0.05 and r_s = -0.63, P<0.05, respectively), indicating higher abundance in less acidic conditions. Numbers of the acid-tolerant *Isoperla grammatica* were significantly negatively correlated with mean streamwater Ca (r_s= -0.68, P<0.05), SO_4 (r_s= -0.75, P<0.01) and NO_3 (r_s= -0.62, P<0.05). Acid-tolerant *Chloroperla torrentum* numbers were significantly negatively correlated with streamwater SO_4 concentrations (r_s= -0.54, P<0.05). Overall, the results for the indicator species show that abundance of both acid-sensitive and acid-tolerant species declines in catchments with high streamwater concentrations of the acid anions SO_4 and NO_3, while abundance of the acid-sensitive *Heptagenia lateralis* declined in catchments with high woodland covers and high streamwater soluble Al concentrations.

4.4.6 Analysis of catchment similarity based on macroinvertebrate composition

Detrended Correspondence Analysis (DCA) was used to assess patterns of similarity between the 11 catchments sampled based on their macroinvertebrate composition at different levels of taxonomical penetration: the family level and the less detailed order level. Mean abundance values were used for all macroinvertebrate families and for the major macroinvertebrate orders present in the catchments. The analysis was also conducted using mean abundance of individual species and mean richness of macroinvertebrate families and orders but the results obtained were not significant due to the low dispersion of the species in the ordination axes.

Results of the DCA using mean abundance values for macroinvertebrate family data are given in Table 4.13 and Figure 4.10. Family abbreviations used in Figure 4.10 are given in Table 4.12. Gammaridae species were not included in the analysis as their high presence in the Ullswater catchments was predominantly due to the low flow levels present during sampling.

Table 4.12 Macroinvertebrate family names and their abbreviations used in Figure 4.10 for the 11 catchments sampled

Family name	Abbreviation	Family name	Abbreviation
Aeshnidae	AESHN	Lymaea	LYMAE
Agelenidae	AGELE	Microvelia	MICRO
Aphididae	APHID	Nemouridae	NEMOR
Baetidae	BAETI	Pediciidae	PEDIC
Chironomidae	CHIRO	Perlodidae	PERLO
Chloroperlidae	CHLOR	Philopotamidae	PHILO
Dixidae	DIXID	Polycentropodidae	POLYC
Dytischidae	DYTIS	Psychomyridae	PSYCH
Elmidae	ELMID	Pyraidae	PYRAL
Emnithidae	EMNIT	Seriata	SERIA
Ephemerellidae	EPHEM	Simulidae	SIMUL
Glossomatidae	GLOSS	Siphlonuridae	SIPHO
Heptagenidae	HEPTA	Taeniopterae	TAENI
Hygrobiidae	HYGRO	Tipulidae	TIPUL
Leuctridae	LEUCT	Vellida	VELII
Limnephillidae	LIMNE		

Table 4.13 Summary statistics for DCA shown in Figure 4.10

	DCA 1	DCA 2	DCA 3	Total
Eigenvalue	0.44	0.19	0.09	2.34
Cumulative percentage variance	22.9	32.6	37.2	

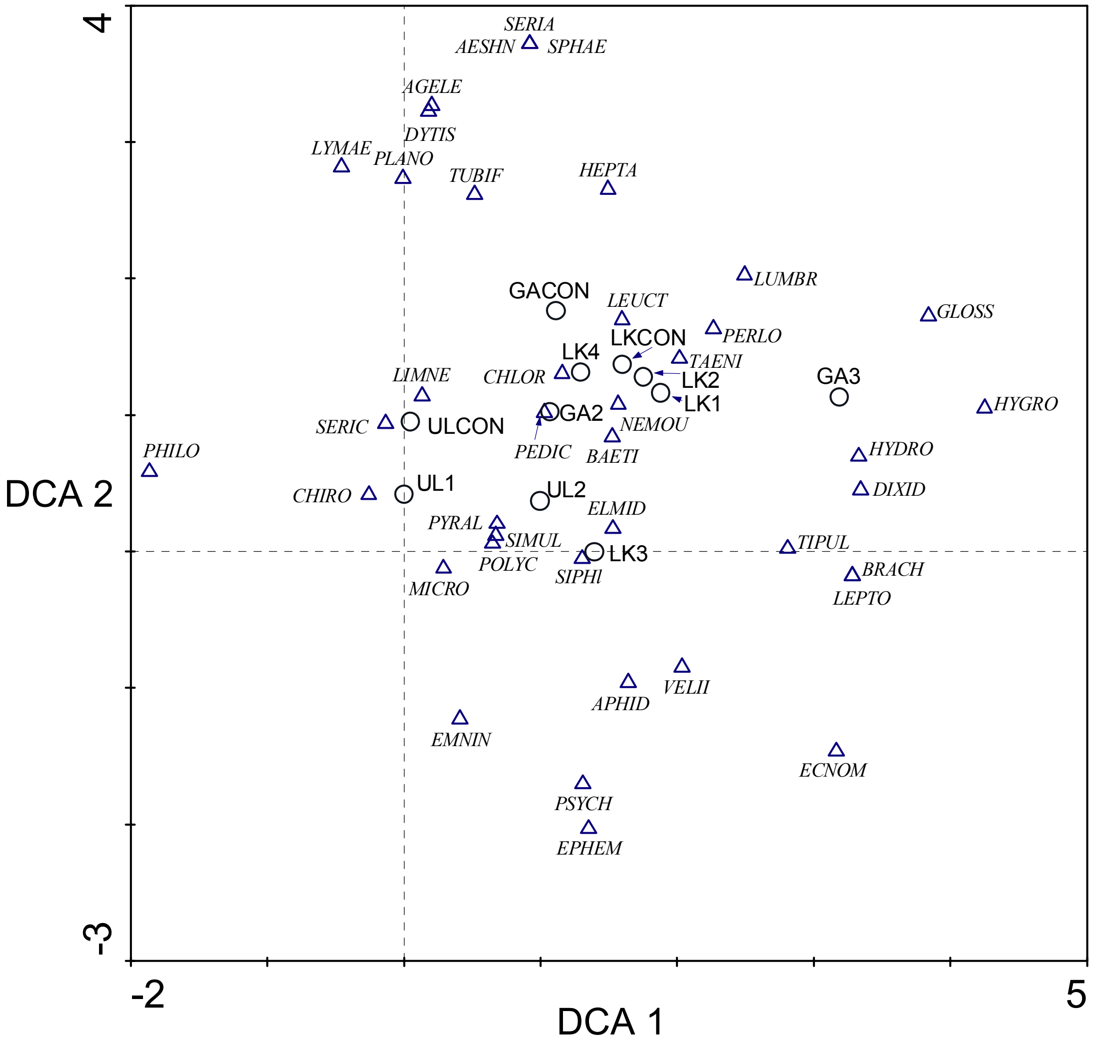


Figure 4.10 Detrended Correspondence Analysis (DCA) ordination diagram of DCA 2 vs. DCA 1 of mean macroinvertebrate family data from the 11 catchments sampled. Macroinvertebrate families (see Table 4.12 for abbreviations) are represented by triangles and catchments are represented by circles. Scale marks are in multiples of standard deviation (s.d.) and the dashed lines represent zero

Eigenvalues above 0.50 usually denote a good separation of families along the axis, while catchments at opposite ends of an axis with a length close to four s.d. should have little similarity in species composition (ter Braak, 1995). The eigenvalue of the first DCA axis was relatively high, indicating good dispersion along this axis, but the eigenvalue of DCA 2 was much lower and the two axes together explained only 32.6% of total variation (Table 4.13).

Some clear catchment groupings emerged in Figure 4.10. LK1, LK2, LK4, LKCON, GA2 and GACON formed one group, while UL2 and LK3 formed a smaller group nearby. Catchments UL1 and ULCON have little similarity in species composition with GA3 because their distance was close to 4 s.d. Most of the common macroinvertebrate families clustered around the largest grouping of catchments in the ordination plot, including both families with acid-sensitive species, such as the Baetidae and Nemouridae, and acid-tolerant species, such as Perlidae and Leuctridae. However, GA3 was closer to the Glossosomatidae and Hydropsychidae families, which included acid-sensitive species such as *Agapetus fuscipes* and *Hydropsyche* (Figure 4.10).

DCA results using mean abundance values for the major macroinvertebrate orders present in the 11 catchments sampled are given in Table 4.14 and Figure 4.11. Macroinvertebrate orders used were Ephemeroptera (EPH), Plecoptera (PLE), Trichoptera (TRI), Coleoptera (COL), Diptera (DIP) and Hemiptera (HEM).

Table 4.14 Summary statistics for DCA shown in Figure 4.11

	DCA 1	DCA 2	DCA 3	Total
Eigenvalue	0.30	0.10	0.01	0.66
Cumulative percentage variance	45.5	60.6	62.1	

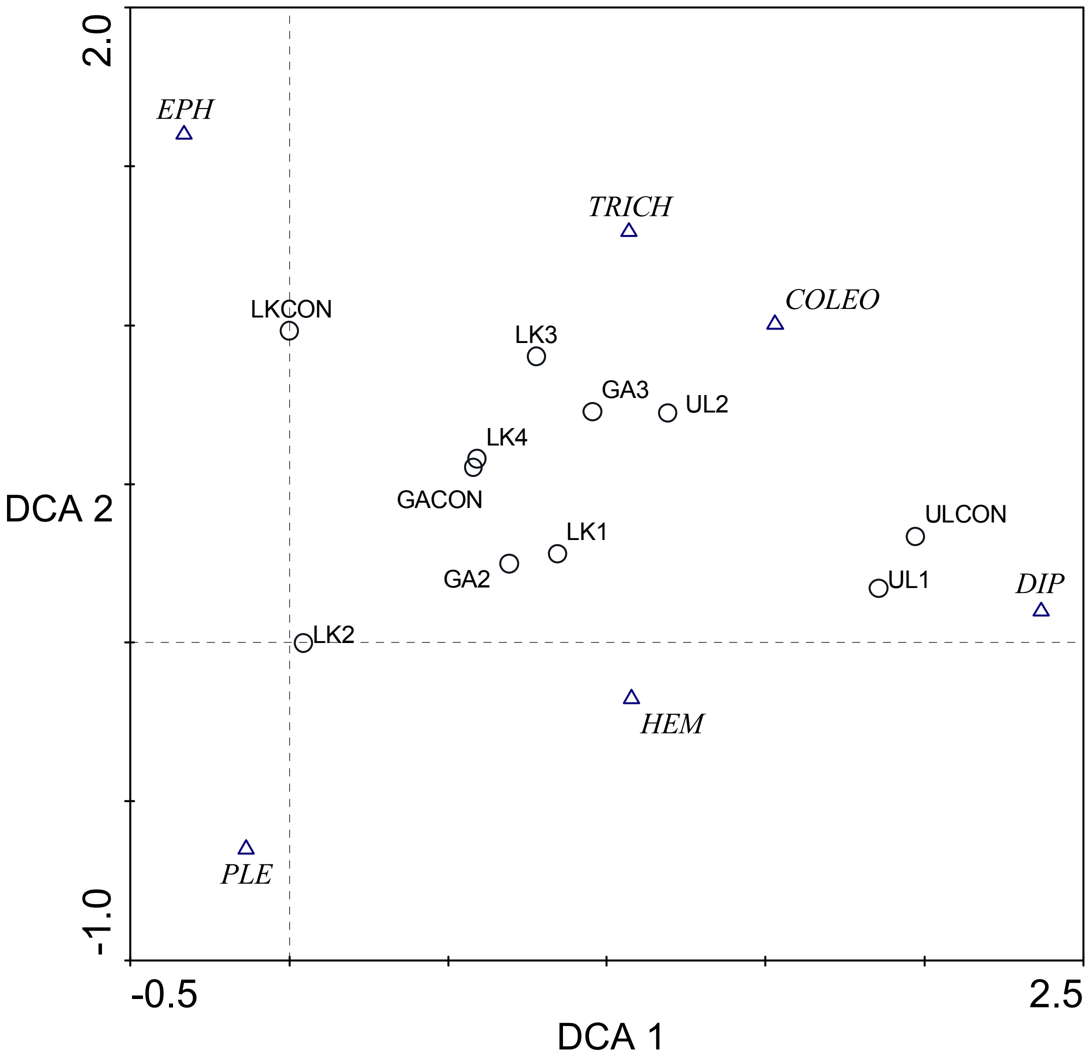


Figure 4.11 Detrended Correspondence Analysis (DCA) ordination diagram of DCA 2 vs. DCA 1 of mean macroinvertebrate order data from the 11 study catchments sampled. Major orders (see text for abbreviations) are represented by triangles and catchments are represented by circles. Scale marks are in multiples of standard deviation (s.d.) and the dashed lines represent zero

The eigenvalues of the first two DCA axes are low, indicating a moderate separation of macroinvertebrate orders, but 60.6% of total variation is explained by these axes (Table 4.14). Moderate separation is also shown by the lengths of DCA 1 and DCA 2 which are 2.5 and 2.0 s.d., respectively. Most catchments form one group and are located between 0 and 1.5 s.d. along DCA 1 and 2, apart from catchments UL1 and UL2 which lie towards the end of DCA 1 and form a separate group (Figure 4.11). Dipteran species fall closest to UL1 and ULCON, Plecopteran closest to LK2 and

Ephemeropteran closest to LKCON, while the remaining catchments were closest to Coleopteran, Trichopteran and Hemipteran species.

Overall, the DCA results for macroinvertebrate data, at both the family and order level, did not reveal clear patterns for the 11 catchments sampled. Most catchments are clustered together, while only macroinvertebrate composition in GA3, and UL1 to a lesser extent, seems to differ from the other catchments. Also, there were no clear associations between macroinvertebrate families or orders and study catchments.

4.5 Discussion of factors controlling streamwater chemistry in the study catchments

The effect of broadleaf woodland cover on high flow streamwater chemistry due to the scavenging effect was expected to be more evident for the atmospherically-derived ions Cl, SO_4, xSO_4 and NO_3, and also for soluble Al concentrations due to incoming mobile anions releasing Al from the soil complex. However, significant positive relationships between broadleaf woodland cover and streamwater chemistry in the study catchments were found only for streamwater NO_3 and soluble Al. Broadleaf woodland effects on streamwater chemistry were probably masked by variability in local conditions, in particular pollution deposition climate, catchment soil type composition and topography. The importance of local conditions for streamwater chemistry in the study catchments was further demonstrated by the catchment groupings identified by multivariate analyses (cluster analysis and PCA) of the streamwater chemistry results which corresponded to the geographical location of the study catchments.

4.5.1 Atmospheric deposition

The study catchments have experienced different past and present pollutant deposition due to different distances from major pollutant sources. The catchments near Ullswater have been probably most impacted by acid deposition, since the region of Cumbria received the highest measured rates of wet non-marine S and total

N deposition in the UK in 1997 of 25 kg S and 25 kg N ha^{-1} yr^{-1}, respectively (NEGTAP, 2001). Cumbria and northern England is one of the areas of the UK most impacted by soil acidification caused by acidic inputs, with soil critical loads exceedance in 1995-97 above 0.5 kg H ha^{-1} yr^{-1} (NEGTAP, 2001). On the other hand, north-west Scotland has never experienced large amounts of anthropogenic pollutant deposition and the acid-sensitivity of freshwaters in this area is mainly due to the poor buffering capacity of soils for acidic inputs (Harriman et al., 2001). The pollution climate in the Trossachs and Devon was similar to the Ullswater area but deposition loads were lower. The contribution of wet deposition to total non-marine S and N deposition corresponded to rainfall inputs in the study catchments, and was highest and lowest in the Loch Katrine and Ullswater areas catchments, respectively.

The rates of pollutant deposition were expected to vary substantially in the study catchments due to the different structure of the broadleaf woodlands present. The aerodynamic resistances used to calculate dry deposition estimates in the UK are determined from the roughness length, z_0, of the canopy, canopy height, h, and wind speed (Smith et al., 2000). The ratio of z_0 to h varies widely depending on canopy density. It is expected to decrease as a canopy closes and the air flow experiences drag only near the top of the canopy while, conversely, as canopy elements become sparse, their drag declines and the ratio also decreases (Schaudt and Dickinson, 2000). Therefore, the maximum z_0/h ratio should occur at some intermediate value of canopy density. Dry deposition loads in the study catchments depend on the actual air pollutant concentration and also on proximity to major pollutant emissions. Calculated z_0 and h values were available only for the birchwoods in the Loch Katrine area (see Chapter 6) but, according to the modelled dry S and N deposition inputs generated with FRAME (see Chapter 5), dry deposition was expected to be higher in the more dense and highly forested catchments in the Ullswater area and Devon than in the more open birchwoods in Glen Arnisdale and the Loch Katrine area catchments, despite the effect of wind speed which could enhance dry deposition inputs in the more upland Scottish catchments.

The study catchments in Glen Arnisdale and the Loch Katrine area had a clear upland character and catchment mean and maximum altitudes and mean slopes were much higher than in the more gentle sloping and lower altitude catchments in the Ullswater area and Devon. Wet deposition in the uplands (typically 300-1000 m in the UK) is subject to orographic enhancement due to the "seeder-feeder" effect, where precipitation from the high level (seeder) cloud effectively washes out aerosol phase pollutant-derived ions (SO_4, NO_3 and NH_4) from hill (feeder) clouds increasing rainfall amount and the concentrations of ions reaching the ground (Metcalfe et al., 1999). In addition, the direct deposition of cloud droplets, containing high concentrations of liquid phase pollutant ions, to vegetation represents an important contribution to deposition totals in upland areas in western UK which are in cloud for a significant fraction of time, especially at elevations above 600 m. Therefore, the "seeder-feeder" and occult deposition mechanisms could result in larger deposition inputs to the Scottish study catchments which generally have mean and maximum altitudes above 300 and 600 m, respectively, and also a high proportion of woodland cover occurring above 300 m. However, despite the lower altitudes of the English study catchments, acid deposition would be expected to be enhanced by higher S and N dry deposition due to the greater broadleaf woodland cover and closer proximity to major pollution sources.

4.5.2 Geological and soil effects on catchment buffering capacity

The interaction between marine inputs and soil weathering rates probably largely determined the buffering capacity of soils in the study catchments. The study catchments were dominated by slow-weathering soil types derived from acidic geological substrates (mainly quartzites and granite), which resulted in low soil buffering capacity to acidic inputs, as demonstrated by the low streamwater alkalinity and base cation concentrations measured at high flows. Different proportions of the main catchment soil types, gleys and podzolic soils, may have an important influence on streamwater chemistry. In particular, streamwater Ca and Mg concentrations were found to be influenced by soil type and were higher in catchments with substantial percentages of gleysols (UL1, UL2 and Glen Arnisdale catchments) indicating possible contributions from gleys of Ca-rich water even at high flows as reported elsewhere in the Acid Waters Survey of Wales (Stevens et al., 1997). On the other hand, streamwater Ca and Mg concentrations were lower in catchments with a substantial proportion of podzolic soils (Loch Katrine area and Devon catchments). More base cations are expected to be available in gleysols because they are less weathered and leached than podzols (Stevens et al., 1997). However, the association with percentage gleysols cover did not stand for non-marine Mg, probably due to greater contributions of Mg from marine inputs rather than chemical weathering.

The maritime influence on streamwater chemistry was clearly evident in the study catchments and was demonstrated by the significant negative association between Na_{dom} values and streamwater alkalinity and Ca concentrations (see Table 4.7). High positive Na_{dom} values indicate soils with low weathering rates, especially for Ca in soils, and the base cation ratio is expected to differ only slightly of that in seawater. This was supported by White et al. (1999) who used Na_{dom} values to successfully predict weathering rates in 59 upland catchments in north-eastern Scotland. Most study catchments had relatively high Na_{dom} values, indicating little soil weathering and subsequently low soil buffering capacity, which was supported by the relatively low mean streamwater Ca concentrations, especially for catchments YAR and NAR (Table 4.4). In addition, Na_{dom} values for the Glen Arnisdale and Loch Katrine area catchments generally agreed with chemistry data, provided by the Macaulay Institute for the soil series present in these catchments, which showed that these catchments had similar and low soil water pH values (4.13-4.79), indicating low soil buffering capacities.

The physical and chemical characteristics of surface soil horizons under different tree species can vary due to differences in litter quality and nutrient status, root nutrient uptake, interception of atmospheric deposition, alterations to the microclimate and the soil biological community associated with the tree species (Alexander and Cresser, 1995). In a study of the impact of different tree species on the chemistry of mineral topsoil in Sweden, pH, base saturation and exchangeable Ca^{2+} concentrations in the upper (0-10 cm) soil layer were significantly lower under spruce than birch or oak, while total Al pools and concentrations were significantly higher under spruce than the deciduous species (Hagen-Thorn et al., 2004). In the same study, soil chemistry under birch and oak was found to be similar and less acidic due to higher litter decay rates and low acidic deposition inputs, and possibly also due to neutralisation of acid deposition in deciduous forests by the leaching of base cations into stemflow, as reported by Levia Jr. and Frost (2003). These results indicate that the birch and oak woodland in the Glen Arnisdale, Loch Katrine area catchments and in YAR should have similar effects on soil chemistry. The mature alderwood in catchments UL1 and UL2 could have caused depletion of soil base cations due to increased nitrification below alder, associated with the atmospheric N fixing ability of this species, leading to NO_3 leaching (Hurd et al., 2001), but there was no evidence of this effect in the results. Streamwater Ca and Mg concentrations in UL1 were similar to most study catchments. In UL2, Mg concentrations were also similar to most catchments but Ca concentrations were the highest in the study catchments, probably due to past application of lime. The effect of alder trees on streamwater NO_3 leaching to streamwater is discussed further below.

4.5.3 Climatic effects

The UK lies at the boundary between a large area of small pollutant emissions, the Atlantic Ocean, and continental Europe with large sources to the south and east. The bulk of the annual precipitation over the UK is associated with depressions approaching from the west. Because rainfall efficiently removes aerosol phase SO_4, NO_3 and NH_4, areas with high rainfall in western Britain tend to receive the largest influx of acidic wet deposition even though the concentration of pollutants is lower than in eastern Britain. Thus the deposition in western Britain of pollutants from industrial activity is highly episodic due to the episodicity of precipitation, combined with the relatively infrequent flow of highly polluted continental air into an area of effective precipitation scavenging (Fowler et al., 2005). This can result in 30 to 50% of the annual wet deposition occurring in only one to three precipitation events. Hence, climatic effects causing the episodicity of acid deposition could have masked any broadleaf woodland scavenging effects. However, streamwater sampling did not apparently capture one of these acidic episodes, since streamwater high flow SO_4 and NO_3 concentrations did not vary much in the study catchments.

In addition, the location of the UK at the north-west edge of Europe makes the atmospheric chemistry very sensitive to air mass trajectories. Thus inter-annual variations in the influence of westerly airflows are expected to affect the annual deposition of both marine and anthropogenic ions (Evans and Monteith, 2000). Peak positive values of the North Atlantic Oscillation (NAO) index are associated with south westerly air flow over the UK, higher wind speeds and the potential for larger marine ion contributions and lower contributions of pollutant-derived ions (SO_4, NO_3 and NH_4) to precipitation chemistry. However, NAO index values for winter/spring of 2004/2005 and 2005/2006, when streamwater sampling occurred in the study catchments, were negative (-0.11 and -0.82, respectively, source: www.cru.uea.ac.uk), indicating a reduced maritime influence and larger contributions from anthropogenic pollutant deposition, although at least one seasalt event still occurred in the Glen Arnisdale catchments. If the study had been conducted in other years with positive NAO index values, the enhanced presence of marine ions might have made it even more difficult to discern the influence of broadleaf woodland cover on streamwater concentrations of acidifying atmospherically-derived anions and soluble Al from episodic acidification due to high seasalt inputs.

4.5.4 Factors influencing chloride concentrations in the study catchments

Streamwater Cl concentrations appeared to be influenced more by distance from the nearest coast rather than by woodland scavenging, especially in the Glen Arnisdale and Loch Katrine area catchments where no apparent difference was observed in Cl concentrations between forested and unforested catchments at present levels of woodland cover (10 to 30%). Only in the UL1 and UL2 catchments, with higher percentage woodland covers (> 50%), was there evidence of enhanced Cl capture by the woodland canopy as streamwater Cl concentrations were significantly higher than in the control catchment (Kruskal-Wallis and non-parametric multiple comparisons, $P<0.01$ for both UL1 and UL2). These differences were easier to observe in the Ullswater area catchments because they are located almost 50 km from the west coast and thus were not as greatly influenced by seasalt inputs as the Glen Arnisdale catchments.

In general, because the study catchments were located close to the nearest coast (2 to 56 km), streamwater chemistry was strongly influenced by seasalt inputs, especially for the marine-derived ions Cl, Na and Mg and to some extent K and SO_4. In addition, data from the UK primary precipitation chemistry measurement stations show that Cl deposition is highly episodic with more than 30% of the wet deposition occurring in less than 5% of the precipitation events, with almost 80% of Cl deposition occurring during winter months (Fowler and Smith, 2000). Results from the UK network also showed that there are climatic controls on Cl deposition as annual NAO index values were significantly associated with Cl (and Na) in precipitation, with the highest concentrations occurring in high NAO years. Therefore, climatic controls on Cl deposition, the episodic nature of Cl deposition and the distance of catchments from the nearest coast can introduce great variability, both spatially and temporally, in streamwater Cl concentrations in the study catchments, making it difficult to identify any effects of broadleaf woodland cover on Cl deposition.

4.5.5 Factors influencing marine and non-marine sulphate concentrations in the study catchments

No significant indication of a woodland effect, via canopy scavenging, on streamwater chemistry emerged for SO_4 and xSO_4. There are a number of explanations for this. Wet S deposition dominated modelled total non-marine S deposition inputs to all the study catchments and especially in the high rainfall catchments in the Loch Katrine area. Since wet S deposition is largely unaffected by the presence of woodland, streamwater SO_4 and xSO_4 concentrations were similar in the forested and unforested catchments in the Loch Katrine and Ullswater areas and Devon catchments. In the Glen Arnisdale catchments, most SO_4 was of marine origin and concentrations seemed to correspond to distance from the nearest coast. Concentrations of both streamwater SO_4 and xSO_4 were highest in the Ullswater area and Devon catchments, probably because they were closer to sources of non-marine S, receiving two and four times higher dry S deposition loads than the Loch Katrine area and Glen Arnisdale catchments, respectively, according to 2002 FRAME deposition data. In south-west England there are also significant S contributions from shipping (Fowler et al., 2005) which could have increased streamwater concentrations in the Devon catchments, especially to NAR which lies closer to the south-western coast (23 km) than YAR (41 km). Dry S deposition can be enhanced in woodland canopies but this was not evident in the study catchments since median streamwater $x\mathrm{SO}_4$ concentrations in the forested UL1 and UL2 catchments were not significantly higher than in ULCON, while the control catchment NAR actually had higher mean streamwater $x\mathrm{SO}_4$ than the forested catchment YAR.

The effect of broadleaf woodland cover on streamwater SO_4 and $x\mathrm{SO}_4$ was probably also masked by processes operating in the catchment soils. The significant negative association between streamwater SO_4 and percentage of catchment podzolic cover could indicate possible SO_4 retention in the Fe and Al-rich horizons of podzolic soils (Barton et al., 1999) which dominate the Devon and Loch Katrine area catchments. However, SO_4 adsorption is concentration dependent, with the capacity of the soil to adsorb/desorb SO_4 changing with the solution SO_4 concentration. For example, Oulehle et al. (2006) reported significant release of SO_4 into soil solution in a heavily acidified area of the Czech Republic as result of marked declines in S deposition. Desorption of SO_4 from the soil was also believed to have delayed chemical recovery from acidification in an acid-sensitive catchment in south-east England (Hill et al., 2002). The catchments in the Ullswater area have received the highest past S deposition loads of the study catchments, with 50 kg ha^{-1} yr^{-1} in Cumbria in 1986 (NEGTAP, 2001), and the current declining trends in S deposition could have stimulated SO_4 release from the acidified soils, thus explaining the similar streamwater concentrations in these catchments, despite the differences in broadleaf woodland cover and soil type composition.

Furthermore, it has been suggested that SO_4 storage by catchment soils may be enhanced following periods of high seasalt inputs, while when seasalt inputs are low and total SO_4 concentration in the soil water declines, stored SO_4 may be released (Fowler and Smith, 2000). Retention of SO_4 was observed during the seasalt event in the Glen Arnisdale catchments, while SO_4 desorption has also been reported in periods of low seasalt inputs in Acid Waters Monitoring Network (AWMN) sites in western Britain (Evans et al., 2001). In contrast, Cl is more mobile in the soil and moves rapidly into catchment runoff. This means that, since a fixed SO_4:Cl ratio in sea water (seasalt correction factor) is used to calculate xSO_4 concentrations, xSO_4 concentrations may be underestimated during periods of high seasalt inputs and overestimated when inputs are low. Hence uncertainty in xSO_4 estimates could have further masked any evidence of an effect of broadleaf woodland in this study. However, Cooper (2005) reported little retention or loss of S in the AWMN catchments in relation to short-term throughput and therefore there should be little uncertainty in streamwater xSO_4 estimates in most of the study catchments, apart from the Glen Arnisdale catchments, where SO_4 retention was observed during the seasalt event resulting in very low mean calculated xSO_4 concentrations.

4.5.6 Factors controlling nitrate concentrations in the study catchments

4.5.6.1 Associations with woodland cover

The significant positive association between streamwater NO_3 concentrations and percentage woodland cover was shaped by the high NO_3 concentrations in the three heavily forested catchments (YAR, UL1 and UL2) and the low NO_3 concentrations in catchments with woodland covers below 30% (see Figure 4.8a). Streamwater NO_3 concentrations in upland catchments in the UK have been reported to vary seasonally, with the highest concentrations in winter/early spring due to the seasonality in N deposition and plant uptake, coupled with generally higher rainfall in these months (Chapman and Edwards, 1999). However seasonal patterns should not have influenced mean NO_3 streamwater concentrations in the study catchments because streamwater sampling was conducted at the same time of year. Low streamwater NO_3 concentrations in the Glen Arnisdale catchments were probably due to the low N deposition inputs, while, despite the high N inputs in the Loch Katrine area, streamwater NO_3 was also low, probably due to dilution by higher rainfall. Higher streamwater NO_3 concentrations in catchments YAR, UL1 and UL2 could be attributed to the high local N deposition inputs and the type and extent of broadleaf woodland cover.

4.5.6.2 Influence of N deposition and woodland structure

According to 2002 modelled deposition generated by FRAME, the Ullswater area and Devon catchments received the highest N loads from dry deposition in the study catchments. N deposition is still relatively high in north-west and south-west England due to proximity to pollution sources such as nitrous oxides from industry and ammonia (NH_3) emissions from livestock agriculture (NEGTAP, 2001). Catchments YAR, UL1 and UL2 lie in low intensity agricultural areas, but emissions from these activities could be important for these catchments since NH_3 deposition tends to occur close to the emission source.

Pollutant scavenging is positively associated with the height and density of the woodland canopy, especially for dry and occult deposition (Nisbet et al., 1995). The dense oak and alder woodlands in YAR and UL1 and UL2 catchments, respectively, are expected to have higher aerodynamic roughness resulting in more pollutant scavenging than the more open birchwoods in the Glen Arnisdale and Loch Katrine area catchments. Although the small sizes of the birch stands in these catchments could result in greater forest edge effects, enhancing the scavenging of pollutants as suggested by Neal et al. (1993), it is unlikely to have influenced streamwater chemistry in the Scottish catchments due to the quite open birchwood canopy.

4.5.6.3 Woodland age effect

The well-established relationship of increasing NO_3 concentrations in streamwater with forest age described by Emmett et al. (1993) suggests that there may be more NO_3 leaching into streamwater from the mature woodlands in the YAR, UL1 and UL2 catchments because of the lower N needs and uptake of mature woodlands. Furthermore, older forests usually accumulate larger amounts of mineral N in the soil during the summer which is then flushed out during the winter, and occult deposition also tends to be higher in old than young forests (Chapman and Edwards, 1999). Although there was no information about the age of the birchwoods in the Scottish catchments, there is unlikely to be any forest age effect on streamwater NO_3 in these catchments covered by birchwoods. Birch is a pioneer species but it is possible that succession has been arrested or slowed down in the harsh Highland conditions, and regeneration would have been limited by deer browsing. Even if the birchwoods were of the same age as the semi-ancient oakwood in YAR, more NO_3 leaching would have been expected from the oakwood due to the greater tree heights and the dense woodland structure which would enhance pollutant scavenging.

4.5.6.4 N fixation and soil processes

Streamwater NO_3 concentrations were much higher in catchments UL1 and UL2 than in the other study catchments. This could be attributed to atmospheric N fixation by symbiotic bacteria in the alder-dominated woodland resulting in enhanced NO_3 leaching to water. Alder species form a root nodule symbiosis with N_2-fixing actinomycetes and bacteria production provides most of the N required by the trees, leading to lower N demands from the soil and subsequent leaching of excess N to waters (Hurd et al., 2001). Various studies have reported this effect. Verburg et al. (2001) measured red alder N fixation rates of the order of 80 kg N ha^{-1} yr^{-1}, while Hurd et al (2001) estimated that speckled alder can fix at least 37-43 kg N ha^{-1} yr^{-1}. In addition, NO_3 concentrations increased more from throughfall to the soil solution in the A horizon below alder than Scots pine, Norway spruce and oak in northern England (Robertson et al., 2000) and were attributed to active nitrification below alder. The influence of alder on streamwater NO_3 concentrations is further demonstrated by the significantly higher median NO_3 concentrations in the forested UL1 and UL2 catchments compared to the unforested, control catchment (ULCON) (Kruskal-Wallis tests and non-parametric multiple comparisons, $P<0.01$).

High N deposition inputs between 10 to 20 kg N ha^{-1} yr^{-1} have been reported to cause soil acidification resulting in enhanced NO_3 leaching to streamwater (Dise and Wright, 1995). Current and past N deposition loads in the Ullswater area have been high (18 kg N ha^{-1} yr^{-1} in the 2002 data for FRAME), however if soil acidification was the main influence on streamwater NO_3 concentrations, then similar concentrations would be expected in the forested and unforested catchments. Therefore, the main cause of the higher streamwater NO_3 concentrations in the forested catchments UL1 and UL2 compared to the control catchment (ULCON) is probably the woodland, through the combined effect of canopy scavenging (especially for dry deposition) and N fixation by alder. There was no indication of an influence from catchment soils on streamwater NO_3 concentrations since mean N denitrification and mobilisation values for the study catchments, according to default values suggested by Hall et al. (1998) for use in the FAB model calculations, were similar (see Table 5.5), apart from the thin rankers in ULCON which had much lower values.

4.5.6.5 Nitrate index association with % woodland cover

The strong relationship between streamwater NO_3 index values and percentage woodland cover (see Figure 4.8c) indicates the important role of NO_3 in streamwater chemistry in catchments with broadleaf woodland cover. NO_3 is the dominant excess acid anion in streamwater from catchments UL1 and UL2 and almost of equal importance to $x SO_4$ in YAR, with NO_3 index values of 0.56, 0.57 and 0.47 for UL1, UL2 and YAR, respectively. Values in the remaining catchments with broadleaf woodland covers below 30% ranged from 0.05 to 0.41, however the relatively high values in the Glen Arnisdale catchments were not due to high NO_3 concentrations but to low $x SO_4$ concentrations caused by SO_4 retention in catchment soils during the seasalt event. The NO_3 index values for UL1, UL2 and YAR were higher than all the AWMN sites (Curtis et al., 2005), and also higher than NO_3 index values, which were calculated using SO_4 instead of $x SO_4$, reported by Chapman and Edwards (1999) for streams in acid-sensitive regions of Europe and North America. Presently, typical rainfall weighted concentrations of reduced and oxidised N exceed non-marine S concentration by a factor of two in the UK (NEGTAP, 2001) and it is expected that the relative role of NO_3 in excess anion loads will probably increase in the future as $x SO_4$ concentrations decline. Therefore, it has been suggested that NO_3 leaching could be a confounding factor in freshwater chemistry recovery from acidification in the UK uplands (Curtis et al., 2005). This seems to be the case in catchments with high broadleaf woodland covers, combined with the presence of tree species such as alder which may further enhance NO_3 leaching to streamwater.

4.5.6.6 Nitrogen saturation status in the study catchments

The concept of N saturation was proposed by Aber et al. (1989) and refers to the situation where N inputs from the atmosphere to forested catchments exceed the biological demand and any excess N is then leached from the soil to surface drainage waters. Hypothetical time scales for the response of forested catchments to N additions have also been defined (Aber et al., 1989) and these stages of terrestrial N saturation were used by Stoddard (1994) to propose four corresponding stages of N loss from terrestrial ecosystems, with different rates of NO_3 leaching to surface waters. At stage 0 the ecosystem is defined as N-deficient and the N cycle is dominated by vegetation and microbial uptake. The demand for N is the major influence on the seasonal pattern of NO_3 in surface waters, which is caused by the seasonality in N uptake from vegetation, N deposition and precipitation (Chapman and Edwards, 1999). At this stage NO_3 concentrations in streamwater are expected to be negligible (< 10 μeq l^{-1}), with maximum concentrations in the range of 20 to 30 μeq l^{-1} during the winter/spring period. According to these criteria, the catchments in Glen Arnisdale and the Loch Katrine area and ULCON and NAR fall into Stage 0 with measured streamwater high flow NO_3 concentrations ranging from 0.12 to 16.3 μeq l^{-1}.

Streamwater NO_3 concentrations in YAR ranged from 32.3 to 47.4 μeq l^{-1}, and this catchment probably falls into Stage 1, which is characterised by the amplification of the seasonal NO_3 pattern in surface waters, with increased winter NO_3 concentrations and relatively low summer NO_3 concentrations. However, the latter could not be verified because streamwater was not sampled during summer in YAR. Maximum recorded NO_3 concentrations in UL1 and UL2 were quite high (> 200 μeq l^{-1}), suggesting that these catchments have probably reached the N saturation stage (Stage 3), and have become net sources of N rather than a sink, with elevated NO_3 concentrations and lack any seasonal trend. However, NO_3 concentrations in one low flow summer sample from UL1 and UL2 were low (<10 μeq l^{-1}) suggesting that symptoms of N saturation are only evident in winter/spring months and that there is still biological demand for N by vegetation in the summer. More streamwater samples would be necessary to accurately assess the N saturation stage of the study catchments.

The debate about whether terrestrial ecosystems can reach the stage of N saturation has led to N addition experiments which showed that only at high rates of N deposition (> 25 kg N ha^{-1} yr^{-1}) does N cycling become uncoupled, stimulating soil acidification and resulting in significant quantities of N leaching to freshwaters (Dise and Wright, 1995). Of the study catchments only the Ullswater area catchments have probably experienced such high N deposition inputs (NEGTAP, 2001), which could partially explain the high N leaching. However, since this occurs only in the forested catchments it highlights the important effect of the alderwood, through N scavenging and N fixation, on the rates of N leaching to streamwater. It is also possible that there has been a reduction in the direct uptake of atmospheric N or N species in throughfall by alder foliage and twigs in UL1 and UL2 because the N requirements of the trees may already be satisfied by root uptake (Hill et al., 2002), resulting in a greater availability of NO_3 for leaching to streamwater.

4.5.7 Factors controlling soluble aluminium concentrations in the study catchments

4.5.7.1 Catchment buffering controls on Al mobilisation

Acidification of soils and surface waters due to acidic deposition has been shown to be responsible for increases in the mobilisation of Al, particularly in acid-sensitive uplands. Mobilisation of Al by inputs of acidic anions and subsequent leaching to streamwater depends on soil base saturation, streamflow conditions and soil flow pathways (Lange et al., 2006). Streamwater alkalinity measured at high flow indicated that all study catchments, apart from UL2 and to a smaller extent ULCON, had a very low to moderate capacity for neutralising acidic inputs as a result of the acidic, base-poor or slowly weathering soil parent materials present. The observed significant positive association between streamwater soluble Al concentrations and percentage woodland cover (see Figure 4.8b) can be attributed to some extent to the enhanced deposition of S and N on woodland canopies and also to NO_3 leaching from mature woodland stands, causing Al displacement from the ion-exchange complex and leaching to streamwater. The highest mean soluble Al concentrations were measured in YAR and UL1 which also had high streamwater SO_4 and NO_3 concentrations. Median streamwater Al concentration in the highly forested UL1 was significantly higher than concentrations in the control catchment (ULCON) (non-parametric multiple comparison tests, $P<0.001$). Some indication of a woodland effect on streamwater Al concentrations was found in LK1, which had the highest broadleaf woodland cover in the Loch Katrine area catchments, and a significantly higher median Al concentration than the less forested LK4 catchment (10.3% woodland cover) and the control catchment LKCON (Kruskal-Wallis tests and non-parametric multiple comparisons, $P<0.001$ for both LK4 and LKCON). However, despite the high streamwater SO_4 and NO_3 concentrations measured in UL2, the higher soil buffering capacity resulted in high Ca concentrations and less leaching of Al from soil to streamwater.

Further evidence of lower leaching of Al to streamwater in soils with higher buffering capacity is provided by the significant negative associations between soluble Al concentrations and alkalinity and ANC and the positive association of Al concentrations with Na_{dom} values in the study catchments (see Table 4.7). Also, a significant negative relationship was found between streamwater Na_{dom} values, which were used as a quantitative indicator of catchment weathering rates, and Al toxicity (represented by ratios of Ca to inorganic Al) in 59 sub-catchments of the River Dee catchment, north-east Scotland (Stutter et al., 2001). In the same study, in upland sub-catchments peaks in streamwater Al concentrations corresponded with elevated discharge and large drops in pH values and were attributed to near surface flow pathways, with Al released from organic surface horizons of peaty and podzolic soils. There was some indication of the influence of high discharge on Al leaching in YAR and in the forested catchments in the Loch Katrine area catchments where podzolic soils were dominant. The two highest streamwater Al concentrations (127 and 110 $\mu g\ l^{-1}$) in YAR were measured in the two highest flow events sampled. In

LK1, where continuous flow data were available, the highest measured Al concentration (100 µg l^{-1}) was measured in the second highest flow event (flow of 0.94 m^3 s^{-1}), which was also the only occasion when streamwater pH dropped below 6.0.

The influence of soil hydrological pathways on Al mobilisation and on streamwater acidity is expected to be important in all the study catchments, with overland flow from saturated upper soil horizons during high rainfall events causing highest Al concentrations in streamwater. The presence of woodland can increase the soil infiltration capacity, resulting in more water entering the soil and interacting with the cation-exchange sites in the soil complex (Ward and Robinson, 2000). Contributions of more Ca-rich subsurface flow could be significant in acid-sensitive catchments with broadleaf woodland cover in reducing incoming acidity and subsequent solubility of inorganic Al. However, overland flow is expected to be higher in the Glen Arnisdale and Loch Katrine area catchments which have high slopes and high rainfall inputs.

The buffering capacity in the Glen Arnisdale and Loch Katrine area catchments was relatively high as indicated by streamwater pH and alkalinity values, despite mean soil water pH values reported for the upper horizons of the soil series present in these catchments (from Macaulay Institute data) being low (4.13-4.79), indicating low soil buffering capacity. One explanation for this in the Glen Arnisdale catchments could be the variability in soil type composition, with brown earth and alluvial soils present in the lower parts of these catchments. Thus it is possible that streamwater chemistry at the catchment outlets was influenced more by these more base-rich soils than by acid-sensitive thinner soils found on upper slopes (Cresser, 2000). Billett and Cresser (1992) showed that the proportions of different soils immediately adjacent to streams in the Scottish Highlands had a much greater effect on streamwater chemistry than the proportional total coverage of the soils in the catchment. Cresser et al. (2000) derived empirical models using streamwater chemistry from 59 sub-catchments within the River Dee catchment to predict streamwater acidity, alkalinity and base cation concentrations using flow routing-weighted CaO concentration of the rock types present in the riparian zone. However, there was little afforestation in these catchments and thus any effects of forests on streamwater chemistry were not included in the modelling approach. These findings highlighted the importance of the riparian area as a mediator of geological, soil and land use effects, and the influence of riparian zones may be particularly significant in catchments where streamwaters are sensitive to diffuse sources of pollution such as acidification (Smart et al., 2001).

4.5.7.2 Influence of dissolved organic carbon on Al leaching

Streamwater Al concentrations in the Loch Katrine area catchments were probably influenced more by soil type composition than broadleaf woodland cover. Acid, organic-rich horizons such as those present in the predominantly podzolic soils of the Loch Katrine area catchments are important sources of mainly organically complexed Al, rather than inorganic (labile) Al which is considered to be the most toxic form of Al for freshwater biota (Stutter et al., 2001). Labile Al was not determined in this study. However, the high streamwater Fe and dissolved organic carbon (DOC) concentrations suggest that most of the Al in streamwater in the Loch Katrine area catchments is organically complexed. Many studies have associated Al mobilisation with DOC. Lange et al. (2006) reported that peak Al concentrations were associated with high Fe and DOC in soil solution in forest soils in Norway, especially when DOC was leached from the upper horizons during heavy rain events. In the River Dee upland sub-catchments in north-east Scotland organically bound Al was significantly positively correlated with total organic carbon (TOC) concentrations in streamwater, with stronger relationships occurring during high flow conditions (Stutter et al., 2001). In the same study, streamwater TOC concentrations were significantly positively correlated with the percentage area cover of organic soil in the sub-catchments. Temporal and spatial variations in total Al and Fe concentrations were also found to be closely related to variations of TOC in soil solution in upland forest and moorland sites in Scotland (Grieve and Marsden, 2001). Therefore, it is possible that in the Loch Katrine area catchments complexation with DOC in the upper organic soil horizons is the major mechanism of Al mobilisation, and also the cause of the high streamwater Fe concentrations.

4.5.7.3 Potential Al mobilisation by marine inputs

Apart from acidic deposition, mobilisation of Al to surface waters can be triggered through exchange of base cations during episodic seasalt deposition events (Andersen and Seip, 1999). Inputs of marine base cations, mainly Na and Mg, displace acid cations, mainly H^+ and labile (inorganic monomeric) Al, or Ca in more buffered soils (Evans et al., 2001). Seasalt inputs could be important in the study catchments due to their location close to the nearest coast.

The Glen Arnisdale catchments are subject to high marine inputs, due to their close proximity to the west coast, and experienced a major seasalt event during streamwater sampling. High seasalt inputs resulted in large increases in streamwater Cl concentrations, while the high negative non-marine Na concentrations indicated high retention of Na in the catchments' soils, probably due to ion-exchange processes. The high marine inputs were expected to result in increases in streamwater Al concentrations due to displacement of Al from the soil complex, but this was not observed in any of the catchments. In contrast, there was evidence of substantial leaching of non-marine Ca in all four catchments in response to the seasalt event, indicating that Ca was the major component of the cation-exchange pool in the catchment soils and that the catchment soils had enough buffering capacity to compensate for the retention of Na. However, in GA3, where streamwater conditions were most acidic, streamwater Mn concentrations were almost seven times higher than those measured before the seasalt event probably due to selective Ca^{2+} and Mg^{2+} displacement of Mn^{2+}.

In general, following seasalt events, Ca is expected to be the major desorbed cation in well-buffered catchments, with labile Al and H^+ desorbed in the more acidic catchments. However these patterns were not found after seasalt events at eight AWMN sites (Evans et al., 2001) and were attributed to local soil conditions such as supply of base cations by weathering and the relative abundance and selectivities of base cations on exchange sites that determine the cation response to seasalt inputs. Furthermore, a study in western Norway (Larssen and Holme, 2006) suggested that the different response of adjacent spruce and birch-covered catchments to a seasalt event was due to differences in soil pH, litter chemistry and concentrations of exchangeable base cations between the two forest types. In a literature review, Alexander and Cresser (1995) suggest that the pH of litter measured in water is generally higher for deciduous than for coniferous species and report a specific study in which the pH of birch litter was measured to be 0.5 pH units higher than spruce litter. These results indicate that the birch and oak tree cover in the Glen Arnisdale catchments could have increased the soil buffering capacity, resulting in low Al leaching to streamwater. Therefore, it is possible that the effects of broadleaf woodland in increasing soil base cation status may reduce Al mobilisation in the forested study catchments despite possible enhancement of acid anion concentrations below broadleaf trees.

A long-term soil water chemistry study from Norway (Lange et al., 2006) suggested that a seasalt event of a given size mobilises less Al when anthropogenic S deposition is lower, and this could explain the low streamwater Al concentrations in the Glen Arnisdale catchments where past and current non-marine S deposition is low. No other seasalt events occurred in the study catchments during the sampling period, but long-term AWMN data for the NAR catchment show that a seasalt event occurred in January 1998, resulting in the lowest pH values and alkalinity concentrations and the highest concentrations of labile Al during the 10 year monitoring period (Evans et al., 2000). NAR has received high past anthropogenic S deposition, and is the only AWMN site with increasing non-marine S deposition and streamwater $x\mathrm{SO}_4$ concentrations, hence seasalt events could lead to more Al leaching to streamwater in NAR than in the Glen Arnisdale catchments.

Data from UK AMWN sites for the impact of seasalt events on streamwater chemistry suggest that the sites most responsive to seasalt inputs are those at an intermediate distance from the coast. Cl concentrations are continuously high at sites close to the coast and, although seasalt episodes occur frequently, their proportional impact is less, while in more inland sites where Cl concentrations are low, occasional seasalt events can generate very large proportional changes in the concentrations of Cl and other marine anions (Evans et al., 2001). This suggests that the impact of a seasalt event of a similar size to the one observed in Glen Arnisdale would be much greater in the more inland Loch Katrine and Ullswater area catchments and in YAR and could result in more Al mobilisation than was observed in the Glen Arnisdale catchments. Furthermore, long-term water chemistry data from the UK AWMN (Evans et al., 2001) and from western Norway (Andersen and Seip, 1999) suggest that, although seasalt events are thought to cause episodic acidification, the long-term nature of marine ion cycles means that equilibria on soil cation-exchange sites adjust to seasalt events over time scales of weeks to months. For example, in catchments in Norway it took three to four months for labile Al and almost a year for Cl concentrations in streamwater to return to pre-seasalt event levels (Andersen and Seip, 1999). These processes could also be occurring in the Glen Arnisdale catchments where streamwater Na and Cl concentrations measured at low flow in April 2005 were double those at high flow in November 2005 before the seasalt event, probably due to a previous seasalt event causing retention of marine ions in the soil, which were gradually released into streamwater over several months.

4.5.7.4 Al toxicity

The interest in the processes controlling Al mobilisation in acid-sensitive catchments is that Al can be toxic to sensitive freshwater biota, resulting in the decline or even loss of important fish populations such as brown trout and perch (Laudon et al., 2005). Organically bound Al is considered far less toxic than the inorganic forms, trivalent Al^{3+}, the hydrolysed species $Al(OH)^{2+}$ and $Al(OH)_2^+$, with the former considered as the most toxic component of the inorganic fraction for salmonids (Driscoll et al., 1980). The presence of complexing organic matter is generally thought to reduce the proportion of inorganic Al toxicity, even though total aluminium concentrations may be greater. However, high levels of DOC in soil water can increase H^+ and can cause, in combination with strong acid inputs from acidic deposition, large declines in pH leading to mobilisation of Al from the soil complex (Laudon et al., 2005). Streamwater Ca is also reported to reduce Al toxicity, but its effect depends on the levels of Ca, pH and labile Al, with fish population losses occurring in catchments with low Ca concentrations ($<50\ \mu mol_c\ l^{-1}$), pH below

5.5 and labile Al concentrations above 50 μg l^{-1} (Stutter et al., 2001). Therefore, the ameliorative effects of DOC and Ca on Al toxicity in streamwater depend greatly on the degree of catchment acid-sensitivity.

Concentrations of the inorganic fraction of streamwater Al were not determined in the study catchments, but Al toxicity was expected to be low due to the low streamwater soluble Al concentrations measured. Only three streamwater samples, one from each of LK1, YAR and UL1, exceeded 100 μg soluble Al l^{-1}, compared to the toxicity threshold of about 100 μg l^{-1} of labile Al (Laudon et al., 2005). The high streamwater DOC concentrations in the Loch Katrine area catchments also suggest that Al toxicity should be low in these catchments. The macroinvertebrate results indicate that the presence of toxic conditions is most probable in UL1 and GA3, because of the low species abundance and diversity. These catchments also had low Ca concentrations and were the only study catchments in which pHs below 5.0 were measured in streamwater (measured in UL1 during the catchment selection process in January 2005).

Significant increases in DOC concentrations have been observed in the past 15-20 years in freshwaters in the UK, Europe and North America (Skjelkvåle et al., 2001), and have been attributed to various causes. For example, Evans et al. (2005) suggested that DOC increases of up to 91% in 22 upland AWMN sites in the UK from 1988 to 2003 may be due to a combination of declining acid deposition and rising temperatures. The study catchments are located in the same geographical area and have similar geological and soil composition and acid deposition levels to the AWMN sites, thus it is safe to infer that DOC concentrations have also been increasing in the study catchments. The long-term implication of increases in streamwater DOC would probably be increased metal transport due to complexation with organic compounds, as evidenced by the significant increases in streamwater organic Al and total Fe concentrations in most of the AWMN sites from 1988 to 2003 (Evans et al., 2005). However, increases in organically-bound Al would probably result in lower Al toxicity in streamwater and thus more favourable conditions for the survival and development of sensitive biota. On the other hand, it is possible that the observed increases in organic acidity in the AWMN sites could, to some extent, offset decreases in mineral acid anions, resulting in slower than expected recovery of pH and alkalinity (Evans et al., 2005). Forest cover is not expected to greatly influence streamwater DOC, since similar concentrations have been reported in both acid-sensitive moorland and conifer catchments in mid-Wales (Neal et al., 2005). However, acidic inputs from pollutant scavenging onto broadleaf canopies, combined with possible increases in streamwater DOC could influence acid-sensitivity or chemical recovery in the study catchments.

4.6 Uncertainty in woodland cover estimates

The main aim of this research was to investigate whether broadleaf woodland cover had an effect on streamwater chemical indicators of acidification, due to enhanced atmospheric pollutant scavenging on woodland canopies. The woodland data used for this investigation were woodland polygons at 1: 25 000 scale, where woodlands were defined as areas of tree cover with a crown density of, or likely to achieve, at least 20%, a minimum width of 50 m and minimum area of 2 ha (Woodland Surveys, 2002). Deposition of S and N, especially via dry and occult deposition, is influenced by the height and structure of the vegetation layer due to the greater air turbulence created by the stand structure (Nisbet et al., 1995). For conifer forests in the UK, woodland area is expected to be similar to the sum of cover of individual trees (the vertical projection of the tree canopy) due to the dense canopy and homogeneous structure of conifer plantations. However, in some of the study catchments the woodland cover and the sum of tree covers are expected to be different, due to the variability in woodland structure depending on the tree species present and the spatial distribution of the woodland in the catchment.

The Glen Arnisdale and Loch Katrine catchments had a quite open canopy with scattered trees on the higher slopes, while woodland cover in the oakwood in YAR and the alderwood in UL1 and UL2 was much more dense and located in the lower and more gently sloping areas of these catchments. Therefore, large differences were expected between woodland cover and the sum of tree covers in the Glen Arnisdale and Loch Katrine area catchments, while woodland and tree cover should be similar in catchments UL1, UL2 and YAR. This was partially verified from estimates of tree cover in the Loch Katrine area catchments derived from higher resolution (1: 10 000) aerial imagery available from Forest Enterprise. Individual woodland patches were digitised and their area was used to calculate percentages of total tree cover for each catchment. Total tree cover was lower than woodland cover by 8.4, 5.9 and 2.2% in LK1, LK2 and LK4, respectively. Total tree cover increased slightly by 0.3% in LK3, while the presence of small woodland patches in the control catchment LKCON gave a total tree cover of 2.6%.

Therefore, it is possible that the use of woodland cover calculated from the vertical projection of tree cover in the catchments would have been more appropriate to investigate woodland effects on streamwater chemistry due to pollutant scavenging. This was tested by assuming the same mean % difference between woodland and tree cover for the Glen Arnisdale and Loch Katrine area catchments, and repeating analysis of the associations between re-calculated woodland cover and streamwater chemistry in the study catchments. The same results were found showing that the significant associations between woodland cover and NO_3 and soluble Al concentrations in streamwater would probably have been unaffected by any uncertainty in woodland cover estimates in catchments with covers $< 30\%$, because broadleaf woodland was found to influence streamwater chemistry only at high woodland covers ($\geq 50\%$).

If higher resolution data had been available, woodland metrics, such as mean patch areas and degree of fragmentation, could also have been used to investigate associations between woodland structure and streamwater acid anions and soluble Al concentrations. Apart from percentage woodland cover, other forest attributes, such as woodland stand volume and proportions of catchment area occupied by tree stands of different ages, could have been used to investigate the effect of woodland on streamwater chemistry. Both stand volume and age are related to base cation and N uptake, evaporation rates and tree height, with the latter largely influencing dry deposition of atmospheric pollutants. The Acid Waters Survey for Wales found significant positive correlations between area-weighted conifer stand age and streamwater Na, Cl, SO_4 and Al concentrations at its study sites, while streamwater NO_3 concentrations increased significantly with increasing plantation age (Stevens et al., 1997). However, woodland attribute data are lacking for the majority of broadleaf woodlands in the UK uplands and thus it was not possible to include them in the study.

4.7 Summary

Chapter 4 presented the results of the chemical analysis and the macroinvertebrate survey in the study catchments and also presented and discussed the results of the statistical analysis of the streamwater chemistry results and catchment characteristics, including percentage broadleaf woodland cover. Multivariate analyses using mean streamwater chemistry found clear catchment groupings based on their geographical location. Significant positive associations were found between percentage broadleaf woodland cover and mean high flow streamwater NO_3 and soluble Al concentrations and calculated streamwater NO_3 index values in the study catchments, with the effect of broadleaf woodland cover on streamwater chemistry being more evident in catchments with woodland covers $\geq 50\%$. Elevated streamwater NO_3 concentrations in the higher forested catchments YAR, UL1 and UL2 were increased probably due to increased scavenging of N pollutants by woodland canopies and enhanced NO_3 leaching under alder in catchments UL1 and UL2. The NO_3 index values calculated for YAR, UL1 and UL2 were higher than most values reported in the literature and NO_3 was becoming or was already the dominant excess acid ion in streamwater, suggesting that NO_3 leaching to streamwater could continue to cause acidification or delay any chemical recovery in these catchments. High streamwater SO_4 and NO_3 concentrations in the higher forested catchments YAR and UL1, probably due to a combination of S and N pollutant scavenging on woodland canopies and nitrification by alder in UL1, seemed to mobilise soluble Al from the soil complex. Overall, some of the effects of broadleaf woodland cover on streamwater chemistry in the study catchments were masked by variability in the local deposition climate, including seasalt influences, and soil type composition influencing catchment soil buffering capacity. Macroinvertebrate data showed that species abundance and richness was lower in catchments with high mean soluble Al concentrations and high broadleaf woodland cover, but no clear catchment groupings emerged based on macroinvertebrate abundance of major taxa. The streamwater chemistry and macroinvertebrate results form the basis for the risk assessment of streamwater acidification in the study catchments presented in Chapter 5.

Chapter 5 Risk assessments for streamwater acidification

The critical loads approach was used to assess the risk of acidification in the study catchments. Section 5.1 presents the streamwater critical loads calculated for the study catchments using the two main methodologies for calculating critical loads from water chemistry: a) the Steady-State Water Chemistry (SSWC) model and b) the First-order Acidity Balance (FAB) model (see Section 3.5). The SSWC model is used for the calculation of freshwater critical loads in the Forests and Water Guidelines for protecting freshwaters from acidification, while the FAB model is currently used for the calculation of freshwater critical loads in the UK by the National Focal Centre.

Exceedance of streamwater critical loads was calculated using modelled non-marine S deposition for 1995-97 and N deposition estimated from NO_3 concentrations in streamwater, following the methodology of the Forests and Water Guidelines, and the most recent available (2002) modelled non-marine S and N deposition for the UK from the FRAME model to investigate differences in critical loads exceedance values between the two time periods. The effectiveness of the SSWC and FAB models for the protection of waters sensitive to acidification was also assessed by comparing the critical loads exceedance estimates calculated using the two different models and the different modelled deposition datasets.

Section 5.2 presents the results of a sensitivity analysis conducted to investigate the effect of using the least and most acidic streamwater chemistry samples and different catchment runoff estimates and critical ANC values on the critical loads and exceedance values generated by the two models. The results of the macroinvertebrate survey presented in Chapter 4 are used in Section 5.3 to predict acid-sensitivity in the study catchments using classifications based on the presence/absence of sensitive species, and these predictions are compared with the critical loads calculations. The chapter concludes by discussing the factors influencing the results of different methods of risk assessment of the study catchments to streamwater acidification.

5.1 Calculations of critical loads exceedance in the study catchments

5.1.1 Calculations of critical loads and exceedance with the SSWC model

Mean streamwater concentrations of base cations (Ca, Mg, Na and K) and major anions (SO_4 and NO_3) for each study catchment were used to calculate critical loads (CL) with the SSWC model (Equation 3.6). Following the standard methodology of the Forests and Water Guidelines, a critical ANC value of 0 μeq l^{-1} was used, while runoff was estimated from the most recent available rainfall data for the study catchments from the British Atmospheric Data Centre (BADC). For UK conditions, the Guidelines assume that 15% of the annual rainfall received by the study catchment areas is lost to evapotranspiration and thus catchment runoff was equal to the remaining 85% (in mm). The main parameters used in the SSWC model for calculating CL values are given in Table 5.1. The derivation of these parameters is described in Section 3.5. Unexpectedly, streamwater non-marine acid anion concentrations ($[AA]_t^*$) in the Glen Arnisdale catchments were lower than the calculated pre-industrial non-marine acid anion ($[AA]_0^*$) concentrations. This was due to SO_4 retention during the seasalt event which resulted in low streamwater xSO_4 concentrations and to relatively low NO_3 concentrations in these catchments. The lower non-marine acid anions concentrations lead to higher pre-industrial base cation concentrations (see Equation 3.11), and consequently to higher CL values. Thus, it is possible that CL values are overestimated in the Glen Arnisdale catchments.

Table 5.1 Mean high flow concentrations of calculated sum of non-marine base cations [BC_t^*], sum of non-marine acid anions [AA_t^*], pre-industrial base cations [BC_0^*] and pre-industrial acid anions [AA_0^*] (all in µeq l^{-1}), mean high flow values of the "F" term, N leaching (N_{leach}) estimated from streamwater NO_3 concentrations (in keq H ha^{-1} yr^{-1}) and estimated runoff (mm) from the most recent available rainfall (year given in brackets) for the study catchments

Catchments	BC_t^*	AA_t^*	F	BC_0^*	N_{leach}	AA_0^*	Runoff
GA1	106	6.00	0.40	116	0.06	32.0	1559 (*2003*)
GA2	95.7	4.22	0.37	105	0.05	30.3	1559 (*2003*)
GA3	90.4	16.0	0.35	95.1	0.05	29.5	1559 (*2003*)
GACON	119	17.7	0.45	127	0.05	34.1	1559 (*2003*)
LK1	94.6	35.0	0.36	92.8	0.19	30.1	2416 (*2005*)
LK2	63.1	28.0	0.25	62.4	0.14	25.1	2416 (*2005*)
LK3	68.8	29.5	0.27	67.9	0.11	26.1	2416 (*2005*)
LK4	104	39.3	0.40	101	0.26	31.6	2416 (*2005*)
LKCON	108	34.2	0.41	107	0.17	32.3	2416 (*2005*)
UL1	127	195	0.48	50.2	1.00	35.2	793 (*2005*)
UL2	443	197	1.00	333	0.99	85.2	793 (*2005*)
ULCON	261	73.7	0.85	246	0.05	56.7	793 (*2005*)
YAR	59.3	87.0	0.23	44.9	0.45	24.5	1088 (*2005*)
NAR	48.6	65.4	0.19	40.5	0.10	22.8	1090 (*2004*)

CL exceedance was determined by comparing the calculated CL values with pollutant deposition estimates (Equation 3.12). N deposition is calculated from streamwater NO_3 concentrations. Two different estimates of non-marine S deposition were used: a) 1995-97 modelled S deposition used by Forest Research for calculating streamwater CL exceedance within the Forests and Water Guidelines framework and b) 2002 estimates generated by the FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) model (Singles et al., 1998) (Table 5.2). The 1995-97 deposition data were derived from a range of models (Tom Nisbet, personal communication). In these models, wet deposition is mainly derived from measured deposition at the UK Acid Deposition Monitoring Network (ADMN) sites which was then amended for altitude enhancement due to the seeder-feeder effect. Occult deposition was modelled using data on cloud base, wind speed, vegetation roughness and concentration enhancement, while S dry deposition was based on a modified “big-leaf” model using measured gaseous concentrations, meteorological data and vegetation roughness values. The FRAME model is a Lagrangian atmospheric transport model used to assess the long-term annual mean deposition of reduced and oxidised N and non-marine S over the United Kingdom (Singles et al, 1998). Both modelled pollutant deposition datasets used had a grid resolution of 5 km.

Modelled non-marine S deposition estimates in both datasets followed the same order, with highest and lowest deposition in the Loch Katrine area and the Glen Arnisdale catchments, respectively, but deposition estimates were lower for 2002 by 47 to 87% for the Devon and Glen Arnisdale catchments, respectively. However, the 2002 FRAME S deposition estimates were more uniform across the catchments, apart from the Glen Arnisdale catchments where modelled deposition was low.

Table 5.2 Deposition estimates (5 km grid) of non-marine S for the 1995-97 and 2002 FRAME datasets for the study catchments in the Glen Arnisdale (GA), Loch Katrine (LK) and Ullswater (UL) areas and YAR and NAR catchments

Catchments	1995-97 (keq H ha^{-1} yr^{-1})	2002 FRAME (keq H ha^{-1} yr^{-1})
GA	0.72	0.09
LK	1.21	0.47
UL	1.14	0.41
YAR	0.85	0.39
NAR	0.86	0.42

5.1.2 Results of critical loads and exceedance calculated with the SSWC model

Critical load and exceedance values for the study catchments calculated with the SSWC model and pollutant deposition for 1995-97 and 2002 are shown in Table 5.3.

Table 5.3 Critical load (CL) and CL exceedance values calculated with the SSWC model and non-marine S deposition for 1997-95 and 2002 FRAME and N leaching measured in runoff (keq H ha^{-1} yr^{-1}) and acid neutralising capacity (ANC) (μeq l^{-1}) for the study catchments

Catchments	CL	Acid deposition 1995-97	Acid deposition 2002 FRAME	CL Exceedance 1995-97	CL Exceedance 2002 FRAME	ANC
GA1	1.82	0.78	0.15	-1.04	-1.66	-16.6
GA2	1.64	0.77	0.14	-0.87	-1.50	10.0
GA3	1.48	0.77	0.14	-0.71	-1.34	-32.3
GACON	1.98	0.77	0.14	-1.20	-1.83	-13.2
LK1	2.24	1.40	0.66	-0.84	-1.58	60.8
LK2	1.51	1.35	0.61	-0.15	-0.90	36.1
LK3	1.64	1.32	0.58	-0.32	-1.06	40.4
LK4	2.44	1.47	0.73	-0.97	-1.71	65.7
LKCON	2.59	1.38	0.63	-1.21	-1.96	74.8
UL1	0.40	2.14	1.42	1.74	1.02	-76.1
UL2	2.64	2.13	1.40	-0.51	-1.24	248
ULCON	1.95	1.19	0.46	-0.77	-1.49	188
YAR	0.49	1.30	0.85	0.81	0.36	-32.9
NAR	0.51	0.96	0.52	0.45	0.01	-19.2

The calculated CL values ranged from 0.40 to 2.64 keq H ha^{-1} yr^{-1}, indicating moderate to high susceptibility to acidification. Values were above 1.50 keq H ha^{-1} yr^{-1} for all catchments, apart from UL1, YAR and NAR. Comparison of the CL values with acid deposition data for 1995-97 (non-marine S and N leaching) showed that CL were exceeded in three catchments: NAR, YAR and UL1 by 0.45, 0.81 and 1.74 keq H ha^{-1} yr^{-1}, respectively (Figure 5.1). NAR remained in the same CL exceedance class as its grid square in the provisional map of CL exceedance, while YAR fell into a higher exceedance class (see Table 3.1). UL1 fell into the highest exceedance class (>1 keq H ha^{-1} yr^{-1}) despite lying in a not-exceeded square. Streamwater CL values were not exceeded in the Glen Arnisdale and Loch Katrine area catchments even though they lie in exceedance squares, while non-exceedance remained in catchments UL2 and ULCON.

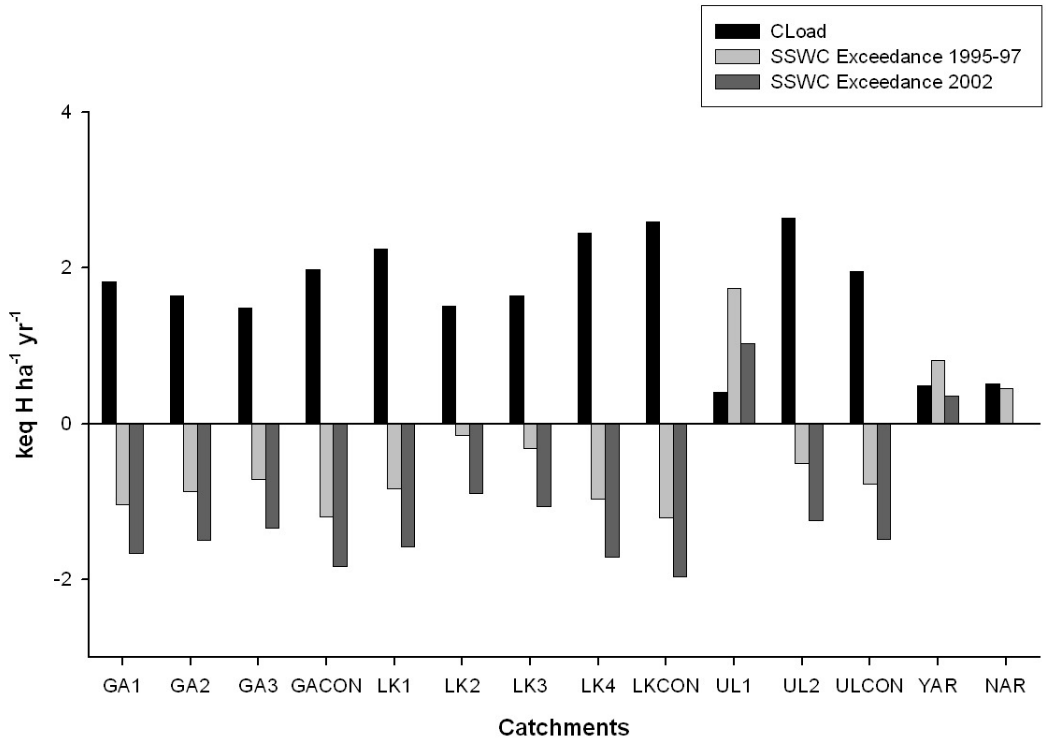


Figure 5.1 CL values and CL exceedances calculated with the SSWC model using modelled non-marine S deposition from 1995-97 and 2002 FRAME datasets and N leaching. Negative values indicate non-exceedance. N.B. The SSWC Exceedance 2002 for NAR is 0.01 keq ha^{-1} yr^{-1}

Using the 2002 FRAME modelled non-marine S deposition and N leaching the CLs were exceeded in the same three catchments as previously: NAR, YAR and UL1 by 0.01, 0.36 and 1.02 keq H ha^{-1} yr^{-1}, respectively (Figure 5.1). NAR was only marginally acid-sensitive, and in the lowest CL exceedance class, while CL exceedance was lower than calculated with the 1995-97 deposition data for both YAR and UL1 (Figure 5.1). Non-exceedance of streamwater CLs in the remaining 11 catchments was also higher when using the 2002 FRAME data and ranged from 0.90 to 1.96 keq H ha^{-1} yr^{-1}. The CL exceedance results for both pollutant deposition datasets show that catchment UL1 is classified in the highest CL exceedance class (> 1.0 keq H ha^{-1} yr^{-1}) despite lying in a not-exceeded CL exceedance square according to the provisional CL exceedance map (see Table 3.1). Non exceedance of CL values in catchments UL2 and ULCON meant that both catchments were still considered not acid-sensitive. CL exceedance in YAR using the 2002 FRAME dataset showed that the catchment was again in a higher exceedance class (0.3-0.5 keq H ha^{-1} yr^{-1}) than its original exceedance grid square, while NAR fell in a lower exceedance class (0.0-0.2 keq H ha^{-1} yr^{-1}) and was only marginally acid-sensitive.

Non-exceedance of CL values was expected to ensure that streamwater ANC values were above the critical value of 0 μeq l^{-1}, necessary for the protection of freshwater biota, while the opposite was expected for acid-sensitive catchments. Mean streamwater ANC was below 0 μeq l^{-1} for the acid-sensitive NAR, YAR and UL1 catchments (Table 5.3). ANC ranged from 36.1 to 248 μeq l^{-1} in the not exceeded catchments in the Loch Katrine area and near Ullswater (UL2 and ULCON). However, despite non exceedance of CLs in the Glen Arnisdale catchments, GA1, GA3 and GACON had negative streamwater ANC, while only GA2 had positive ANC (Table 5.3).

5.1.3 Critical loads and exceedance calculated with the FAB model

Mean streamwater chemistry was also used to calculate critical loads for S and N deposition individually and total critical load exceedance using the FAB model and Equation 3.22 since there has been no forest harvesting in the study catchments. The critical leaching of acid anions used by the FAB model was calculated with the SSWC model and has the same values as the calculated CL values (Table 5.3). FRAME modelled deposition data for 2002, both for non-marine S and N, were used to calculate CL exceedance, but modelled deposition for 1995-97 was not used because it only includes non-marine S but not N deposition.

Total modelled N deposition for 2002 modelled by FRAME ranged from 0.13 to 1.28 keq H ha^{-1} yr^{-1} and was lowest in the Glen Arnisdale catchments and highest in the catchments near Ullswater (Table 5.4). Total N deposition in the Ullswater area catchments was almost 10 times higher than in the Glen Arnisdale catchments, and twice that in the Loch Katrine area catchments. Overall, total modelled S and N deposition ranged from 0.22 to 1.69 keq H ha^{-1} yr^{-1}. Total deposition was similar in all the catchments and ranged from 1.13 to 1.69 keq H ha^{-1} yr^{-1}, apart from the Glen Arnisdale catchments where it was considerably lower (0.22 keq H ha^{-1} yr^{-1}).

Table 5.4 Estimates of reduced (NH_x) and oxidised N (NO_y), total N, non-marine S (SO_y) and total S and N deposition generated by FRAME for 2002 (keq H ha^{-1} yr^{-1}). % wet deposition is given in brackets

Catchments	NH_x	NO_y	Total N deposition	SO_y	Total S and N deposition
GA	0.05 (*77*)	0.08 (*78*)	0.13 (*78*)	0.09 (*78*)	0.22 (*78*)
LK	0.31 (*91*)	0.35 (*92*)	0.66 (*91*)	0.47 (*91*)	1.13 (*91*)
UL	0.89 (*47*)	0.39 (*69*)	1.28 (*54*)	0.41 (*77*)	1.69 (*59*)
YAR	0.62 (*63*)	0.48 (*80*)	1.10 (*70*)	0.39 (*82*)	1.49 (*73*)
NAR	0.55 (*73*)	0.35 (*82*)	0.90 (*76*)	0.42 (*83*)	1.32 (*78*)

The 2002 FRAME dataset also included the modelled fractions of wet and dry deposition for reduced and oxidised N and non-marine S. The contribution of wet to total modelled deposition varied considerably and was highest in the high rainfall catchments in the Loch Katrine area and lowest in the low rainfall catchments near Ullswater. The contributions of wet S and NO_y were high and similar in most catchments, but were slightly lower in the Ullswater area catchments (Table 5.4). The contribution of dry NH_x deposition was quite variable and was more important than wet deposition in the Ullswater area catchments, contributing 53% of total NH_x deposition, and was also relatively high in YAR. Thus, dry deposition on woodland canopies could be a significant process in the catchments UL1 and UL2 and also in YAR which had high percentage woodland covers, particularly for streamwater NO_3 concentrations due to the high dry NH_x pollutant load.

The FAB model takes into account N retention (N_{ret}) in catchment soils as long term N immobilisation (N_{imm}) and denitrification (N_{den}) (see Sections 3.5.5.1 and 3.5.5.2). Default N_{imm} values for the soils present in the study catchments ranged from 0.07 keq H ha^{-1} yr^{-1} (or 1 kg N ha^{-1} yr^{-1}) for rankers and stagnogleys to 0.21 keq H ha^{-1}

yr^{-1} (or 3 kg N ha^{-1} yr^{-1}) for podzols and peaty gley soils (Hall et al., 1998). Default N_{den} values ranged from 0.07 keq H ha^{-1} yr^{-1} (or 1 kg N ha^{-1} yr^{-1}) for rankers and stagnogleys to 0.29 keq ha^{-1} yr^{-1} (or 4 kg N ha^{-1} yr^{-1}) for peaty and stagno-gley soils (Hall et al., 1998). Catchment N_{imm} and N_{den} values were calculated from the default values and percentage cover of different soil types in the study catchments and are shown in Table 5.5.

Table 5.5 Catchment N immobilisation (N_{imm}), denitrification (N_{den}) and retention (N_{ret}) values (keq H ha^{-1} yr^{-1}) calculated for the study catchments

Catchments	N_{imm}	N_{den}	N_{ret}
GA1	0.17	0.11	0.28
GA2	0.18	0.11	0.29
GA3	0.17	0.14	0.31
GACON	0.17	0.14	0.31
LK1	0.20	0.08	0.28
LK2	0.19	0.07	0.27
LK3	0.21	0.09	0.30
LK4	0.20	0.08	0.28
LKCON	0.21	0.08	0.29
UL1	0.20	0.27	0.47
UL2	0.18	0.24	0.42
ULCON	0.10	0.03	0.13
YAR	0.21	0.07	0.28
NAR	0.21	0.14	0.35

Mean catchment N_{imm} values were similar for most catchments, apart from catchment ULCON which had the lowest N_{imm} value due to the high cover from rankers. Mean catchment N_{den} and N_{ret} values were more variable with the highest values in UL1 and UL2 and the lowest in ULCON (Table 5.5). The highest values occurred in catchments UL1 and UL2 because of the high percentage cover of anaerobic gleysols, whilst the lowest was in catchment ULCON which is predominantly (70.4%) covered by thin podzolic rankers. Catchments in Glen

Arnisdale, the Loch Katrine area and in Devon had similar values because of the dominant podzolic soil cover, with smaller contributions from gleysols.

The critical loads for S and N and total exceedance calculated with the FAB model are shown in Table 5.6. The FAB model does not use a single value to represent the critical load (CL) for total acidity but calculates critical loads for S and N individually (see Section 3.5.5.3). $CL_{max}(S)$ values are the same as CL values calculated with the SSWC model (see Equation 3.17) and have already been described. $CL_{min}(N)$ values were equivalent to N_{ret} values (see Equation 3.20) and ranged from 0.13 to 0.47 keq ha^{-1} yr^{-1} (Table 5.5). $CL_{max}(N)$ values were the sum of CL and $CL_{min}(N)$ values (see Equation 3.21) and were quite high (>1.77 keq H ha^{-1} yr^{-1}) for the study catchments, apart from UL1, YAR and NAR where they were considerably lower.

Table 5.6 Critical loads for S ($CL_{max}(S)$) and N ($CL_{min}(N)$ and $CL_{max}(N)$) and total CL exceedance (all in keq H ha^{-1} yr^{-1}) calculated with the FAB model and 2002 FRAME modelled deposition data

Catchments	$CL_{max}(S)$	$CL_{min}(N)$	$CL_{max}(N)$	Total exceedance
GA1	1.82	0.28	2.10	-1.87
GA2	1.64	0.29	1.93	-1.71
GA3	1.48	0.31	1.79	-1.57
GACON	1.98	0.31	2.29	-2.07
LK1	2.24	0.28	2.52	-1.40
LK2	1.51	0.27	1.77	-0.65
LK3	1.64	0.30	1.94	-0.82
LK4	2.44	0.28	2.72	-1.60
LKCON	2.59	0.29	2.88	-1.76
UL1	0.40	0.47	0.87	0.82
UL2	2.64	0.42	3.06	-1.36
ULCON	1.95	0.13	2.08	-0.38
YAR	0.49	0.28	0.78	0.72
NAR	0.51	0.35	0.87	0.46

Calculated total exceedance with FAB found that CLs were exceeded in three catchments: UL1, YAR and NAR by 0.82, 0.72 and 0.46 keq ha^{-1} yr^{-1}, respectively (Table 5.6). CL was exceeded in UL1 despite lying in a not exceeded grid square, while YAR fell in a higher exceedance class (0.5-1.0 keq ha^{-1} yr^{-1}) and NAR remained in the same exceedance class (0.2-0.5 keq ha^{-1} yr^{-1}) as the original exceedance grid squares (see Table 3.1). CL values were not exceeded in the remaining catchments by 0.38 to 2.07 keq H ha^{-1} yr^{-1}. Non-exceedance was highest in catchment GACON and lowest in ULCON.

The Critical Load Function (CLF, see Section 3.5.5.3) was used to assess the deposition reductions required to protect the study catchments from acid deposition (Figure 5.2). The Glen Arnisdale catchments fell in the unshaded (white) area because $CL_{max}(S)$ and $CL_{min}(N)$ were both higher than S and N deposition, respectively, and therefore these catchments were considered protected from acid deposition. In the Loch Katrine area catchments $CL_{max}(S)$ exceeded S deposition and N deposition was higher than $CL_{min}(N)$ but lower than $CL_{max}(N)$. This meant that the Loch Katrine area catchments fell in either the white area or the blue area of the CLF (reductions of either N or S). However, since CL were not exceeded in the Loch Katrine area catchments it seems that no further deposition reductions are necessary and the catchments were considered protected from acid deposition. For UL1, both S and N deposition exceeded $CL_{max}(S)$ and $CL_{max}(N)$, respectively, meaning that the catchment lies in the black area of the CLF and reductions in both S and N deposition are necessary to protect it from acid deposition. For catchments UL2 and ULCON, $CL_{max}(S)$ and $CL_{max}(N)$ were higher than S and N deposition values respectively, so both catchments fell in the white area of the CLF and were considered protected from acid deposition. For catchments YAR and NAR, $CL_{max}(S)$ was higher than the S deposition estimate, but $CL_{max}(N)$ was exceeded by modelled N deposition inputs, meaning that both catchments fell in the red area of the CLF. Therefore, to protect both YAR and NAR from acid deposition initial reductions in N deposition are necessary, followed by further reductions in either S or N deposition.

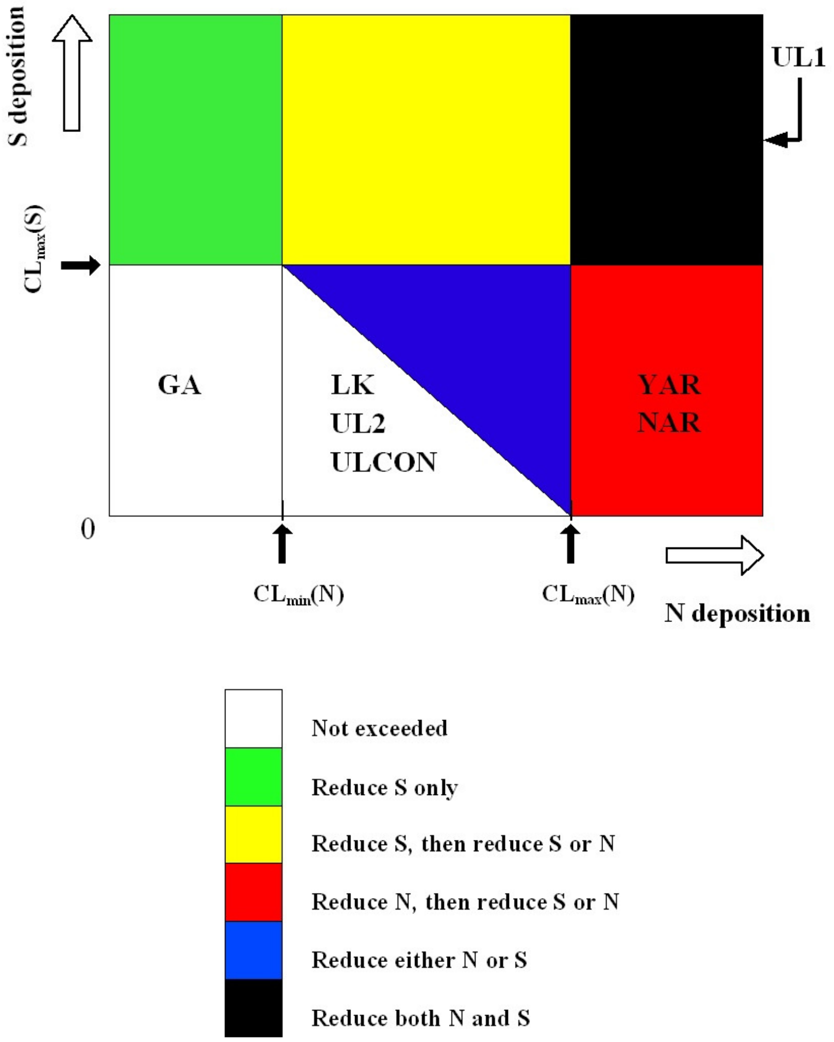


Figure 5.2 Position of study catchments in the Critical Load Function (CLF) (UK National Focal Centre, 2004). GA = Glen Arnisdale and LK = Loch Katrine area catchments

5.1.4 Comparison of critical loads exceedance calculated with SSWC and FAB models

CL exceedances calculated using the SSWC and FAB models and 2002 FRAME pollutant deposition showed in both cases that CL were exceeded in three catchments: UL1, YAR and NAR. However, the magnitude of CL exceedance and non-exceedance differed between the two different models. The FAB model is usually more sensitive (i.e. more protective of freshwaters) than SSWC and calculates higher CL exceedance and lower non-exceedance values than the SSWC model due to the way FAB models N processes in catchment soils (Henriksen and Posch, 2001). However, comparison of the model outputs for the study catchments showed mixed results (Figure 5.3). In the Loch Katrine area and Devon catchments and in ULCON SSWC non-exceedance values were higher than the FAB model values as expected, but the opposite pattern occurred in the Glen Arnisdale catchments and in UL1 and UL2. Since the same modelled S deposition data were used in both models, the differences observed in CL exceedance values are due to the different treatment of incoming N deposition and calculation of N leaching to streamwater in the SSWC and FAB models.

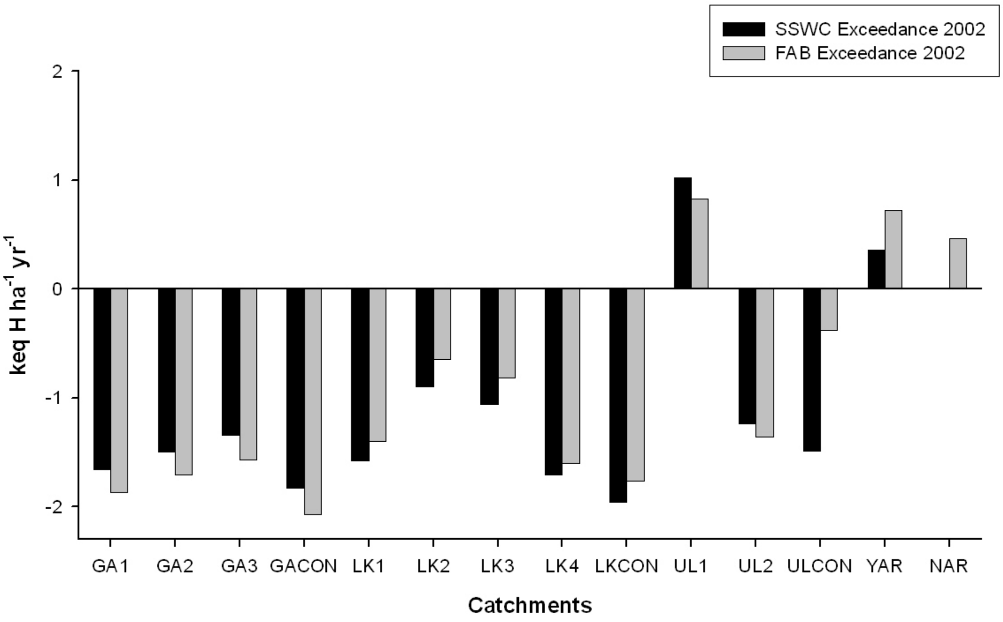


Figure 5.3 CL exceedance values calculated with the SSWC model using 2002 FRAME modelled non-marine S deposition and N leaching and with the FAB model using 2002 FRAME modelled deposition. Negative values indicate non-exceedance. N.B. NAR SSWC Exceedance: 0.01 keq ha^{-1} yr^{-1}

The FAB model assumes that N leaching to streamwater (N_{output}) is equal to the N deposition remaining after N retention in the soil ($N_{output} = N_{dep} – N_{ret}$) while SSWC calculates N leaching (N_{leach}) from measured streamwater NO_3 concentration which is converted to a N flux using the estimated runoff for each catchment (Table 5.1). N_{ret} in FAB depends on the default N immobilisation and denitrification values for each soil type while SSWC does not directly take account of any N soil processes. The N_{output} and N_{leach} values calculated for the study catchments are shown in Figure 5.4. N_{leach} values were lower than N_{output} in the Loch Katrine area catchments and in ULCON, YAR and NAR resulting in lower non-exceedance and higher CL exceedance values, respectively, calculated with FAB than with SSWC (Figure 5.3). The lower N_{leach} values compared to the N_{output} values for the Loch Katrine area and Devon catchments and ULCON suggest that the measured streamwater NO_3 fluxes were lower than expected according to modelled N deposition and N soil retention and that either catchment soils appear to remove more N or less N was deposited than modelled in FAB. Broadleaf woodland could possibly retain some N but this does not explain the big difference between N_{output} and N_{leach} values in NAR which has almost no woodland cover (2%). Seasonal variability in streamwater NO_3 concentrations also does not explain the results since concentrations are expected to be higher in the winter months when there is little biological activity to take up N and when N deposition is highest (Chapman and Edwards, 1999). Another explanation for the difference between N_{output} and N_{leach} values in the Loch Katrine area catchments could be the runoff estimate used to calculate N_{leach}, dilution during high rainfall events and lower than expected streamwater NO_3 concentrations or possible overestimation of N deposition by the FRAME model.

In contrast, values of N_{output} were lower than N_{leach} in the Glen Arnisdale catchments and in UL1 and UL2 (Figure 5.4), resulting in higher non-exceedance and lower CL exceedance values calculated with FAB than with SSWC. The higher N_{leach} values compared to N_{output} values indicate that either these catchments retained less N than calculated with the default values in FAB, or that more N was deposited than modelled by FRAME. The calculated N_{output} values for the Glen Arnisdale catchments were negative because N deposition was lower than the net N removal by catchment soils. However, low NO_3 concentrations were measured in streamwater from the Glen Arnisdale catchments and N_{leach} were low at 0.05 to 0.06 keq H ha^{-1} yr^{-1}. A possible explanation for the larger than expected N leaching in UL1 and UL2 could be lower N uptake from soils due to N fixing by the woodland alder trees as well as enhanced dry N deposition on the woodland canopies, especially for reduced

N. Also, N_{leach} could be overestimated due to overestimation of runoff, since evapotranspiration of more than 15% of the annual rainfall might occur for the dense forest canopy.

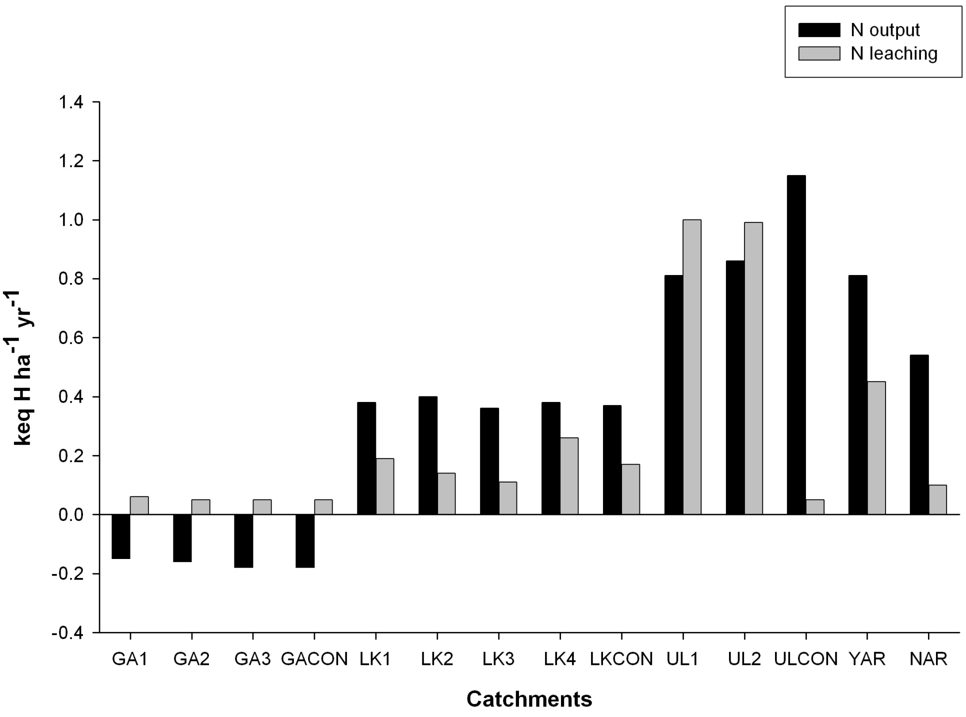


Figure 5.4 Comparison of calculated N output in the FAB model and N leaching in the SSWC model for the study catchments

5.2 Sensitivity analysis of critical load calculations

There have been many efforts to quantify the uncertainty in critical loads estimates because the implementation of important policies, such as those controlling emissions of acidic pollutants in Europe, depends on the outputs of critical load models (Skeffington, 2006). Uncertainties in critical loads estimates are associated with the variables used in the critical load model formulations. An important part of uncertainty analysis is sensitivity analysis in which the extent is investigated to which changes in input variables affect changes in model outputs. Analysis of uncertainty in critical loads and exceedance estimates is important for assessing the effectiveness of the Forests and Water Guidelines methodology for protecting acid-sensitive freshwaters from the expansion of broadleaf woodlands. This section presents the results of a "single" parameter sensitivity analysis in which the effect of changing one input variable in the SSWC and FAB models, while others were held constant, on the critical loads and exceedance estimates for the study catchments was assessed. Input variables used in the sensitivity analysis were different runoff estimates, formulation for weathering rates and critical ANC values and chemistry data from the most and least acidic streamwater sample.

5.2.1 Effect of different runoff estimates on critical loads and exceedance

Annual rainfall is used in the SSWC model to convert critical load (CL) values to fluxes and measured streamwater NO_3 concentrations to NO_3 fluxes, as part of the CL exceedance calculations for each catchment. Runoff is assumed to be 85% of the annual rainfall. In order to investigate the effect of using different runoff estimates, CL and CL exceedance values were re-calculated using the SSWC and FAB models and runoff estimates derived from the minimum, mean and maximum annual rainfall amounts available from the BADC for each study catchment (Table 5.7).

Table 5.7 Annual runoff estimates (mm) from the minimum, mean and maximum annual rainfall available from the British Atmospheric Data Centre (BADC) for the study catchments. Years of minimum and maximum rainfall are given in brackets

Catchments	No. of years of record	Minimum runoff	Mean runoff	Maximum runoff
Glen Arnisdale	36	1383 (*1972*)	1790	2498 (*1990*)
Loch Katrine	35	1453 (*1969*)	1978	2172 (*1990*)
Ullswater	29	632 (*2003*)	878	1089 (*1974*)
YAR	37	714 (*1975*)	1148	1509 (*2000*)
NAR	36	1053 (*1976*)	1451	1873 (*1974*)

CL and CL exceedance values calculated with runoff from minimum, mean and maximum annual rainfall for each study catchment and the SSWC and FAB models using 1995-97 deposition data and the 2002 modelled deposition generated by FRAME are shown in Figure 5.5.

As expected, according to the SSWC model formulation, increases in runoff resulted in increases in CL values (see Equation 3.6) and N leaching to streamwater (see Equation 3.12) in the study catchments. CL non-exceedance increased and CL exceedance decreased in the study catchments as runoff increased, despite increases also in N leaching, apart from UL1, which was the only study catchment where NO_3 exceeded the sum of non-marine base cations in streamwater. Therefore, it seems that CL exceedance with the SSWC model increases with increasing runoff only when streamwater NO_3 exceeds non-marine base cations, while CL non-exceedance will always increase as runoff increases because streamwater non-marine base cations always exceed acid anions in not-exceeded catchments. The effect of runoff on CL exceedance calculated with the FAB model is straightforward because changes in runoff do not affect modelled S and N deposition used to calculate exceedance and thus higher CL values will always result in either higher CL non-exceedance or lower CL exceedance depending on the catchment's acid sensitivity. The results also show that, according to the Forests and Water Guidelines methodology, i.e. CL calculated with the SSWC model and exceedance from 1995-97 non-marine S deposition and N leaching, catchments LK2 and LK3 would also be considered acid-sensitive for years with low rainfall.

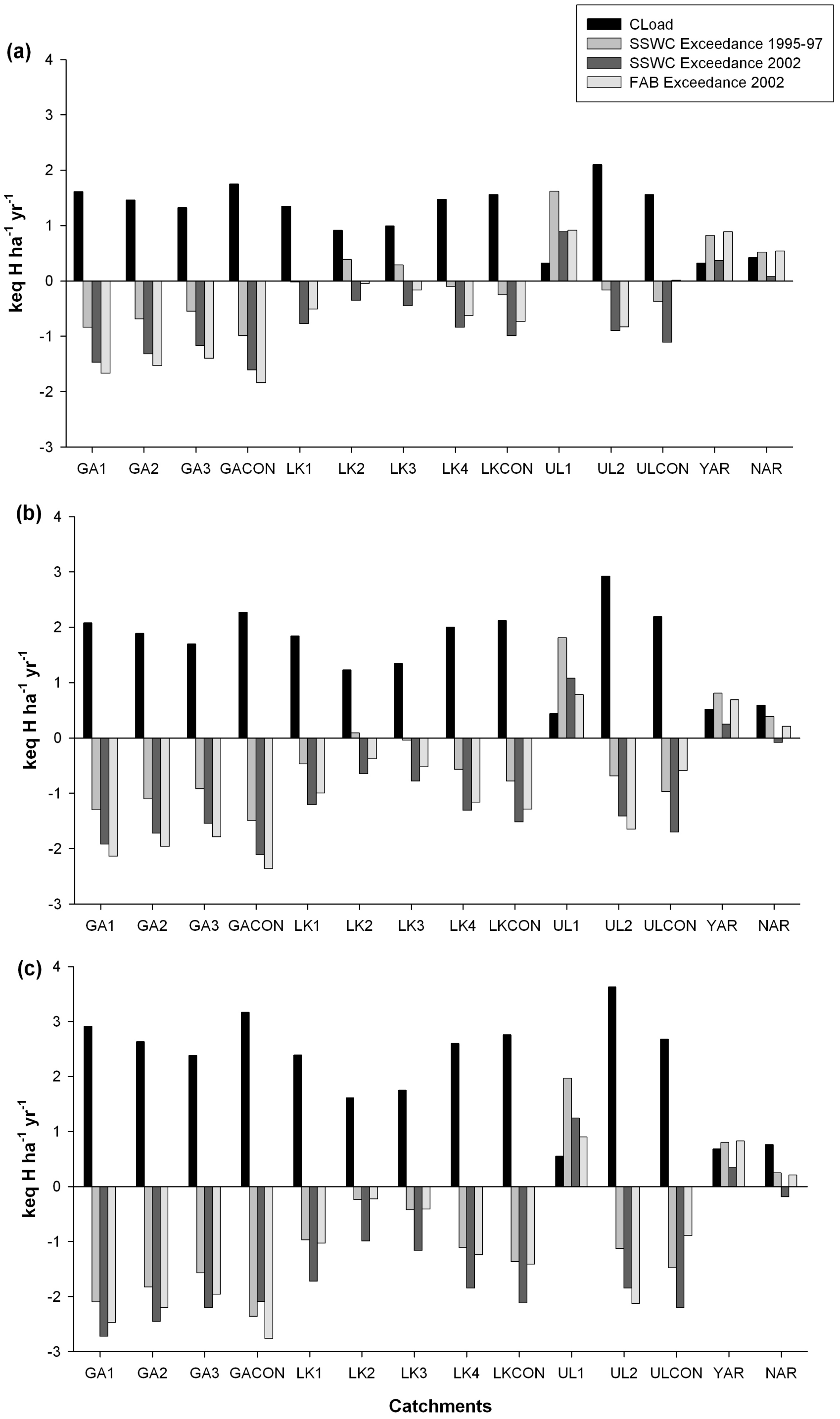


Figure 5.5 CL and CL exceedance values calculated with runoff from (a) minimum, (b) mean and (c) maximum rainfall for each study catchment and the SSWC model using 1995-97 and 2002 FRAME non-marine S deposition and N leaching and the FAB model using 2002 FRAME modelled deposition. Negative values indicate non-exceedance

Regardless whether higher or lower estimates are used to calculate CL values and subsequent CL exceedance in the SSWC and FAB models, the streamwater base cation and acid anion concentrations remain the same. However, streamwater concentrations could possibly decrease as flow increases due to dilution and this was observed in catchment LK1 where streamwater Ca and marine SO_4 were significantly negatively correlated with discharge (r_s= -0.71, P= 0.002 and r_s= -0.58, P= 0.014, respectively). A similar dilution effect has been reported by Stevens et al. (1997) for winter streamwater solute concentrations in the Acid Waters Survey of Wales catchments. For lakes, CL are calculated using a single sample collected in autumn which has been proven to be representative of the yearly flow-weighted average water chemistry (Henriksen and Posch, 2001), but since water chemistry is more variable in rivers, more accurate estimates of streamwater CL values would be obtained if yearly flow-weighted average chemistry was used. However, deriving these values would require considerably higher effort and cost in flow monitoring and water sampling and analysis compared to the methodology used by the Forests and Water Guidelines. Also, the Guidelines' methodology aims to assess the "worst-case" scenario by sampling streamwater with the most acidic rather than average chemistry. Therefore, there is probably no need for the Guidelines' methodology to use flow-weighted chemistry, but improvements to the SSWC formulation, such as the one described in Section 5.2.2, could be used by the Guidelines for more accurate estimates of CL values.

5.2.2 Effect of weathering rates on critical loads and exceedance calculations

The calculation of CLs with the SSWC model depends on the estimation of weathering rates in the catchment soils which supply the system with non-marine base cations. Catchment weathering rates are represented in the SSWC model by the "F" term, which is defined as a function of measured streamwater non-marine base cation concentrations ($[BC]_t^*$, see 3.5.3). The "F" term was originally derived from Norwegian lake data and for an average value of runoff (Henriksen and Posch, 2001). However, if two catchments have similar soils and geology and similar weathering rates but different runoff their base cation fluxes should be similar but their streamwater concentrations would differ considerably. Thus, Henriksen and

Posch (2001) recommend that the “F” term should be calculated as a flux instead of a concentration:

$$F = \sin\left(\left(\frac{\pi}{2}\right) \cdot Q \cdot \frac{[BC]_t^*}{S}\right) \qquad \text{(Equation 5.1)}$$

where Q is the annual runoff (in m yr^{-1}) and S has been estimated to be 400 μeq l^{-1} (see Section 3.5.3). The formulation shown in Equation 5.1 is also recommended by the latest Manual on Methodologies for Modelling and Mapping Critical Loads (UBA, 2004).

The effect of the new formulation of the “F” term on the assessment of acid-sensitivity of the study catchments was investigated by calculating CL and CL exceedance values with the “F” term values converted to fluxes using runoff for each catchment estimated from most recent rainfall. CL and CL exceedance was calculated using mean high flow chemistry and the SSWC model using modelled non-marine S deposition for 1995-97 and 2002 FRAME and N leaching and the FAB model with 2002 FRAME modelled S and N deposition and the results are shown in Table 5.8.

Table 5.8 Values of the "F" term calculated as a flux (F_{flux} in m yr^{-1}), and re-calculated pre-industrial base cation concentration ($[BC]_0^*$) (μeq l^{-1}) and critical load (CL) values with the F_{flux} term and CL exceedance values using total (S and N) 1997-95 and 2002 FRAME modelled deposition (keq H ha^{-1} yr^{-1}) and an acid neutralising capacity (ANC) of 0 μeq l^{-1} for the study catchments

Catchments	F_{flux} term	$[BC]_0^*$	CL	SSWC CL Exceedance 1995-97	SSWC CL Exceedance 2002	FAB CL Exceedance 2002
GA1	0.60	122	1.90	-1.12	-1.75	-1.95
GA2	0.55	110	1.72	-0.94	-1.57	-1.71
GA3	0.53	97.5	1.52	-0.75	-1.37	-1.57
GACON	0.67	130	2.03	-1.26	-1.89	-2.07
LK1	0.78	90.9	2.19	-0.79	-1.53	-1.35
LK2	0.56	61.5	1.49	-0.13	-0.87	-0.63
LK3	0.61	66.7	1.61	-0.29	-1.03	-0.79
LK4	0.83	97.6	2.36	-0.88	-1.63	-1.52
LKCON	0.85	106	2.57	-1.19	-1.94	-1.74
UL1	0.38	65.0	0.52	1.63	0.90	0.71
UL2	0.98	333	2.64	-0.51	-1.24	-1.37
ULCON	0.73	248	1.97	-0.78	-1.51	-0.40
YAR	0.25	43.7	0.47	0.83	0.37	0.73
NAR	0.21	39.8	0.50	0.46	0.03	0.47

As expected, "F" term values calculated as a flux (F_{flux}) were higher than the values calculated as concentrations (F_{conc}) (compare with Table 5.1) in the catchments in Glen Arnisdale, Loch Katrine area and in YAR and NAR where runoff was above 1000 mm and decreased in the Ullswater area catchments where runoff was 793 mm. The greatest increases occurred in the high rainfall catchments in Glen Arnisdale and the Loch Katrine area. Higher F_{flux} values were expected to result in lower pre-industrial non-marine base cation concentrations ($[BC]_0^*$) and CL values according to Equations 5.2 and 5.3 (for explanation see Section 3.5.3):

$$[BC]_0^* = [BC]_t^* - F \cdot \left([AA]_t^* - [AA]_0^*\right) \qquad \text{(Equation 5.2)}$$

$$Critical\ Load = \left([BC]_0^* - [ANC_{crit}]\right)\cdot Q \qquad \text{(Equation 5.3)}$$

The higher F_{flux} values gave lower $[BC]_0^*$ and CL values in the Loch Katrine and in YAR and NAR but higher values in the Glen Arnisdale catchments compared to when F_{conc} values were used for these catchments (compare with Table 5.1). In addition, the lower F_{flux} values in catchments UL1 and ULCON resulted in higher $[BC]_0^*$ and CL values, while there was no change in the values in UL2. Consequently, CL non-exceedance was lower in the Loch Katrine catchments and CL exceedance was higher in YAR and NAR for both the SSWC and FAB models and 1995-97 and 2002 deposition. CL non-exceedance was higher in the Glen Arnisdale catchments and ULCON, whilst CL exceedance was lower in UL1 while non exceedance remained the same in UL2.

The unexpected lower $[BC]_0^*$ and consequently CL values in the Glen Arnisdale catchments are explained by the low estimated streamwater non-marine acid anion concentrations ($[AA]_t^*$) in these catchments, which were lower than the pre-industrial non-marine acid anion ($[AA]_0^*$) concentrations mainly due to the effect of seasalt inputs. Thus, the difference between $[AA]_t^*$ and $[AA]_0^*$ becomes negative, resulting in increases in $[BC]_0^*$ values (Equation 5.2) until a threshold concentration where $[AA]_t^*$ exceeds $[AA]_0^*$ values and $[BC]_0^*$ values start decreasing, causing lower CL values. For example, in catchment GA1 non-marine acid anion concentrations need to increase from the current 6 to 32 μeq l^{-1} before $[BC]_0^*$ values start to decrease. Thus, for present acid anion streamwater concentrations, the use of higher F_{flux} values resulted in higher $[BC]_0^*$ and CL values in the Glen Arnisdale catchments.

For UL1 and ULCON, the unexpected increases in CL values with decreasing F_{flux} values were due to the high $[AA]_t^*$ concentrations, especially in UL1 where they exceeded non-marine base cation concentrations. The difference between $[AA]_t^*$ and $[AA]_0^*$ was positive and when multiplied with lower F_{flux} values resulted in higher $[BC]_0^*$ and CL values. No change was observed in UL2 because the $[BC]_t^*$ concentration was higher than the S value of 400 μeq l^{-1} (Equation 5.1).

These results suggest that CL values calculated with F_{conc} can overestimate CL values and thus underestimate CL exceedance in catchments with high annual runoff (> 1000 mm). However, due to the way AA_0^* is calculated in the SSWC model, the effect of F_{flux} on CL values also depends on the non-marine acid anion concentrations and how these compare with pre-industrial acid anion and non-marine base cation concentrations. In the absence of flow-weighted chemistry data for the study catchments, inclusion of F_{flux} in the SSWC model formulation should provide more certainty in the calculation of CL values. The same increase in certainty is expected from the inclusion of F_{flux} in the FAB model calculations since this model uses the CL values calculated in SSWC.

5.2.3 Critical loads and exceedance calculated with ANC_{crit} of 20 μeq l^{-1}

For the calculation of CLs with the SSWC and FAB models an ANC_{crit} = 0 μeq l^{-1} was used, following the methodology of the Forests and Water Guidelines (Forestry Commission, 2003). However, an ANC_{crit} value of 20 μeq l^{-1} is also currently being used for the mapping of freshwater CL exceedance in the UK (UK National Focal Centre, 2004) and therefore CLs for the study catchments were recalculated using an ANC_{crit} = 20 μeq l^{-1} in order to investigate CL exceedance in the study catchments under more stringent CL values, which provide a higher probability of protection for brown trout.

CLs and exceedance were calculated using the same mean streamwater chemistry and modelled pollutant deposition datasets as previously and the only difference was the inclusion of ANC_{crit} = 20 μeq l^{-1} instead of 0 μeq l^{-1} in the CL formulation used by the SSWC model. As expected, the re-calculated CL values were lower in all study catchments, resulting in higher CL exceedance values and lower non-exceedance values. Decreases in CL values were generally small in the catchments near Ullswater and greater in the Loch Katrine area catchments (Table 5.9).

Table 5.9 CL and CL exceedance values calculated using ANC_{crit}= 0 (ANC_0) and ANC_{crit}= 20 µeq l^{-1} (ANC_{20}) and the SSWC model using 1995-97 and 2002 FRAME non-marine S deposition and N leaching and the FAB model using 2002 FRAME modelled deposition (all in keq H ha^{-1} yr^{-1})

Catchments	CL		CL exceedance 1995-97 (SSWC)		CL exceedance 2002 (SSWC)		CL exceedance 2002 (FAB)	
	ANC_0	ANC_{20}	ANC_0	ANC_{20}	ANC_0	ANC_{20}	ANC_0	ANC_{20}
GA1	1.82	1.50	-1.04	-0.73	-1.66	-1.35	-1.87	-1.56
GA2	1.64	1.33	-0.87	-0.56	-1.50	-1.18	-1.71	-1.40
GA3	1.48	1.17	-0.71	-0.40	-1.34	-1.02	-1.57	-1.26
GACON	1.98	1.66	-1.20	-0.89	-1.83	-1.52	-2.07	-1.76
LK1	2.24	1.76	-0.84	-0.36	-1.58	-1.58	-1.40	-0.92
LK2	1.51	1.02	-0.15	0.33	-0.90	-0.90	-0.65	-0.17
LK3	1.64	1.16	-0.32	0.16	-1.06	-1.06	-0.82	-0.34
LK4	2.44	1.95	-0.97	-0.48	-1.71	-1.71	-1.60	-1.11
LKCON	2.59	2.11	-1.21	-0.73	-1.96	-1.96	-1.76	-1.28
UL1	0.40	0.24	1.74	1.90	1.02	1.18	0.82	0.99
UL2	2.64	2.48	-0.51	-0.35	-1.24	-1.08	-1.36	-1.21
ULCON	1.95	1.79	-0.77	-0.61	-1.49	-1.33	-0.38	-0.22
YAR	0.49	0.27	0.81	1.03	0.36	0.57	0.72	0.94
NAR	0.51	0.26	0.45	0.70	0.01	0.26	0.46	0.71

Since the same pollutant deposition estimates were used for re-calculating CL exceedance, the absolute changes in CL exceedance values were the same magnitude as the ones for CL values. With the 1995-97 modelled non-marine S deposition and N leaching and ANC_{crit}= 20 µeq l^{-1}, CLs were exceeded in five catchments: LK2, LK3, NAR, YAR and UL1. Lower re-calculated CL values meant that catchments LK2 and LK3 were now considered acid-sensitive. Using the 2002 FRAME modelled non-marine S deposition and N leaching and ANC_{crit}= 20 µeq l^{-1}, CL values were only exceeded in the same three catchments NAR, YAR and UL1, as when the lower ANC_{crit} value was used.

Re-calculated total CL exceedance for an ANC_{crit}= 20 μeq l^{-1} with the FAB model and using the 2002 FRAME modelled deposition again found that CL values were exceeded in NAR, YAR and UL1, but by more than when the lower ANC_{crit} value was used. Calculated critical deposition loads in the FAB model ($CL_{max}(S)$, $CL_{min}(N)$ and $CL_{max}(N)$) for ANC_{crit} = 20 μeq l^{-1} showed that all the catchments lay in the same position as before, apart from YAR and NAR. For these catchments, both S_{dep} and N_{dep} were higher than $CL_{max}(S)$ and $CL_{max}(N)$, respectively, and this meant that they no longer fell in the red but in the black area of the CLF meaning that both S and N deposition had to be reduced to protect the catchments from acidic deposition.

These results indicate that if a higher ANC_{crit} value of 20 μeq l^{-1} was used, more catchments would have been found to be acid-sensitive according to the Forests and Water Guidelines methodology, i.e. CL exceedance calculated with the SSWC model and modelled non-marine S and N leaching. Also, examination of the CLF in the FAB model formulation showed that recommended deposition reductions would have changed for some catchments.

5.2.4 Critical loads and exceedance calculated with minimum and maximum ANC

The Forests and Water Guidelines (Forestry Commission, 2003) use the mean streamwater chemistry of high flows sampled during January-March for the calculation of CL and CL exceedance values because streamwater is expected to be most acidic in these conditions. However, the effect of the most and least acidic streamwater sampled on CL and CL exceedance values from the study catchments (worst and best case scenario, respectively) was also investigated in order to: a) assess effects of episodic acidification on catchment acid-sensitivity and b) assess whether catchment acid-sensitivity changes when less acidic streamwater samples are used, which in most cases were sampled at lower flow than more acidic streamwater. The chemistry results of the streamwater samples with the lowest and highest ANC values (ANC_{min} and ANC_{max}) for each catchment were used to represent the most and least acidic conditions, respectively. CL and CL exceedance values were calculated from these streamwater samples using the same methods as before and an $ANC_{crit} = 0$ µeq l^{-1}.

Figure 5.6 shows the minimum, mean and maximum calculated ANC values for streamwater sampled at high flow from the study catchments. Streamwater ANC_{min} values were negative in 10 catchments, while only UL1 had negative streamwater ANC_{max}.

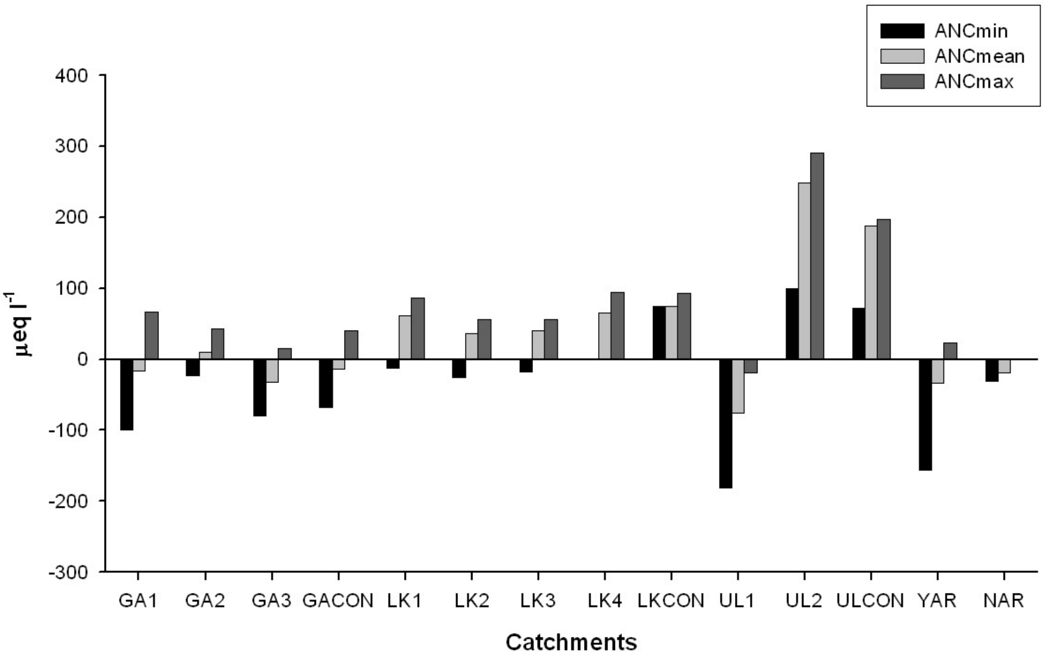


Figure 5.6 Streamwater high flow minimum, mean and maximum ANC values for the study catchments

Table 5.10 gives the CL and CL exceedance values calculated using streamwater chemistry from the samples with minimum and maximum ANC from the study catchments.

Table 5.10 CL and CL exceedance values calculated using streamwater chemistry from samples with $\mathrm{ANC_{min}}$ and $\mathrm{ANC_{max}}$ and the SSWC model using 1995-97 and 2002 FRAME non-marine S deposition and N leaching and the FAB model using 2002 modelled deposition generated by FRAME (all in keq H ha^{-1} yr^{-1}). ANC values given in μeq l^{-1}

Catchments	CL		CL exceedance 1995-97 (SSWC)		CL exceedance 2002 (SSWC)		CL exceedance 2002 (FAB)		ANC	
	$\mathrm{ANC_{min}}$	$\mathrm{ANC_{max}}$	$\mathrm{ANC_{min}}$	$\mathrm{ANC_{max}}$	$\mathrm{ANC_{min}}$	$\mathrm{ANC_{max}}$	$\mathrm{ANC_{min}}$	$\mathrm{ANC_{max}}$	$\mathrm{ANC_{min}}$	$\mathrm{ANC_{max}}$
GA1	3.31	1.21	-2.53	-0.44	-3.16	-1.06	-3.37	-1.27	-99.2	66.0
GA2	2.41	0.77	-1.64	0.01	-2.27	-0.62	-2.48	-0.89	-22.6	42.6
GA3	2.39	0.56	-1.61	0.21	-2.24	-0.42	-2.47	-0.65	-79.6	14.9
GACON	3.00	0.98	-2.23	-0.21	-2.86	-0.83	-3.09	-1.07	-67.3	41.0
LK1	2.09	2.90	-0.65	-1.52	-1.40	-2.26	-1.25	-2.06	-12.4	87.0
LK2	1.32	2.14	0.06	-0.76	-0.68	-1.50	-0.46	-1.28	-25.4	55.9
LK3	1.64	2.04	-0.25	-0.72	-0.99	-1.47	-0.82	-1.22	-18.0	55.6
LK4	2.25	3.20	-0.73	-1.81	-1.47	-2.55	-1.41	-2.36	0.41	94.9
LKCON	2.13	3.07	-0.71	-1.73	-1.45	-2.47	-1.30	-2.24	74.6	92.8
UL1	0.02	0.59	2.79	0.66	2.07	-0.06	1.21	0.63	-181	-19.5
UL2	1.38	3.25	1.34	-0.77	0.61	-1.50	-0.11	-1.98	100	290
ULCON	1.09	2.00	0.13	-0.86	-0.60	-1.59	0.48	-0.44	72.4	197
YAR	0.38	0.97	0.96	0.39	0.50	-0.06	0.83	0.24	-156	23.3
NAR	0.47	0.60	0.55	0.31	0.11	-0.13	0.50	0.37	-31.0	0.99

As expected, CL values calculated with ANC_{max} were higher than those calculated with ANC_{min}, apart from for the Glen Arnisdale catchments. Unexpectedly, CL values in the Glen Arnisdale catchments for the samples with ANC_{min}, which corresponded to streamwater sampled after the seasalt event (see 4.1.3), were higher than the ones calculated with either mean chemistry or chemistry from samples with ANC_{max}. The higher CL values calculated with ANC_{min} were due to the removal by the SSWC formulation of the marine ion component, which was high due to the seasalt event, leading to high non-marine streamwater base cation concentrations but low concentrations of non-marine acid anions.

The number of catchments which exceeded their CL increased when using streamwater chemistry for ANC_{min} compared to mean streamwater chemistry. CLs were exceeded in six catchments when using the SSWC model and 1995-97 non-marine S deposition and N leaching and in four catchments for both the SSWC and FAB models using 2002 FRAME deposition. Overall, CLs were exceeded in fewer catchments when using streamwater chemistry for ANC_{max}, while none of the catchments was considered acid-sensitive for CL exceedance calculated with the SSWC model and 2002 FRAME non-marine S deposition and N leaching.

Critical deposition loads ($CL_{max}(S)$, $CL_{min}(N)$ and $CL_{max}(N)$) calculated in the FAB model for ANC_{min} showed that all catchments lay in the same position as when mean streamwater chemistry was used, apart from YAR and ULCON (Figure 5.2). For ANC_{min}, YAR fell in the black area of CLF indicating that reductions in both S and N deposition were necessary to protect it from acidic deposition, while ULCON fell in the red area of the CLF so initial reductions in N deposition were necessary followed by further reductions in S or N deposition to protect it from acidic deposition. Deposition loads in the FAB model for ANC_{max} showed that all catchments lay in the same position as when mean streamwater chemistry was used, apart from UL1, YAR and NAR. UL1 fell in the red area of the CLF indicating that initial reductions in N deposition were necessary followed by further reductions in S or N deposition to protect the catchment from acidic deposition, while both YAR and NAR fell in the blue area of the CLF indicating that reductions in either N or S were necessary to protect these catchments. Overall, less stringent reductions in acid deposition were recommended for the acid-sensitive catchments by the CLF in the FAB model when streamwater chemistry for ANC_{max} was used.

The results show that calculated CL values are lower and CL exceedance occurs more frequently when using streamwater chemistry from the most acidic sample, while the opposite occurs when the least acidic streamwater samples are used. In the context of the Forests and Water Guidelines (i.e. CL exceedance with the SSWC model and 1995-97 non-marine S deposition and N leaching), the calculations for ANC_{min} gave twice the number of acid-sensitive catchments than when ANC_{max} was used. However, CLs were exceeded in the same catchments when mean high flow chemistry and chemistry from the sample with ANC_{max} were used. Thus sampling the most acidic streamwater may not be so important for assessment of the risk of streamwater acidification within the methodology recommended by the Guidelines.

Catchments GA2 and GA3 where streamwater chemistry was affected by seasalt events were not considered acid-sensitive when either ANC_{min} or ANC_{max} were used, indicating that the methodology failed to take account of the potential adverse impacts on freshwater biota posed by the excess acid anion loads in streamwater. Thus, the critical loads methodology seems to underestimate the risk of episodic streamwater acidification in catchments receiving high seasalt inputs, probably due to the inability of both the SSWC and FAB models to take account of seasalt inputs on ion-exchange processes in catchment soils which may result in the leaching of inorganic Al to streamwater (UK Focal Centre, 2004).

5.3 Catchment acid-sensitivity assessed with the Rutt model

5.3.1 Catchment classification with the Rutt model

The results from the macroinvertebrate sampling were analysed to provide information on the effects of catchment acidification using models of macroinvertebrate presence/absence, because macroinvertebrates often respond strongly to acid-base status. For this purpose, the Rutt model was used to classify the

11 catchments sampled and assign them, on the basis of indicator taxa, into one of four groups, which differ markedly in their streamwater chemistry conditions (Rutt et al., 1990). The Rutt model was developed from TWINSPAN classification and Multiple Discriminant Analysis of macroinvertebrate and streamwater chemistry (pH, Ca, Al and hardness) data sampled from streams across Great Britain and predicts catchment acid-sensitivity using macroinvertebrate family level indicators. In the Rutt model, group number increases as acid-sensitivity increases (i.e. Group 4 represents the most acidic conditions). The 11 catchments sampled were assigned to the four groups according to the presence or absence of the indicator macroinvertebrate families shown in Figure 5.7 and the results are shown in Table 5.11.

Table 5.11 Classification of the 11 catchments sampled for the Rutt model

Group 1	Group 2	Group 3	Group 4
GA2	LK1	GA3	UL1
GACON	LK2	ULCON	
UL2	LK3		
	LK4		
	LKCON		

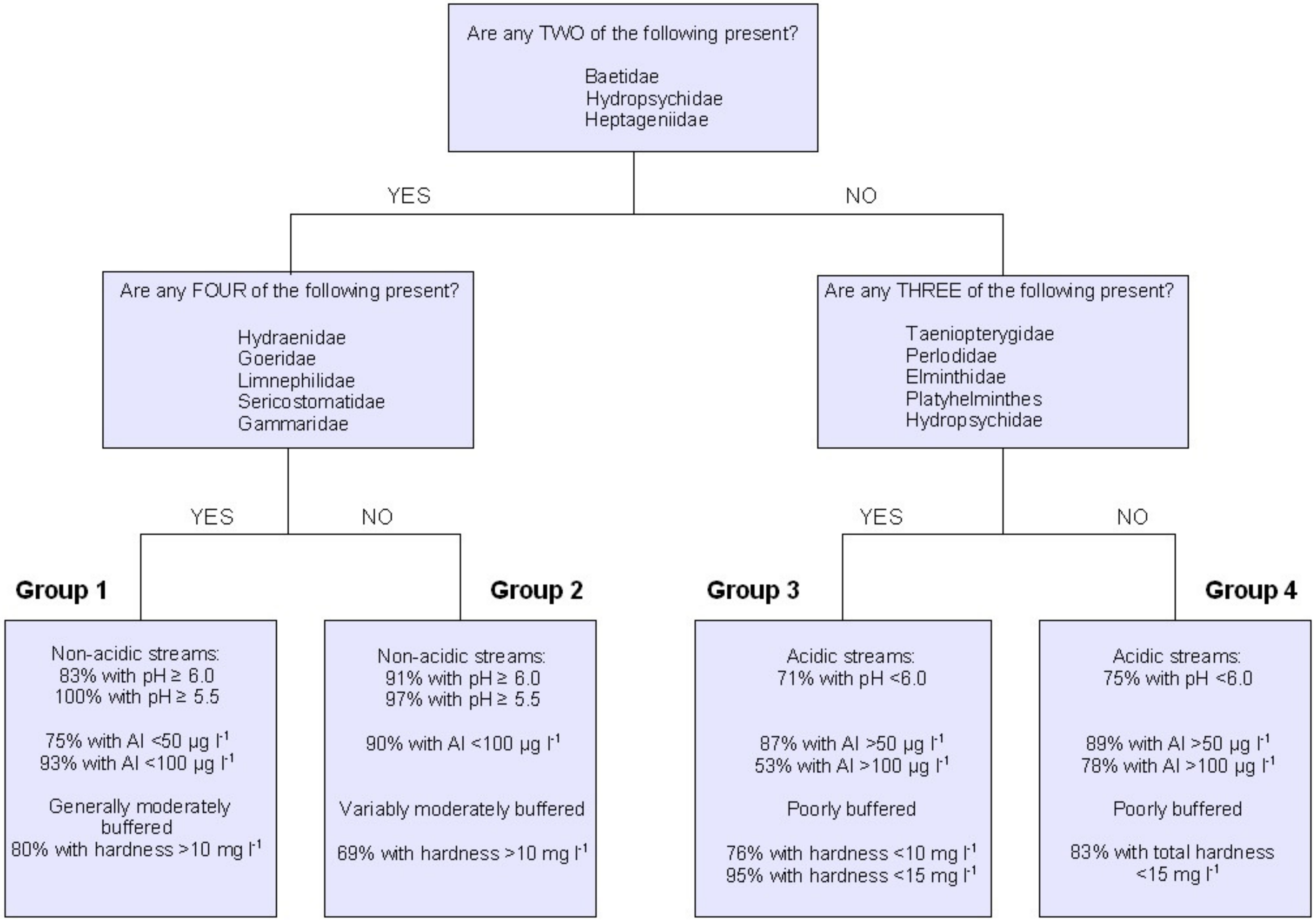


Figure 5.7 The classification procedure of the Rutt model based on absence/presence of indicator macroinvertebrate families. Hardness is given in mg l^{-1} CaCO$_3$

According to the Rutt model, the Loch Katrine area and Glen Arnisdale catchments, apart from GA3, were assigned to Groups 2 and 1, respectively, and were classified as non-acidic. ULCON and GA3 were both assigned to Group 3 and UL1 was assigned to Group 4, so streamwater in these catchments was classified as acidic. Mean streamwater pH in the Loch Katrine area catchments and GA2 and GACON was above 6.0 and streamwater soluble Al was below 100 and 50 μg l^{-1}, agreeing with the predictions made by the Rutt model for Groups 2 and 1. However streamwater hardness (calculated as ([Ca] * 2.5 + [Mg] * 4.1), in mg l^{-1} $CaCO_3$) in the Loch Katrine catchments and GA2 and GACON ranged from 5 to 7 mg l^{-1} $CaCO_3$ and was below the threshold value of 10 mg l^{-1} $CaCO_3$ indicated by the Rutt model for Groups 1 and 2. In GA3, streamwater pH was 5.5, hardness was 4 mg l^{-1} $CaCO_3$ and mean streamwater soluble Al was 55 μg l^{-1} in good agreement with the streamwater chemistry indicated by Group 3 in the Rutt model.

On the other hand, mean streamwater pH and soluble Al concentrations in ULCON were lower than the threshold values indicated by the Rutt model for Group 3 and streamwater hardness equalled the higher threshold value of 15 mg l^{-1} $CaCO_3$. UL1 had mean streamwater pH of 6.2 and mean streamwater Al concentration of 65 μg l^{-1}, which were higher than the threshold values. However, the mean streamwater hardness in UL1 of 17 mg l^{-1} $CaCO_3$ exceeded the 15 mg l^{-1} $CaCO_3$ threshold for Group 4. High mean pH and hardness values in UL1 and ULCON were caused by the high pH value and streamwater Ca and Mg concentrations in the one low flow sample collected from these catchments. However, if this low flow sample was excluded from the analysis, mean streamwater high flow chemistry in both UL1 and ULCON corresponded better to the Rutt model predictions. Mean streamwater soluble Al concentrations in UL1 increased to 87 μg l^{-1} but remained almost the same in ULCON (16 μg l^{-1}). However, streamwater hardness decreased in both catchments and was 8 and 13 mg l^{-1} $CaCO_3$ for UL1 and ULCON, respectively, below the 10 and 15 mg l^{-1} $CaCO_3$ thresholds specified by the Rutt model for Groups 3 and 4. However, it has to be noted that the Rutt model streamwater chemistry predictions are given as percentage probability, so some study streams could lie in the percentages that do not meet the probabilities.

5.3.2 Comparison of Rutt model predictions with critical load calculations

There was good agreement between measured and predicted streamwater chemistry with the Rutt model for the 11 catchments sampled based solely on the presence/absence of indicator macroinvertebrate families. In addition, the assessment of catchment status from the Rutt model predictions mostly agreed with the acid-sensitivity status determined with the critical loads (CL) approach for each study catchment. Streamwater high flow CL values were not exceeded in the Loch Katrine area, UL2, GA2 and GACON catchments, for both SSWC and FAB models and the 1995-97 and 2002 FRAME deposition datasets, indicating that these catchments were not acid-sensitive, and these catchments were also classified as non-acidic by the Rutt model. Furthermore, UL1 which had the highest CL exceedance in the study catchments was classified in the most acidic group of the Rutt model. GA3 and ULCON were classified as acidic by the Rutt model, but CLs were not exceeded in either catchment. However, GA3 had the lowest mean streamwater pH of the study catchments (pH 4.9) and it is possible that GA3 is actually acid-sensitive, but CLs were not exceeded due to the inability of the SSWC model to distinguish between anthropogenic and seasalt induced deposition causing acidification, as discussed earlier. However, CL was exceeded in GA3 with the SSWC model and for 1995-97 non-marine S deposition and N leaching using streamwater chemistry from the sample with ANC_{max} (Table 5.10), which could be considered more representative as mean streamwater chemistry in GA3 was greatly influenced by the seasalt event.

Catchment ULCON was also classified as acidic by the Rutt model despite its CL non-exceedance, but the CL was exceeded in ULCON using streamwater chemistry from the sample with ANC_{min} with the SSWC model and for 1995-97 non-marine S deposition and N leaching (Table 5.10), indicating that ULCON could be classified as acid-sensitive when streamwater chemistry is most acidic. Overall, the results suggest that macroinvertebrate samples are an effective means of identifying catchment acid-sensitivity in conjunction with models such as the Rutt model and in the absence of available streamwater chemistry data. In addition, the Rutt model predictions generally agree with acid-sensitivity determined using the critical loads approach within the Forests and Water Guidelines. Thus the Guidelines' methodology should ensure good ecological quality in water from catchments where CLs are not exceeded and which are regarded as not acid-sensitive.

5.4 Discussion

5.4.1 Introduction

All the catchments included in the study were considered acid-sensitive (i.e. critical loads were exceeded), or potentially acid-sensitive in the case of the Ullswater area catchments, according to the provisional critical load exceedance dataset used by the Forests and Water Guidelines. However, calculated streamwater critical load values with the SSWC and FAB models were only exceeded by deposition from the 1995-97 and 2002 FRAME modelled deposition datasets in catchments UL1, YAR and NAR, in decreasing order of CL exceedance. These three catchments had the highest streamwater concentrations of non-marine acid anions and also modelled S and N deposition inputs of the study catchments. In addition UL1 and YAR were the catchments where broadleaf woodland cover affected streamwater chemistry the most, with woodland cover positively associated with streamwater NO_3 concentrations. A similar increase in streamwater NO_3 related to the presence of woodland was observed in UL2 but the critical load was not exceeded due to the high soil buffering capacity in this catchment. The influence of various factors on critical loads and critical loads exceedance in the study catchments is discussed below.

5.4.2 Acid-sensitive catchments UL1, YAR and NAR

The high critical load exceedance observed in catchment UL1 was due to the highest measured streamwater $x\mathrm{SO}_4$ and NO_3 concentrations in the study catchments, probably caused mainly by the relatively high S and N deposition inputs. Streamwater NO_3 concentrations were also greatly influenced by the extensive alderwood cover in UL1, probably through both enhanced dry N deposition (mainly of NH_3) and increased nitrification. Woodland cover did not appear to influence $x\mathrm{SO}_4$ concentrations, which seemed to be controlled by internal soil processes. Streamwater concentrations of non-marine base cations in UL1 were relatively high, probably due to cation-exchange in the soil in response to the high inputs of acid anions, but they comprised only 60% of the mean sum of non-marine acid anions, resulting in the third lowest pre-industrial base cation concentration in the study catchments. The Ullswater area catchments received the lowest rainfall of the study catchments, and thus the lowest estimated runoff resulting in the lowest calculated critical load in UL1. Total modelled deposition was highest in the Ullswater area and consequently critical load exceedance in UL1 was highest in the study catchments, falling in the highest critical load exceedance class of the provisional dataset used by the Forests and Water Guidelines. Thus, according to FAB model calculations, reductions in present pollutant deposition levels for both S and N are necessary to protect UL1 from streamwater acidification. In addition, results of the macroinvertebrate analysis showed low species abundance and diversity in UL1 and it was classified as the most acidic, according to the Rutt model, of the 11 study catchments where macroinvertebrates were collected, suggesting that the streamwater chemistry in UL1 could have adverse impacts on freshwater biota. The fact that UL1 is highly acid-sensitive, despite lying within a not-exceeded square, shows the high variability in freshwater chemistry within each 10 km^2 critical load square and the necessity for also conducting streamwater assessments in areas adjacent to exceeded squares, as recommended by the Forests and Water Guidelines.

Critical load exceedance in YAR and NAR was probably due to a combination of low catchment buffering capacity and high pollutant deposition. Mean streamwater Ca concentrations were the lowest within the study catchments, probably due to the low buffering capacity of the dominant podzolic soils in these catchments. Mean non-marine base cation concentrations in YAR and NAR were also the lowest in the study catchments, since a large fraction of streamwater Mg and Na was of marine origin. NO_3 concentrations in YAR were relatively high, probably due to the presence and extent of the oakwood, while streamwater SO_4 concentrations were relatively high and similar for both YAR and NAR. Deposition of S has increased in parts of south-west England from 1987 to 2001, probably due to significant S contributions from shipping (Fowler et al., 2005). Data from the AWMN suggest that streamwater $x\mathrm{SO}_4$ concentrations in NAR have risen in the past decade, due to increases in S deposition but there are also indications of desorption of stored SO_4 in the soil in this catchment (Evans et al., 2000). A similar situation may exist also in YAR since the two catchments lie in the same region and have similar past and current pollutant deposition, topography and soil composition. In addition, long-term data from the ADMN station in Yarner Wood, which was located 200 m downstream of the YAR outlet point in this study, showed small but significant positive trends in NO_3 concentrations in precipitation between 1988 and 1997, which were attributed to an increase in the deposition of aerosol NO_3 and/or HNO_3 at Yarner Wood (Fowler and Smith, 2000). Thus, the high critical load exceedance in YAR can be largely attributed to increasing N deposition inputs, which were possibly enhanced by pollutant scavenging from oak canopies. Calculations using the FAB model suggest that in order to protect YAR and NAR from streamwater acidification initial reductions in present levels of N deposition are necessary, followed by further reductions in either S or N deposition.

Streamwater acid-sensitivity in YAR and NAR was further demonstrated by the negative streamwater ANC concentrations calculated for both catchments. There were no available macroinvertebrate data from YAR to assess the ecological water quality, but AWMN data for NAR showed that this catchment has the greatest macroinvertebrate diversity in the Network. During the first five years of the monitoring period NAR was rather impoverished in macroinvertebrate abundance but both species richness and abundance has increased since 1993, indicating improved streamwater conditions (Evans et al., 2000). Macroinvertebrate improvements in NAR were attributed to significant positive trends in streamwater pH and alkalinity concentrations, despite a significant increase in $x\mathrm{SO}_4$ concentrations the same time period. Although this catchment remains moderately acidic, streamwater conditions in NAR were more acidic in the past.

5.4.3 Non-exceeded study catchments

5.4.3.1 Catchments UL2 and ULCON

Calculated mean streamwater critical load values for UL2 and ULCON were not exceeded giving the same classification in the provisional critical load exceedance dataset as not acid-sensitive. However, mean concentrations of acid anions in UL2 and ULCON were amongst the highest in the study catchments. Streamwater $x\text{SO}_4$ concentrations were similar in both catchments, indicating possible SO_4 desorption from catchment soils due to declining S deposition (Oulehle et al., 2006). However, mean streamwater NO_3 concentration in UL2 was the second highest in the study catchments, probably due to enhanced N deposition on the alderwood canopy and NO_3 leaching caused by N fixation. Mean streamwater NO_3 concentration in ULCON was similar to or higher than some forested catchments in Glen Arnisdale and the Loch Katrine area, probably due to greater input of wet reduced N deposition (see Table 5.4). Nevertheless, both UL2 and ULCON had the highest mean streamwater alkalinity and Ca concentrations, and consequently the highest mean non-marine base cation concentrations in the study catchments. Therefore, non-exceedance in UL2 was probably mainly due to the high soil buffering capacity, despite the high streamwater NO_3 concentration caused by the presence of woodland, while non-exceedance in ULCON was probably due to a combination of both high soil buffering capacity and the absence of woodland cover which resulted in lower mean streamwater NO_3 concentration.

However, critical load calculated with the SSWC model was exceeded by 1995-97 modelled deposition in UL2 and ULCON when streamwater chemistry was used from the sample with ANC_{min}, which had the highest streamwater $x\text{SO}_4$ and NO_3 concentrations measured in this catchment. There was no clear reason for these high acid anion concentrations in UL2 and ULCON, but since the highest acid anion concentrations were also measured in UL1 at the same time, it is possible that S and N deposition was high prior to that particular sampling occasion. Therefore, it is possible that UL2 and ULCON can suffer from episodic acidification during high pollutant deposition events, despite the relatively high soil buffering capacity.

As expected, mean calculated streamwater ANC concentrations for both catchments were much higher than the ANC_{crit} values of 0 and 20 $\mu\text{eq l}^{-1}$ used in the critical load calculations, indicating waters well-buffered to acidification. However, macroinvertebrate results showed low species richness and abundance in both catchments and the Rutt model classified ULCON as acidic but UL2 as not-acidic. These results appear to contradict the measured streamwater chemistry and the results of critical load calculations, but could be attributed to the difficulty of representative sampling of macroinvertebrates in both catchments in summer low flow conditions.

5.4.3.2 Loch Katrine area catchments

Mean streamwater critical load values calculated with both the SSWC and FAB models for the Loch Katrine area catchments were not exceeded by either 1995-97 or 2002 FRAME modelled deposition and thus these catchments were not considered acid-sensitive compared to the original exceedance map grid squares. The Loch Katrine area catchments received high S and N loadings, predominantly as wet deposition, but streamwater concentrations of SO_4, xSO_4 and NO_3 were relatively low. Significant negative correlations were found in LK1, where flow monitoring data were available, between measured discharge and streamwater SO_4 (r_s= -0.58, P= 0.014) and xSO_4 (r_s= -0.54, P= 0.022) concentrations, indicating that the relatively low concentrations of these anions were probably due to dilution by high rainfall amounts. Streamwater NO_3 was not associated with discharge but rather seemed to follow the typical seasonal pattern of NO_3 concentrations in surface waters in the UK, with the highest concentrations occurring in winter/spring (Chapman and Edwards, 1999). Nevertheless, streamwater NO_3 concentrations were lower than expected from modelled N deposition inputs and soil N retention estimates in the FAB model based on default values. This indicates that N deposition could either have been overestimated in the Loch Katrine area catchments, or that, due to the presence of extensive waterlogged areas in the Loch Katrine catchments, the soils had a higher capacity for denitrification than predicted using default values. N uptake by vegetation in these catchments could also be more than expected.

Significant negative correlations were also found in LK1 between measured discharge and streamwater pH values (r_s= -0.80, P= 0.000), Ca (r_s= -0.71, P= 0.002) and calculated ANC (r_s= -0.68, P= 0.004) concentrations indicating that the catchment's buffering capacity declined during high flow events. However, mean streamwater non-marine base cation concentrations were almost three times higher than mean non-marine acid anion concentrations in the Loch Katrine area catchments, resulting in relatively high critical load values calculated with the SSWC model. Thus the incoming modelled acid deposition load did not exceed the streamwater critical load values. Non-acidic conditions in streamwater were also evident in the positive calculated mean ANC concentrations for the Loch Katrine area catchments which were above the ANC_{crit} values of 0 and 20 μeq l^{-1}. However, mean streamwater alkalinity was negative in LK2 and close to zero in LK3, and critical loads calculated with the SSWC model for both catchments were exceeded by 1995-97 deposition when an ANC_{crit} value of 20 μeq l^{-1} (see Table 5.9) was used and also when streamwater chemistry from the sample with the lowest ANC was used (see Table 5.10). Thus, it is possible that LK2 and LK3 could suffer from streamwater acidification during high flow events when pH and alkalinity are depressed. Nevertheless, the macroinvertebrate results for the Loch Katrine area catchments showed good ecological conditions in both species richness and abundance and the catchments were classified as non-acidic by the Rutt model. Therefore, the Loch Katrine area catchments should not be affected by streamwater acidification, except possibly LK2 and LK3 during high rainfall events, and streamwater conditions should be favourable for the survival and development of freshwater biota.

5.4.3.3 Glen Arnisdale catchments

Pollutant deposition in the remote Glen Arnisdale catchments was very low while concentrations of non-marine base cations were relatively high and consequently critical loads were not exceeded. As mentioned earlier, mean streamwater chemistry in the Glen Arnisdale catchments was calculated from only two samples, with one sample taken during a seasalt event which strongly influenced streamwater chemistry by increasing concentrations of non-marine Ca, probably due to cation-exchange, and also SO_4. However, most SO_4 in streamwater during the seasalt event was derived from marine inputs, and since the SSWC removes the marine component of major base cations and acid anions, calculated xSO_4 concentrations were actually very low. Streamwater NO_3 concentrations were unaffected by the seasalt event but were the lowest in the study catchments. The high critical load non exceedances in the Glen Arnisdale area catchments were expected to be reflected in streamwater ANC concentrations above the ANC_{crit} value of 0 µeq l^{-1} used in the SSWC model calculations. However, mean streamwater ANC was negative for three of the four catchments, indicating excess acid anion loads in streamwater. Thus, these catchments are probably acid-sensitive with episodic streamwater acidification caused by seasalt events rather than anthropogenic deposition.

The observed non exceedance of critical loads probably results from the SSWC model's inability to deal satisfactorily with streamwater chemistry influenced by high seasalt inputs, especially during storm events (UK National Focal Centre, 2004). During the seasalt event, SO_4 was retained in the soil complex and thus the use of the fixed ratio of SO_4 in seawater to calculate xSO_4 in streamwater resulted in negative values in GA3 and GACON. To overcome this, streamwater xSO_4 concentrations were calculated using the known ratio of SO_4:Na instead of SO_4:Cl in seawater. The SSWC model uses certain assumptions to quantify pre-industrial acid anion streamwater concentrations, which are used to calculate the pre-industrial non-marine base cation leaching and eventually the critical load values. However, due to the low streamwater xSO_4 and NO_3 concentrations in the Glen Arnisdale catchments, the calculated sum of non-marine acid anions was actually lower than the modelled pre-industrial value, implying that streamwater acidity was higher in pre-industrial times. This was clearly problematic and led to overestimations of critical load values and consequently underestimation of critical load exceedance by the SSWC model in the Glen Arnisdale catchments. Since the FAB model uses the same critical load value calculated with the SSWC model, there was also overestimation of the critical deposition load for S ($CL_{max}(S)$), but the effect was less pronounced for the critical deposition values for N ($CL_{min}(N)$ and $CL_{max}(N)$) and for total critical load exceedance due to the treatment of N processes in catchment soils in the FAB model.

Non-exceedance of critical loads in the three Glen Arnisdale catchments with negative streamwater ANC concentrations does not necessarily indicate that they are not acid-sensitive since seasalt induced episodic acidification could adversely impact freshwater biota in these catchments (Larssen and Holme, 2006). The macroinvertebrate analysis results showed moderate and high species abundance and diversity in GA2 and GACON, respectively, and both catchments were classified as non acidic by the Rutt model. However, GA3 was taxonomically poor and was classified by the Rutt model as acidic. This was expected for GA3 since mean streamwater alkalinity and calculated ANC concentrations were negative and pH values were below 5.0 at high flow, and below 5.5 at spring low flow, and were the lowest values measured in the Scottish catchments.

Critical load values calculated using streamwater chemistry from the sample before the seasalt event in the Glen Arnisdale catchments were lower than those calculated with mean streamwater chemistry due to the much lower non-marine base cation concentrations, and were exceeded by 1995-97 modelled S deposition and NO_3 leaching in GA2 and GA3. In the light of the above discussion, these critical load calculations can be regarded as more representative for the Glen Arnisdale catchments, especially for GA3, the most acid-sensitive catchment in Glen Arnisdale. However, it is difficult to determine how representative the sample before the seasalt event was of streamwater chemistry conditions, due to the small number of high flow samples collected from the Glen Arnisdale catchments. Assuming that seasalt events occur frequently (i.e. on an annual time scale) in the Glen Arnisdale catchments, streamwater chemistry can be influenced by marine inputs and Cl concentrations may remain higher than pre-event levels for long periods as suggested by Andersen and Seip (1999). Thus, more high flow streamwater sampling would have been necessary in the Glen Arnisdale catchments to investigate thoroughly the effects of marine inputs on streamwater chemistry and provide a more accurate assessment of acid-sensitivity in these catchments.

5.4.4 Trends in atmospheric pollution deposition

5.4.4.1 Acid-sensitivity for different pollution deposition estimates

Non-exceedance of critical load values was lower and critical load exceedance, calculated with both the SSWC and FAB models, was higher in the study catchments when 1995-97 rather than 2002 modelled deposition generated by FRAME was used, mainly because S deposition estimates for 2002 with FRAME were much lower than those for the 1995-97 dataset. The differences between the values calculated with the two deposition datasets can be mainly attributed to marked reductions particularly in S, but also in N emissions, and subsequent deposition in the UK, due to international agreements. Trends in S and N deposition and streamwater SO_4 and NO_3 concentrations are discussed further below using data from the UK AWMN sites and the UN/ECE International Cooperative Programme (ICP) Waters sites in central/north Europe and North America. The study catchments have a similar geographical location to the AWMN sites, and therefore trends in S and N deposition occurring in the AWMN sites are expected to be important for understanding the processes influencing current acid-sensitivity in the study catchments. Data from ICP Waters sites provide a wider insight into the transboundary pollution effects on streamwater chemistry in the main acid-sensitive areas in the Northern Hemisphere.

5.4.4.2 Trends in sulphur deposition

In the past two decades national and international regulations and agreements, such as the UN/ECE Convention on Long-Range Transboundary Air Pollution (LRTAP) protocols, have led to widespread declines in acidic deposition, especially for S, across large regions of North America and Europe. Long-term data from ICP Waters showed declines in SO_2 concentrations in air and precipitation of 63% and 40%, respectively, between 1985 and 1996 in north/central Europe (Stoddard et al., 1999). Similar but smaller decreases were observed in S concentrations in air and precipitation in the United States and Canada. In the UK, it is estimated that S emissions declined by 71% between 1987 and 2001 while deposition of non-marine S declined by 60% for the same period (Fowler et al., 2005). Emissions of S in 1987 were 1937 kTonne and declined to 563 in 2001, while total non-marine S deposition was 524 and 205 kTonne in 1987 and 2001, respectively (Fowler et al., 2005). There was a much larger reduction in dry S deposition (74%) than wet deposition (45%), with reductions in dry S deposition being greater than those in S emissions, probably due to a gradual increase in the deposition velocity for SO_2 through increased dry co-deposition with NH_3 as atmospheric concentrations of NH_3 have increased (Fowler et al., 2005). Therefore regions that have benefited most from the reductions in emissions have been those in which dry S deposition dominated total S inputs, primarily across the English Midlands, which were also closest to major pollution sources (NEGTAP, 2001). However, many areas in the UK, including most upland regions in the west, show reductions in S deposition of less than 60% from 1987 to 2001, and therefore a smaller improvement in deposition than expected from the 71% reduction in emissions (Fowler et al., 2005). Data from the AWMN sites in high rainfall areas in Devon, Cumbria and Scotland show that the magnitude of S reduction in deposition in these areas is small relative to reduction in S emissions in the UK as a whole or even Europe, partially due to significant S emissions from shipping sources to the west of the UK (Fowler et al., 2005). Nevertheless, declining trends of SO_4 concentrations in precipitation are significant for all AWMN sites (Fowler et al., 2005). This suggests that significant but less than expected reductions in S deposition should have occurred in the study catchments, especially for the high rainfall Glen Arnisdale and Loch Katrine area catchments.

Long term data from the AWMN sites indicate that as levels of S deposition have decreased, surface water concentrations of $x\text{SO}_4$ have fallen accordingly (Davies et al., 2005). However, the magnitude of downward trends in streamwater $x\text{SO}_4$ decreases in a north-westerly direction in the UK, with the smallest and non-significant trends occurring in the most remote sites in north-west Scotland. Due to the geographical location of the study catchments it is expected that downward trends in streamwater $x\text{SO}_4$ have been lower than in eastern areas of the UK, with perhaps no changes in streamwater $x\text{SO}_4$ concentrations in the remote Glen Arnisdale catchments.

5.4.4.3 Trends in nitrogen deposition

In contrast to the significant declines in S emissions and deposition in the past two decades, total N deposition has remained fairly constant in the UK, while small increases have been reported in coastal areas of western Britain. Reductions in NO_3 concentrations in precipitation have been significant only in eastern England, amounting to 20% from 1986 to 2001, which are comparable to N emission reductions in the UK and EU of 35 and 25%, respectively, for the same period (Fowler et al., 2005). Annual wet deposition in the UK of oxidised N has remained fairly constant at about 100 kTonne N, while dry deposition of NO_2 has declined from about 60 to 30 kTonne N (Fowler et al., 2005). Currently the contribution of HNO_3 to total N deposition is also significant (60 kTonne N), but deposition occurs mainly in the heavily polluted areas in eastern England, such as in the Midlands, and is considered to be negligible in western areas (NEGTAP, 2001) so contributions of HNO_3 to total N inputs are expected to be small in the study catchments. Dry deposition of reduced N has declined by about 10% from 1996 (when dry deposition monitoring began) to 2000 and wet deposition has declined by about 10% between 1986 and 2001, corresponding to a 10% reduction in NH_3 emissions in the UK for similar timescales. However, NH_3 deposition is highly spatially variable and is expected to be high in areas with agricultural activity (Metcalfe et al., 1999), such as in the Ullswater area and to a lesser extent in the area around YAR.

The small declines in N deposition have not been accompanied by declines in streamwater NO_3 concentrations at the AWMN sites (Davies et al., 2005), and also there have been no significant changes in NO_3 in the ICP Waters sites (Skjelkvåle et al., 2001). The absence of significant trends in NO_3 has been mainly attributed to temporal variability in streamwater concentrations caused by the degree of N saturation, which is site specific, and the influence of climatic factors, most notably the NAO index. Davies et al. (2005) suggested that NO_3 leaching was enhanced in the AWMN sites during cold (negative NAOI) winters when a greater duration and intensity of soil freezing enhanced biocidal effects, releasing more N by mineralisation, while low soil temperature may also slow down assimilation of N by soil biota. They also suggest that this relationship may be influenced by inter-annual variability in prevailing wind direction and hence supply of N pollutants. Streamwater NO_3 concentrations in the highly forested study catchments were clearly influenced more by the presence and extent of broadleaf woodland cover, while a number of factors discussed earlier could have influenced concentrations in the study catchments with lower (<30%) woodland covers.

5.5 Summary

Chapter 5 presented the results and the discussion of the critical loads calculations for the study catchments using the SSWC and FAB models. Critical loads were exceeded in catchments NAR, YAR and UL1 using both models and the different pollutant deposition datasets. Critical load exceedance in the higher forested catchments YAR and UL1 was mainly caused by the high streamwater NO_3 concentrations, which were probably due to N scavenging by woodland canopies and nitrification by alder in UL1, while exceedance in the almost unforested NAR was attributed to past high acidification and current high S deposition inputs. Non-exceedance of critical loads in the remaining study catchments was mainly attributed to marked reductions in the deposition of anthropogenic S in the UK at the end of the twentieth century, as the result of pollutant abatement policies, and due to high soil buffering capacity in UL2. However, calculated streamwater ANC values were negative in three of the Glen Arnisdale catchments, indicating that they could suffer from seasalt induced, episodic acidification, and the SSWC model had difficulty in dealing with high marine inputs from seasalt events in these catchments. Catchment acid-sensitivity determined by the Rutt model using macroinvertebrate data from the study catchments showed good agreement with the outcomes of the critical loads calculations, especially for the not-exceeded catchments. Catchment GA3 was classified as acidic by the Rutt model which further indicates that marine inputs could cause streamwater acidification and adversely influence streamwater ecology. Trends in pollutant deposition indicate that S deposition should continue to decline in the future in the UK, but smaller reductions are expected in the deposition of reduced and oxidised N and it is possible that NO_3 in streamwater will confound chemical recovery or continue to acidify the most acid-sensitive waters.

Results of a sensitivity analysis of the critical loads calculated for the study catchments showed that the use of a critical ANC value of 20 μeq l^{-1}, different runoff estimates and chemistry of the most and least acidic streamwater sampled resulted in small changes in the number of study catchments where critical loads were exceeded, especially for critical loads exceedance calculated using the SSWC model and 1995-97 modelled deposition. However, for the parameters examined, the analysis found that critical loads were exceeded in the same three catchments (NAR, YAR and UL1), suggesting that critical loads exceedance calculated with mean streamwater chemistry at high flow and the standard ANC value and runoff estimates was sufficient to identify the study catchments at most risk of streamwater acidification.

Chapter 6 Modelling dry deposition onto birch canopies

6.1 Introduction

Previous chapters have shown some evidence of the scavenging effect of broadleaved woodland on streamwater chemistry. Chapter 6 investigates the scavenging mechanism in more detail through a case study. Forests are aerodynamically rough surfaces and can induce more turbulent diffusion than other land categories, such as grass fields or open water, thus increasing the dry deposition rates of atmospheric pollutants. The aerodynamic resistances used by atmospheric pollutant models to calculate dry deposition estimates in the UK are determined from the roughness length, z_0, of the canopy, canopy height, h, and wind speed (Smith et al., 2000). These models use default z_0 and h values determined only for conifer forests. Broadleaves are considered less aerodynamically rough than conifers (Neal, 2002) and the dry deposition of atmospheric pollutants on broadleaf canopies is expected to be smaller than on conifers. Therefore, it is possible that atmospheric pollutant models may overestimate the magnitude of pollutant inputs via dry deposition to areas covered by broadleaf woodlands, resulting in overestimates of surface water acid-sensitivity when these values are used to calculate critical loads exceedance in catchments covered with broadleaf woodlands. In this chapter, dry deposition onto the birchwoods of the Loch Katrine area catchments was modelled using parameters specific to these deciduous woodlands.

6.2 Case study aims

The aim of this case study was to calculate more accurate estimates of dry pollutant deposition onto the birchwoods covering the Loch Katrine area catchments and to use these pollutant estimates and modelled wet deposition to assess acid-sensitivity in the catchments by calculating critical loads exceedance.

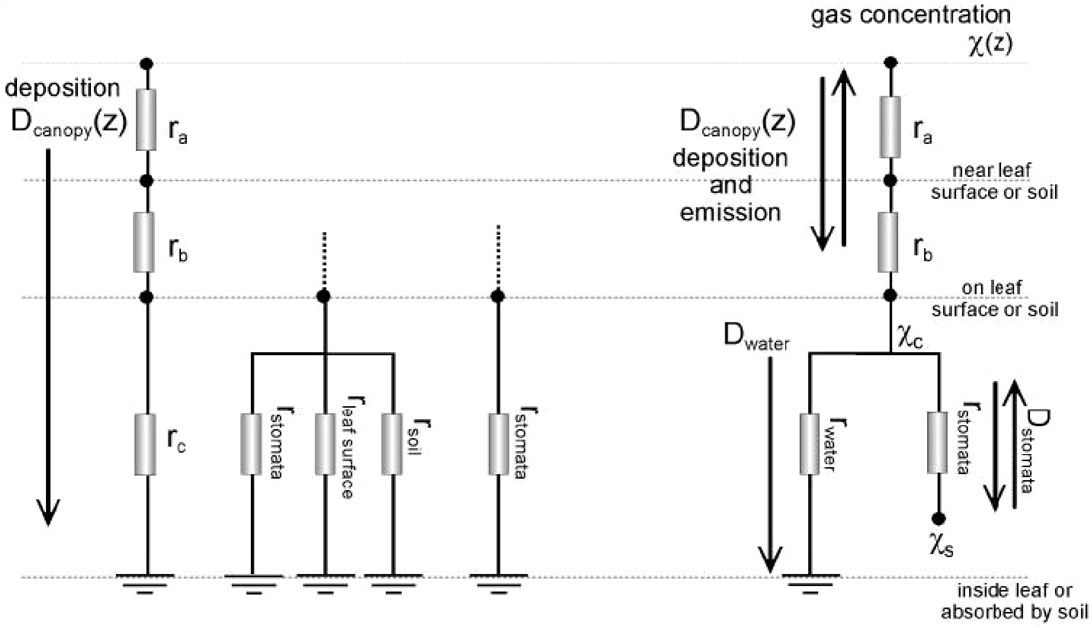
The birchwoods covering the Loch Katrine area catchments were selected for the case study because: a) upland birchwoods are the most widespread woodland type in the Scottish uplands (Forestry Commission, 2006); b) more high flow streamwater samples were available from these catchments for calculating critical loads; c) aerial imagery necessary for the case study was available for the Loch Katrine area; and d) the Loch Katrine area has been recently selected for the establishment of the largest broadleaf woodland in Scotland comprising 2000 ha of native broadleaf woodland (Forestry Commission, 2005) and the birchwoods covering the study catchments will be used as the core woodlands for new tree planting and natural regeneration (Russell Lamont, Forest Enterprise, Aberfoyle, personal communication). Thus, assessment of the effect of new broadleaf woodland planting on streamwater chemistry and the risk of freshwater acidification is of great importance in the Loch Katrine area.

6.3 Modelling pollutant dry deposition

The case study focused on modelling the dry deposition of ammonia (NH_3) and sulphur dioxide (SO_2) because these two species are the major contributors to dry deposition of reduced N (NH_x) and oxidised S (SO_y) and their deposition is largely influenced by the aerodynamic roughness of the vegetation layer (Metcalfe et al., 1999). In contrast, deposition of oxidised N species (NO_y), such as nitrogen dioxide (NO_2), is largely controlled by stomatal processes and is less influenced by the vegetation roughness, while the deposition of the highly reactive nitric acid (HNO_3) is rapid to all surfaces, regardless of surface roughness (Metcalfe et al., 1999).

6.3.1 Dry deposition mechanisms

The process of dry deposition is described by three phases which are quantified in models as resistances to the flow of pollutant gases (Figure 6.1). These resistances are (Smith et al., 2000): a) r_a is the aerodynamic resistance and describes the transport of gas molecules from the well-mixed planetary boundary layer to the immediate vicinity of absorbing surfaces (e.g. leaves and stems) via turbulent diffusion, whose rate is controlled by the wind velocity and aerodynamic roughness of the surface; b) r_b describes the transport of molecules through the viscous, quasi-laminar boundary layer of air close to absorbing surfaces via molecular diffusion, the rate of which depends on the physical properties of the gas; and c) r_c describes the removal of gases from the atmosphere whose rate is controlled by the physical and chemical properties of the gas and the absorbing surface.



a) SO_2 b) NO_2 c) NH_3

Figure 6.1 The various resistance components used in models describing the dry deposition of a) SO_2, b) NO_2 and c) NH_3 (Smith et al., 2000)

The deposition of a pollutant gas to the ground, D_g(z) from a fixed height z, in the atmosphere is the product of the gas concentration, χ(z), and the deposition velocity, V_g(z), assuming that gas concentration at the absorbing surface is zero and the deposition velocity is independent of the gas concentration.:

$$D_g(z) = \chi(z) V_g(z) \qquad \text{(Equation 6.1)}$$

The deposition velocity is the combined total resistance to deposition, comprising the aerodynamic resistance (r_a(z)), the laminar boundary layer resistance (r_b), and the bulk canopy resistance (r_c):

$$V_g(z) = \frac{1}{r_a(z) + r_b + r_c} \qquad \text{(Equation 6.2)}$$

For vegetation, the bulk canopy resistance is the net effect of resistances to uptake and potential sinks. For SO_2 these resistances are the stomata, the leaf surface and the soil (Figure 6.1). For NO_2 the bulk canopy resistance equals the stomatal resistance, while for HNO_3 the bulk canopy resistance is assumed to be zero. With NH_3, the gas is emitted through stomata as well as deposited and this bi-directional exchange leads to a more complex model (Figure 6.1) described by Sutton et al. (1995).

6.3.2 Modelling dry deposition with FRAME

Dry deposition of reduced and oxidised N and oxidised S was modelled using the FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) model (Singles et al., 1998). FRAME is a Lagrangian atmospheric transport model which was initially developed to focus on the transport and deposition of reduced N but, due to recent developments in the treatment of S and oxidised N, it can now be used to assess mean annual deposition of reduced and oxidised N and non-marine S at 5 km x 5 km grid squares over the United Kingdom. FRAME simulates an air column moving along straight-line trajectories. Emissions of NH_3 are estimated for each 5 km grid square using national data of farm animal numbers (cattle, poultry, pigs and sheep) as well as fertiliser application, crops and non-agricultural emissions (including traffic and contributions from human sources and wild animals). Emissions of SO_2 and NO_x are taken from the National Atmospheric Emissions Inventory for the United Kingdom. For the case study, dry and wet deposition was modelled for 2002 to be consistent with FRAME modelled deposition data used in Chapter 5. FRAME runs were done by Dr. Massimo Vieno of the School of GeoSciences, University of Edinburgh.

6.3.2.1 Dry deposition estimates for ammonia and oxidised N

Deposition of NH_3 in FRAME is calculated for each grid square using a canopy resistance model (Singles et al., 1998). The deposition velocity is generated from the sums of the aerodynamic resistance, the laminar boundary layer resistance and the bulk canopy resistance (Figure 6.1). The calculation of these resistances, and consequently of NH_3 deposition, is land cover specific and is defined using a UK land cover database (Fournier et al., 2002). Land cover is divided into five different categories (arable, forest, moorland, grassland, and urban) (RGAR, 1997), and total dry deposition is the average deposition for the different land categories present in each 5 km x 5 km grid square.

Dry NH_3 deposition was estimated for the 5 km x 5 km square containing the Loch Katrine area catchments using z_0 and h values derived from specific data to the birchwoods in the Loch Katrine area. Heights of 50 trees were measured with a Haglöf Laser Vertex Hypsometer in five 30 m radius randomly selected circular plots located within the Loch Katrine area catchments, and these heights were used to calculate the mean height h of the birchwoods. Values of z_0 and the zero-plane displacement height, d, were determined using the simplified equations of Raupach (1994) (method R94) described in Section 6.3.3. The z_0 and d values and wind speed were used to calculate the atmospheric resistances r_a and r_b for NH_3, which were then inserted in FRAME to calculate the NH_3 deposition estimates. FRAME calculates dry deposition by first assuming that each land category covers the whole area of the grid square and then calculates mean dry deposition based on the proportional cover of each land category within the grid square. Therefore, it was necessary to calculate the z_0 value assuming that the whole grid square was covered by birchwood. Dry deposition of oxidised N was also calculated in FRAME using the standard formulation.

6.3.2.2 Dry deposition for sulphur dioxide

In FRAME, the dry deposition of SO_2 is calculated using deposition velocity derived from the "big leaf" model (Smith et al. 2000) which calculates atmospheric resistances (r_a and r_b) from z_0 and wind speed. The model normally assumes that z_0 and d are functions of the canopy height, h, ($z_0 = 0.1h$ and $d = 0.7h$) (Smith et al., 2000). However, in the case study a specific SO_2 deposition velocity for the birchwoods was determined by inserting the site-specific z_0 and d values in a spreadsheet which included the model formulation for the specific 5 km x 5 km grid square and parameters, provided by Dr. Ron Smith, Centre of Ecology and

Hydrology (CEH), Edinburgh. SO_2 dry deposition was then estimated by incorporating the calculated deposition velocity in FRAME.

6.3.2.3 Canopy resistance controls

Due to the large surface area of forests, r_c dominates the calculation of the deposition velocity for NH_3 and consequently NH_3 deposition, especially during light hours when the stomata are open. FRAME assigns a specific value of r_c to each land cover category to describe land-dependent dry deposition, with the forest r_c value of 20 s m^{-1} referring to conifer forests (Fournier et al., 2002). In the context of the case study this value was replaced by an r_c value of 80 s m^{-1}, which is the daytime r_c value for deciduous trees used in the UK Met Office rainfall and evaporation calculation system (MORECS, Hough and Jones, 1997). MORECS has been developed for British climatic conditions and thus the r_c value for deciduous trees was considered appropriate to use within FRAME for the calculation of dry deposition onto the birch canopy.

6.3.2.4 Land-use classification

Woodland patches and individual trees were digitised in the Loch Katrine area catchments (Figure 6.2) in ArcMap, from aerial imagery (1: 10 000 scale) covering the area of the 5 km x 5 km grid square, provided by Forest Enterprise in Aberfoyle. This procedure provided a more accurate estimate of the total birch woodland area, required to calculate the canopy roughness, than the 1: 25 000 NIWT-IFT woodland polygons used previously to estimate percentage woodland cover.

Birchwoods covered 139 ha or 5.58% of the 2500 ha of the grid square and most of the woodland was located within the Loch Katrine area catchments (Figure 6.2). Other woodland (conifer and mixed) covered only 0.37 ha (0.02%), while most of the grid square was covered by grassland and bare rock (2291 ha or 91.6% cover), with the remaining 69 ha (2.76%) being open water (Loch Katrine). Thus, the birchwoods comprised the dominant woodland cover within the 5 km x 5 km grid square which enabled the study to focus exclusively on dry deposition to these woodlands.

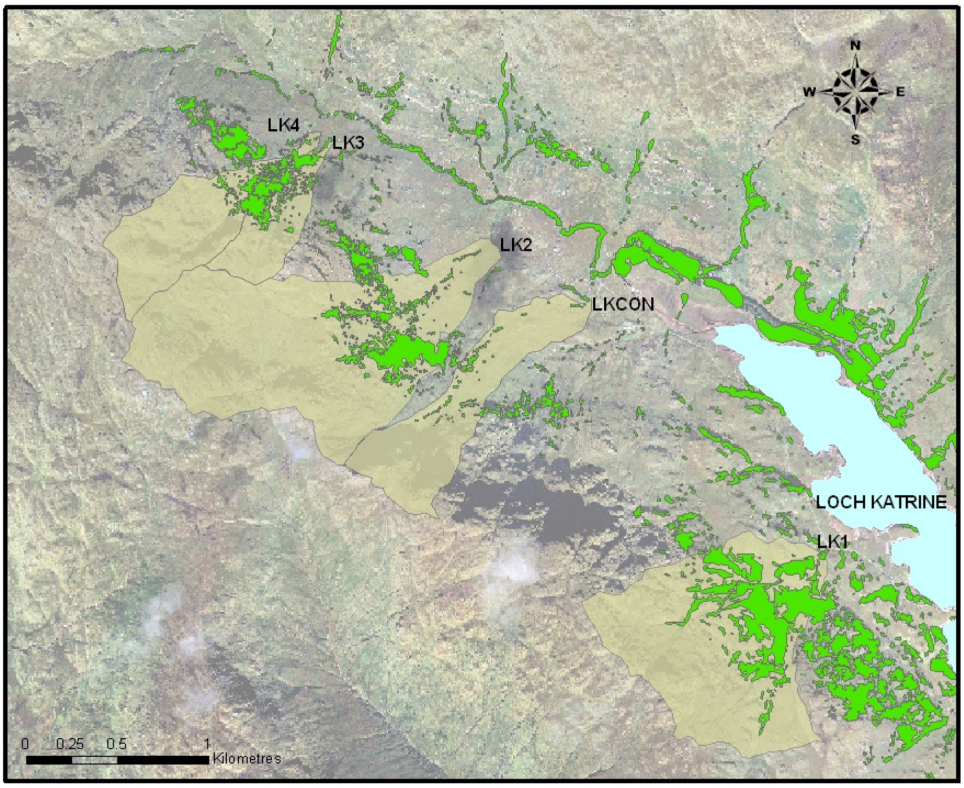


Figure 6.2 Digitised birch woodland cover (shown in green shading) derived from aerial imagery within the 5 km x 5 km grid square containing the Loch Katrine area catchments marked

6.3.3 Calculation of birchwood roughness length

The R94 method (Raupach, 1994) is currently used to calculate canopy roughness by models in the UK, such as FORESTGALES, which predict critical wind speeds for damage to different tree species (Gardiner et al., 2000). In the R94 method the z_0 and d values are calculated by first determining from the mean wind direction per unit ground area the frontal area index, λ, which represents the frontal area of the roughness elements, in this case the birch trees:

$$\lambda = \frac{1}{S}\sum_{i=1}^{n}\left(b_i \cdot \frac{S_t}{2}\right)\cdot c \qquad \text{(Equation 6.3)}$$

where S is the grid square area (25 km^2) and b_i is the vertical projection of the canopy of an individual tree within area S. Since a 100% woodland cover is assumed, the sum of individual tree covers also equates to 25 km^2. c is an empirical coefficient (≈0.5) determined by the rate at which an element wake spreads in the cross-stream directions. The dimensionless coefficient S_t adjusts the frontal area to account for streamlining (Gardiner et al., 2000) and reflects the combined effects of the skin friction as the air moves over the surface of the drag element and the pressure differential between wind ward and leeward sides of the element (Vollsinger et al., 2005). Consequently, S_t depends on the shape and surface roughness of the drag element and, because tree crowns are both porous and flexible, the frontal area presented by the crown and the shape and orientation of its component drag elements varies with wind speed. S_t is determined from power function fits to experimental data:

$$S_t = c_d \cdot {u_h}^{-n} \qquad \text{(Equation 6.4)}$$

where $10 < u_h < 25$ is the mean canopy top wind speed (m s^{-1}) and c_d and n are coefficients that are species dependent. Values of S_t in Equation 6.3 are divided by two to account for the triangular shape of the canopy.

S_t values for the birchwoods were calculated from relationships from wind tunnel studies reported by: a) Mayhead (1973) for Scots pine (Pinus sylvestris) and used in FORESTGALES as an approximation for broadleaf tree species in the UK and b) more recent data from Vollsinger et al. (2005) for paper birch (Betula papyrifera).

Mean monthly wind speed for the specific grid square, measured from the UK wind network at an effective height of 10 m above ground, ranged from 5 to 6 m s^{-1} (Massimo Vieno, personal communication), so a canopy top wind speed of 10 m s^{-1}

was used in Equation 6.4. Using specific data for Scots pine and paper birch $S_{t(Mayhead)} = 0.66$ and $S_{t(Vollsinger)} = 0.37$, respectively.

In the R94 method the frontal area index λ is replaced with the canopy area index Λ, the total (single-sided) area of all canopy elements per unit ground area. For isotropically oriented elements $\Lambda = 2\lambda$.

Roughness length z_0 is related to the bulk drag coefficient, γ, of a rough surface at mean tree height h and to the zero-plane displacement height, d:

$$\frac{z_0}{h} = \left(1 - \frac{d}{h}\right) \cdot e^{(-\kappa\gamma + \Psi_h)} \qquad \text{(Equation 6.5)}$$

which when solved for z_0 becomes:

$$z_0 = (h - d) \cdot e^{(-\kappa\gamma + \Psi_h)} \qquad \text{(Equation 6.6)}$$

The mean measured tree height for the birchwoods was $h = 10.2$ m. κ (≈ 0.4) is the von Karman constant and Ψ_h is the roughness sub-layer influence function, describing the departure of the velocity profile just above the roughness generated by the canopy from the inertial-sub-layer logarithmic law, and has a value of 0.19.

$\gamma = U_h / u_*$, where u_*, is the friction velocity and U_h the mean wind velocity at height h. γ can also be determined using the canopy area index Λ as shown in Equation 6.7:

$$if\ \Lambda > 0.6 \Rightarrow \gamma = \frac{1}{\sqrt{C_S + C_R \cdot 0.3}} \quad else\ \gamma = \frac{1}{\sqrt{C_S + C_R \frac{\Lambda}{2}}} \qquad \text{(Equation 6.7)}$$

Values of $\Lambda > 0.6$ are interpreted as the onset of “over-sheltering”, when adding further roughness elements to the surface does not affect the bulk drag because additional elements simply shelter each other. $C_S = 0.003$ is the drag coefficient of the substrate surface at height h in the absence of roughness elements (trees) and C_R= 0.3 is the drag coefficient of an isolated tree mounted on the surface.

The zero-plane displacement height, d, relates to the vertical distance through which the shear layer spreads before it reaches the next element downwind, and is given by:

$$d = \left(1 - \frac{1 - e^{-\sqrt{c_{d1}\Lambda}}}{\sqrt{c_{d1}\Lambda}}\right) \cdot h \qquad \text{(Equation 6.8)}$$

where c_{d1} = 7.5 and is a free parameter.

Using these formulations, roughness length z_0 was calculated in the Loch Katrine area study catchments.

6.4 Case study results

The results of the roughness length calculations and dry pollutant deposition estimates for Scots pine and paper birch are presented in this section. Critical loads exceedance for the Loch Katrine area catchments were calculated using the modelled deposition estimates for present birch woodland cover and for the proposed woodland planting within the grid square.

6.4.1 Present birch woodland cover

The results of the R94 calculations for the birchwoods, using S_t values for Scots pine (Mayhead, 1973) and paper birch (Vollsinger et al., 2005) and assuming a 100% cover, are given in Table 6.1.

Table 6.1 Values of the canopy area index (Λ), zero-plane displacement height (*d*) and roughness length (z_0) calculated with the R94 method for Scots pine (Mayhead, 1973) and paper birch (Vollsinger et al., 2005)

Tree species	Λ	*d* (m)	z_0 (m)
Scots pine	0.33	5.06	1.09
Paper birch	0.18	4.18	0.73

The calculated z_0 for Scots pine was very close to the default z_0 value of 1 m used for conifers in FRAME. As expected, the z_0 value for paper birch was lower than for Scots pine and other conifer trees.

Table 6.2 shows dry deposition estimates of NH_3, oxidised N and SO_2 calculated using FRAME. Dry deposition was estimated for the present birch woodland cover (5.58%) by multiplying pollutant estimates for 100% cover by 0.0558.

Table 6.2 Modelled 2002 dry deposition in FRAME for NH_3, oxidised N (NO_y) and SO_2 (keq H ha^{-1} yr^{-1}) for Scots pine (Mayhead, 1973) and paper birch (Vollsinger et al., 2005) for present woodland cover within the Loch Katrine area grid square

Dry deposition	Scots pine	Paper birch
NH_3	3.1×10^{-3}	3.0×10^{-3}
NO_y	2.5×10^{-3}	2.5×10^{-3}
SO_2	3.0×10^{-3}	3.0×10^{-3}

Modelled dry deposition estimates for NH_3 and SO_2 were almost identical for both Scots pine and paper birch despite the difference in the z_0 values. This is mainly due to the higher contribution of the fixed parameter canopy resistance r_c to total resistance compared to the atmospheric resistances (r_a and r_b), which depend on the z_0 values. For example, mean monthly values of r_c for SO_2 ranged from 128 to 137 s m^{-1}, while the combined atmospheric resistance (r_a and r_b) for paper birch was 11 s m^{-1}.

The dry deposition estimates for the birchwoods present cover were used along with wet deposition estimates for reduced and oxidised N (NH_x and NO_y) and non-marine oxidised S (SO_y) to calculate critical loads (CL) exceedance in the Loch Katrine area catchments. Since the dry deposition estimates were almost the same for the two tree species investigated, only the ones for paper birch, considered more representative of the Loch Katrine area birchwoods, were used in the CL exceedance calculations. Total modelled deposition for present cover is given in Table 6.3, which also gives the total modelled deposition for the proposed woodland area within the grid square covering the Loch Katrine area described in Section 6.4.2. The wet deposition was grid average estimates calculated in FRAME using the standard parameters and formulation. Total deposition of reduced and oxidised N and oxidised S was dominated by wet deposition in the Loch Katrine area catchments. Dry modelled deposition of NH_3, NO_y and SO_2 onto the birch canopies for present day cover accounted for only 1, 0.8 and 0.7% of total deposition, respectively. Therefore, the effect of the birchwoods on the total pollutant deposition inputs was very small in the Loch Katrine area catchments, where rainfall totals are high.

Table 6.3 Total (dry and wet) modelled deposition from FRAME for 2002 for reduced and oxidised N and oxidised non-marine S (keq H ha^{-1} yr^{-1}) for the present day birchwoods and proposed woodland area within the grid square covering the Loch Katrine area

Deposition	Present birchwood cover	Proposed woodland cover
NH_x	0.277	0.297
NO_y	0.338	0.354
SO_y	0.455	0.475
Total deposition	1.070	1.126

CL values were calculated using mean high flow streamwater chemistry and the SSWC model using an acid neutralising capacity (ANC) of 0 and 20 μeq l^{-1}, and were the same as the ones presented in Chapter 5. The FAB model was used to calculate CL exceedance because it can identify the effect of different S and N deposition scenarios. The CL and re-calculated CL exceedance values for the Loch Katrine area catchments based on modelled deposition for present birchwood cover and proposed woodland area are shown in Table 6.4. CLs were not exceeded in any of the Loch Katrine area catchments for both ANC values of 0 and 20 μeq l^{-1} for present birchwood cover, and CL exceedance values were similar to those calculated with grid average dry NH_3, NO_y and SO_2 deposition estimates in FRAME 2002 not taking account of the broadleaf woodland cover. Therefore, all catchments were not considered acid-sensitive with present birch woodland cover and 2002 modelled pollutant deposition.

Table 6.4 CL exceedance values for the Loch Katrine area catchments calculated using the FAB model and modelled deposition for present birchwood cover and proposed woodland area within the grid square covering the Loch Katrine area for ANC = 0 and 20 μeq l^{-1} ($Ex(CL_0)$ and $Ex(CL_{20})$) (keq H ha^{-1} yr^{-1})

Catchments	Present birchwood cover		Proposed woodland area	
	$Ex(CL_0)$	$Ex(CL_{20})$	$Ex(CL_0)$	$Ex(CL_{20})$
LK1	-1.45	-0.97	-1.40	-0.91
LK2	-0.70	-0.22	-0.65	-0.16
LK3	-0.87	-0.39	-0.82	-0.33
LK4	-1.65	-1.17	-1.59	-1.11
LKCON	-1.81	-1.33	-1.76	-1.27

6.4.2 Effect of proposed planting in the Loch Katrine area

The Loch Katrine area has been selected for a major native broadleaf woodland planting and restoration project aiming to expand the area of the existing native woodland over the next 10-20 years by an additional 2000 ha. Of this area it is estimated that 800 ha will be planted, while the remaining 1200 ha will be achieved through natural regeneration (Russell Lamont, personal communication). The final location of this expansion will depend on site suitability, browsing and landscape constraints. The digitised birchwoods from the aerial imagery show that currently birchwoods within the grid square extend from 205 to 450 m elevation. Using a

DEM (1: 10 000, PROFILE®, EDINA Digimap) in ArcMap, the potential area for woodland planting and restoration within the grid square, based on the observed altitude range of woodland, was estimated to be 1051 ha. This is an estimate of the maximum available area since a substantial proportion will be unsuitable for new woodland planting due to high slope gradients present or other site characteristics preventing the establishment of new woodland. The estimated woodland expansion would increase woodland cover within the grid square from the present 5.58 to 42.0%.

Modelled dry deposition, derived from 2002 FRAME runs for the proposed woodland area, assuming 42.0% coverage, was 0.023, 0.019 and 0.023 keq H ha^{-1} yr^{-1} for NH_3, NO_y and SO_2, respectively. Total modelled deposition estimates for reduced and oxidised N and oxidised S for the proposed woodland area are given in Table 6.3. The contribution of dry to total deposition for the proposed woodland area increased to 8, 5 and 5% for NH_3, NO_y and SO_2, respectively. Overall, total (dry and wet) deposition for the proposed woodland increased by 0.056 keq H ha^{-1} yr^{-1} compared to the total deposition estimate for current woodland cover within the grid square (Table 6.3).

CL exceedance for the Loch Katrine area catchments calculated with the FAB model and using the modelled deposition data for the proposed woodland area is shown in Table 6.4. As expected, non-exceedance of CLs decreased due to the increases in dry deposition inputs from the greater woodland cover. However, these deposition increases were small and did not result in the exceedance of CL values for both an ANC of 0 and 20 μeq l^{-1}, and the catchments were not considered acid-sensitive. CL non-exceedance was mainly attributed to the dominance of wet deposition inputs to pollutant deposition in the Loch Katrine area, and also to the buffering capacity of the catchments resulting in calculated CLs which exceeded total acidic inputs at present (2002) deposition rates.

6.5 Case study conclusions

The results showed that, despite the substantial difference between calculated roughness length values for Scots pine and paper birch, there was only a very small difference in modelled dry pollutant deposition estimates, due to the dominance of canopy resistance compared to the sum of atmospheric resistances. Overall, the effect of modelled dry pollutant deposition onto birch canopies on critical loads exceedance in the Loch Katrine area catchments was small at present levels of woodland cover and pollutant deposition. Modelled dry deposition onto the birch canopies contributed only a very small proportion of total deposition to the Loch Katrine area catchments, due to the high rainfall received by this area and also the distance from major pollutant sources. However, the influence of pollutant scavenging by broadleaf canopies on streamwater acidification could be more important in highly forested areas where the contribution of wet deposition is smaller and pollutant loadings are higher than in the Loch Katrine area.

CL values in the Loch Katrine area catchments were not exceeded when modelled dry pollutant deposition for the proposed woodland area was used, indicating that the catchments were protected from pollutant scavenging from new woodland planting at present (2002) deposition levels. Again, the proportion of dry to total deposition onto the proposed woodland canopies was much smaller than the contribution from wet deposition. Non-marine S deposition is expected to continue to decline in the UK, while smaller reductions in reduced and oxidised N are also expected (Fowler et al., 2005). Therefore it is safe to assume that the Loch Katrine area catchments should not be at risk of streamwater acidification from new woodland planting, even if all the potential land within the grid square is covered with broadleaf, mainly birch, woodland. However, the effect of new planting on streamwater chemistry in the Loch Katrine area catchments is not restricted to the inputs of acidifying pollutants but will also depend on the balance between these inputs, base cation uptake and the effect on the N cycle (Reynolds, 2004). The Loch Katrine area catchments had relatively low mean streamwater high flow alkalinity values and Ca concentrations (see Table 4.2), indicating a relatively low capacity for buffering of streamwater. Hence increased uptake of base cations from the soil by new woodland could further reduce the relatively low capacity for buffering acidic pollutant (especially non-marine S) inputs. On the other hand, the establishment of new woodland will increase the uptake and retention of N from atmospheric N inputs and the soil pool and consequently there should not be any increases in NO_3 leaching to streamwater in the Loch Katrine area catchments. Also, current best management practices used for new broadleaf woodland planting should protect streamwater chemistry from planting operations (Farmer and Nisbet, 2004).

There are certain weaknesses in the modelling methodology used to calculate dry pollutant deposition onto woodland canopies. The FRAME model takes account of the "seeder-feeder" effect at higher altitude which can influence wet deposition rates (Singles et al., 1998) and the "big leaf" model formulation also takes into account the altitudinal variation in wind speed for the calculation of deposition velocities for SO_2 (Smith et al., 2000). However, the effect on dry pollutant deposition of spatial variability of woodland cover within each grid square, and in particular the elevation at which woodland is located, is not taken account of by the FRAME model formulation for reduced and oxidised N, since dry deposition of N species onto woodlands is simply calculated using the woodland percentage cover of each grid square. This is problematic since dry pollutant deposition for the same percentage woodland cover is expected to be higher at higher elevations, usually above 300 m in the UK, where wind speeds are higher and cloud contribution may be locally important (NEGTAP, 2001). In addition, the spatial resolution of the FRAME model output cannot account for the high spatial variability of NH_3 deposition, which is expected to vary substantially within each 5 km x 5 km grid square (Metcalfe et al., 1999). This is expected to be of less importance in the Loch Katrine area catchments because there are no major NH_3 sources within the grid square. However, dry NH_3 deposition inputs, especially close to forest edges, could be more important for forested catchments located close to agricultural activities (NEGTAP, 2001). Deposition of reduced N currently dominates total N deposition and the relative contribution of reduced N deposition is expected to increase in the future (Fowler et al., 2005). Therefore the issue of the spatial variability of dry NH_3 deposition needs to be addressed in the context of the modelling approaches used in the UK to quantify pollutant deposition and thereby predict the effects of deposition on surface water acidification.

Chapter 7 Assessment of the Forests and Water Guidelines

The Forests and Water Guidelines are used in the UK to identify freshwaters at risk of acidification where broadleaf woodland is expanding. Assessing the effectiveness of the Guidelines' methodology is important for protecting areas sensitive to acidification from the woodland scavenging effect. Chapter 7 presents the results and the discussion of an assessment of the effectiveness of the Forests and Water Guidelines methodology for identifying catchments at risk of acidification. The assessment focused on the more intensively studied Loch Katrine area catchments and parameters assessed were the inter-sample streamwater chemistry variability and the uncertainty in critical loads and exceedance calculations for the Loch Katrine area catchments, presented in Sections 7.1 and 7.2, respectively. The chapter concludes by discussing the main parameters influencing the effectiveness of the Forests and Water Guidelines methodology for protecting catchments at risk of acidification, incorporating also the outcomes of the sensitivity analysis of the critical loads and exceedance estimates for the study catchments presented in Chapter 5.

7.1 Streamwater chemistry variability and sampling assessment

Mean streamwater chemistry for the study catchments, used to calculate streamwater critical loads as recommended by the Forests and Water Guidelines, was determined from different numbers of samples. For this reason the more intensively sampled Loch Katrine area catchments were used to assess how representative a few samples are of streamwater chemistry as only limited samples could be collected from most of the study catchments. Parts of the Forests and Water Guidelines methodology were tested by investigating the effect of the number and timing of high flow samples on streamwater chemistry variability and whether high flow conditions represent the most acidic conditions in streamwater.

7.1.1 The effect of number of samples on assessing mean streamwater chemistry

The effect of the number and timing of samples collected on the errors associated in calculating the mean streamwater chemistry variability was investigated using high flow samples collected from the five Loch Katrine area catchments. Standard errors of mean streamwater concentrations of base cations (Ca, Mg, Na and K), acid anions (Cl, SO_4 and NO_3) and soluble Al were calculated for the increasing number of high flow samples collected from each catchment over time. It was expected that calculated standard errors would decrease as the number of samples increased. The results were similar for all catchments and only those for LK1 are presented in Figure 7.1.

Standard errors for Ca, Na, K, Cl and SO_4 displayed a similar pattern, decreasing after the first two high flow samples and then remaining relatively constant. Standard errors for Mg, NO_3 and Al did not follow the expected pattern, with the standard error for nine/ten samples almost equal to the standard error for two/three samples, but error values were quite low (Figures 7.1b, f and h).

The results for LK1 indicate that for most chemical parameters three to four high flow streamwater samples were adequate to reduce variability and increase the probability of sampling representative streamwater concentrations for the calculation of representative CL values. Thus, high flow samples collected from the study catchments (three to ten samples) should be representative of streamwater chemistry, apart from the Glen Arnisdale catchments where only two high flow samples were collected.

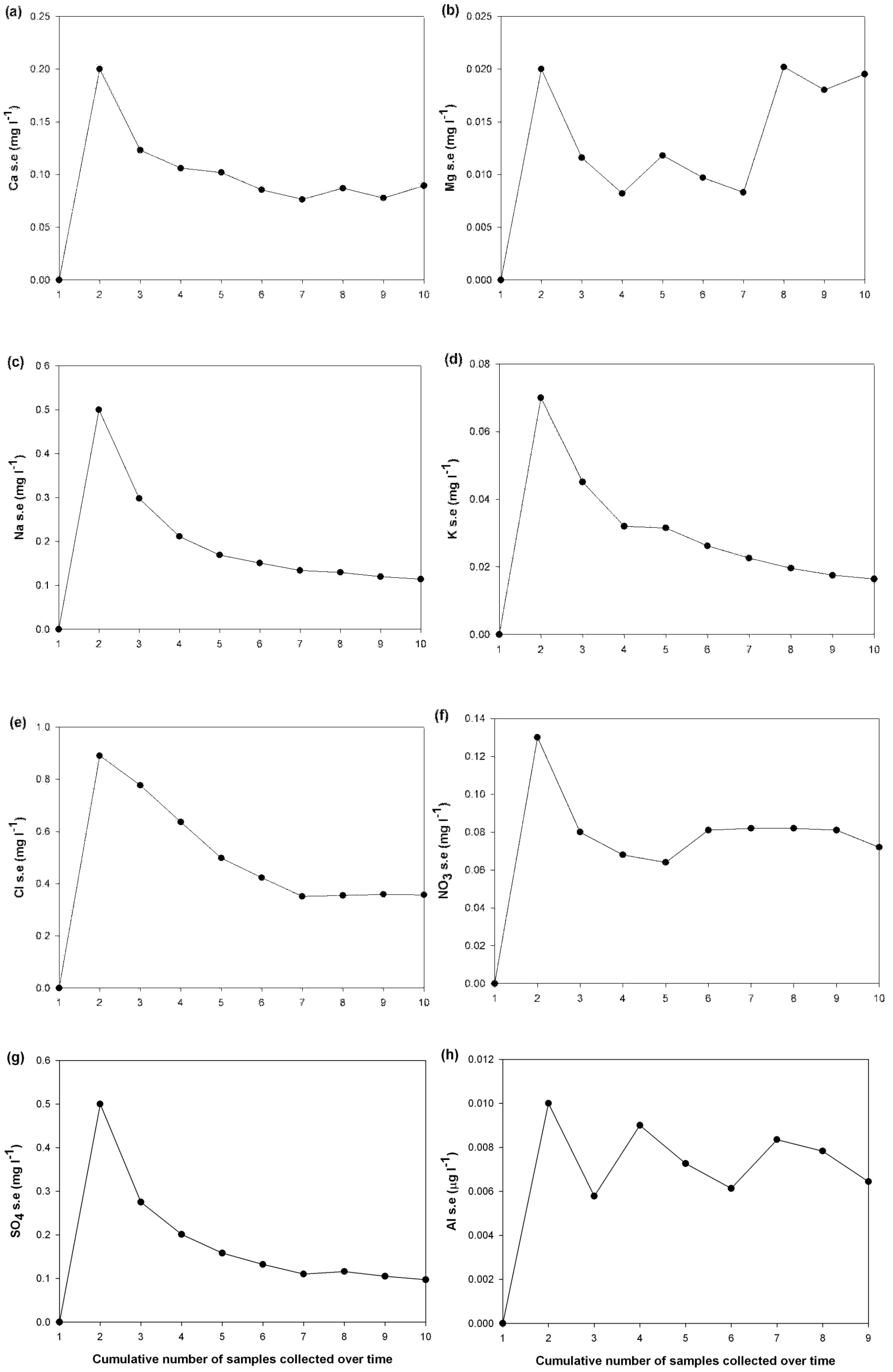


Figure 7.1 Standard errors (s.e) of mean streamwater (a) Ca, (b) Mg, (c) Na, (d) K, (e) Cl, (f) NO$_3$, (g) SO$_4$ and (h) soluble Al concentrations for increasing number of high flow samples from LK1 over time

7.1.2 The effect of flow conditions on assessment of streamwater chemistry

Low flow samples were also collected from the Loch Katrine area catchments and mean low flow streamwater chemistry was determined to assess whether streamwater at low flows in winter/spring is less acidic than in high flow conditions, as recommended by the Forests and Water Guidelines (Forestry Commission, 2003), and also the effect of flow conditions on mean streamwater chemistry. Four low flow samples were collected in March and April 2005 and in late March 2006. Low flow was defined as <0.1 $m^3 s^{-1}$ for LK1 and from rule readings for the remaining catchments. Mean low flow streamwater pH, Gran alkalinity and calculated ANC values and concentrations of base cations (Ca, Mg, Na and K), acid anions (Cl, SO_4 and NO_3) and soluble Al were calculated and compared to mean high flow streamwater chemistry using Mann-Whitney *U* tests.

There were no significant differences between high and low flow concentrations of Gran alkalinity, Mg, Na, K, Cl and soluble Al in the Loch Katrine area catchments. As expected, low flow pH was significantly higher than the high flow values in LK2 (P= 0.006) and LK3 (P= 0.040) and streamwater Ca at low flow was significantly higher than at high flow in LK1 (P= 0.042), LK2 (P= 0.048) and LK3 (P= 0.033). Low flow SO_4 was significantly higher than high flow values in LK1 (P= 0.020) and LK4 (P= 0.006). Low flow NO_3 concentrations were significantly higher than at high flow in LK1 (P= 0.040), LK2 (P= 0.020), LK3 (P= 0.024) and LK4 (P= 0.006). Streamwater SO_4 and NO_3 concentrations were expected to be higher at high flow due to higher S and N deposition during rainfall events. However, the observed higher mean streamwater SO_4 and NO_3 concentrations at low flow were caused by the influence of snowmelt on streamwater chemistry on one sampling occasion in which the highest SO_4 and NO_3 concentrations were measured at low flow. Streamwater ANC was significantly higher at low compared to high flow only in LK1 (P= 0.040).

Despite the lack of significant differences between low and high flow concentrations of some chemical parameters tested, the results generally suggest that samples collected for conducting streamwater chemistry assessments in the context of the

Forests and Water Guidelines should be collected at high flow to represent the most acidic conditions.

7.2 Assessment of uncertainty in critical loads and exceedance

The high flow streamwater chemistry data from the Loch Katrine area catchments and the discharge data from LK1 were used to assess the effectiveness of the Forests and Water Guidelines methodology for identifying catchments at risk of streamwater acidification. The assessment aimed to investigate: a) whether the three high flow samples recommended by the Guidelines were sufficient for calculating CL and CL exceedance values representative of catchment streamwater chemistry, b) the importance of high flow levels for identifying catchment acid-sensitivity with the critical loads methodology used by the Guidelines and c) the effect of measured runoff and estimated runoff from rainfall, using default evapotranspiration values, on the acid-sensitivity status of the Loch Katrine area catchments.

7.2.1 The effect of number of samples on critical loads and exceedance

CL and CL exceedance values were calculated for five runs for each Loch Katrine area catchment using mean streamwater chemistry of three high flow samples selected at random. CL exceedance was calculated using both SSWC and FAB models and modelled pollutant deposition for 1995-97 and N leaching and 2002 (FRAME) and the results are shown in Figure 7.2.

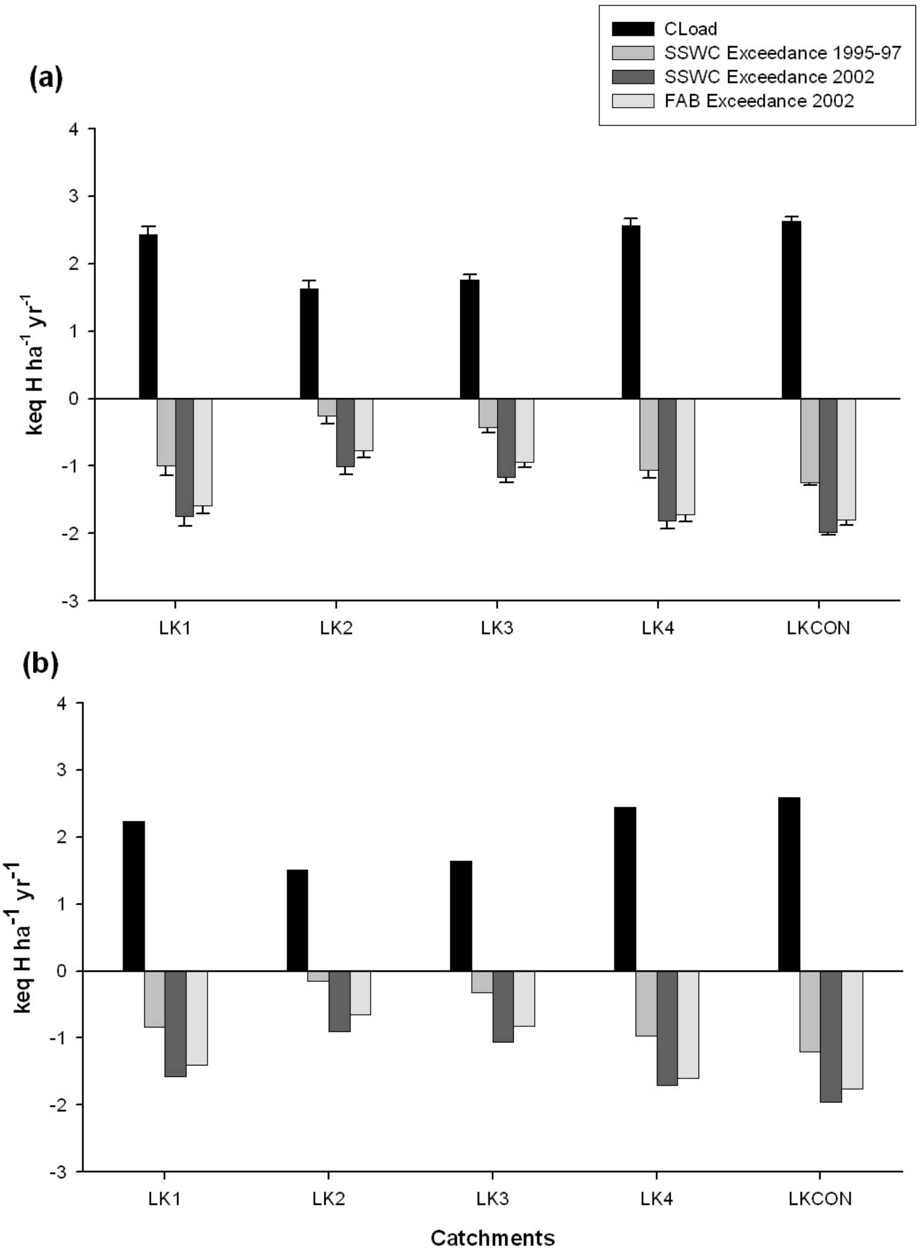


Figure 7.2 CL and CL exceedance values for the Loch Katrine area catchments calculated (a) for five runs using mean streamwater chemistry of three randomly selected high flow samples and (b) mean high flow streamwater chemistry with the SSWC model using 1995-97 and 2002 FRAME non-marine S deposition and N leaching and the FAB model using 2002 FRAME modelled deposition. Negative values indicate non-exceedance. Error bars represent standard error

Mean catchment CL and non-exceedance values calculated for the five runs using randomly selected high flow streamwater samples were slightly higher by 0.04 to 0.19 keq H ha^{-1} yr^{-1} (5-8% increase) than the corresponding values calculated using mean streamwater chemistry for each Loch Katrine area catchment for both the SSWC and FAB models and for 1995-97 and 2002 FRAME deposition data. The results suggest that CL and CL exceedance values calculated from three high flow streamwater samples were very close to values calculated with mean streamwater chemistry for a larger number of samples (nine to ten samples for the Loch Katrine area catchments). Therefore, although a smaller number of high flow samples was collected in the other study catchments, assessments of the CLs and CL exceedances should still be accurate. Furthermore, the results support the methodology used by the Forests and Water Guidelines for risk assessments in acid-sensitive catchments, since three high flow samples should be sufficient for identifying catchments at risk of streamwater acidification.

7.2.2 Critical loads and exceedance using highest flow samples

CL and CL exceedance values were calculated using the mean streamwater chemistry of the three highest flow samples from the five Loch Katrine area catchments to assess whether it is important to sample the highest possible flows to assess the catchment acid sensitivity. The samples occurring at the highest flows were identified from the flow data at LK1 and water depth measured at LK2, LK3, LK4 and LKCON.

CL and non-exceedance values calculated using mean streamwater chemistry from all high flow samples were higher for LK1, LK4 and LKCON by 0.13, 0.08 and 0.31 keq H ha^{-1} yr^{-1} respectively and lower for LK2 and LK3 by 0.02 and 0.05 keq H ha^{-1} yr^{-1} respectively, than the corresponding values calculated using mean chemistry from the three highest flow samples. CL values were not exceeded in any of the five catchments with either the SSWC or FAB model and with the 1995-97 and 2002 FRAME deposition datasets.

The observed reductions in CL and subsequent increases in CL exceedance values in LK2 and LK3, which have the lowest streamwater base cation and ANC concentrations of the Loch Katrine area catchments, were very small and overall did not affect their status as non acid-sensitive catchments. Thus, it is not crucial to obtain the highest flow streamwater samples in order to be confident in the assessment of the acid-sensitivity in the study catchments and it should be sufficient to sample streamwater under general high flow conditions, determined for each catchment from flow monitoring and/or observation. It is also recommended that the Forests and Water Guidelines methodology should not encourage the collection of streamwater samples from catchments at extreme flows, which can pose safety hazards to the sampler, since catchment acid-sensitivity should be identifiable from less extreme high flow samples.

7.2.3 Critical load and exceedance in LK1 using measured runoff

CL and CL exceedance values were calculated for LK1 using the measured catchment runoff for March 2005 to May 2006 (data for only 10 months in this period) and compared with those calculated using runoff estimated from 2005 rainfall. The measured runoff for LK1 was 3833 mm and was higher by 1417 mm than the runoff estimated as 85% of the 2005 rainfall in the Loch Katrine area. Runoff was estimated from rainfall data from the meteorological station at Stronachlachar at an altitude of 117 m, while the altitudes of LK1 ranged from 128 to 683 m. Thus the high measured runoff is probably due to altitudinal differences and the orographic enhancement of rain in LK1, along with contributions from snowmelt, fog and cloud water that are not included in the rainfall value. Also, during the summer months and dry periods the discharge at the outlet of LK1 was still in the range of 0.01 to 0.03 $m^3 s^{-1}$, probably due to contributions from deeper soils, and consistent dry weather flow contributed significantly to annual measured runoff.

Mean high flow streamwater chemistry from LK1 was used in the CL calculations and CL exceedance was calculated with both the SSWC and FAB models using the 1995-97 and 2002 FRAME deposition data. The CL value calculated with the measured runoff was higher than the value calculated with runoff from the rainfall estimate (Figure 7.3), corresponding to an increase in CL value of 37%. Accordingly, the non-exceedance of CL values was higher in all cases when measured rather than estimated runoff was used because increases in base cation weathering estimates outweighed the increases in NO_3 leaching values (see 5.2.1). Interestingly, N leaching calculated with the SSWC model with measured runoff was 0.31 keq ha^{-1} yr^{-1} and very close to the N output value calculated for LK1 within the FAB model (0.38 keq ha^{-1} yr^{-1}), suggesting that the use of measured runoff data does yield realistic estimates.

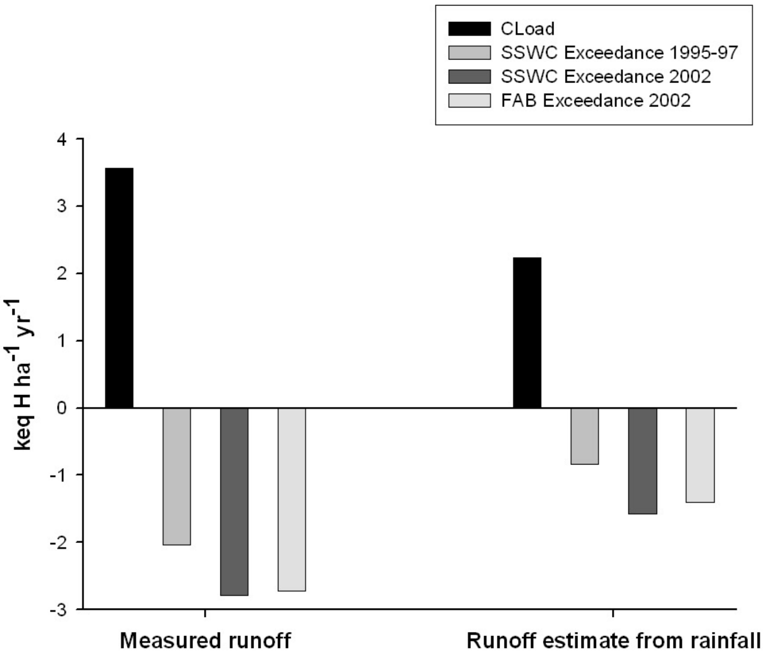


Figure 7.3 CL and CL exceedance values calculated with mean streamwater chemistry using measured and estimated runoff for LK1 with the SSWC model using 1995-97 and 2002 FRAME modelled non-marine S deposition and N leaching and the FAB model using 2002 FRAME modelled deposition. Negative values indicate non-exceedance

The results suggest that by using runoff estimated from rainfall, CL values can be underestimated in catchments with high altitudes and high rainfall, such as the Loch Katrine area catchments, leading to an overestimation of acid-sensitivity. Therefore, the Forests and Water Guidelines methodology is considered conservative.

7.3 Assessment of the Forests and Water Guidelines methodology

The Forests and Water Guidelines methodology for the protection of freshwaters from acidification where broadleaf woodland is expanding was assessed from the research results. The following aspects are discussed below: the suitability of the

30% broadleaf woodland cover threshold and the critical loads approach used by the Guidelines, streamwater sample frequency and timing and the effects of flow levels on critical loads calculations.

7.3.1 Broadleaf woodland cover threshold

The finding that critical loads were not exceeded in all catchments with broadleaf woodland covers below 30%, apart from NAR (see Chapter 5), seems to indicate that the 30% woodland cover threshold is a sensible one for use within the Forests and Water Guidelines. This conclusion is further supported by the exceedance of critical loads in the highly forested catchments UL1 and YAR, with percentage woodland cover of 49.9 and 53.4%, respectively. Non exceedance of critical loads in UL2, which was the most forested study catchment with woodland cover of 78.7%, was probably due to the high soil buffering capacity of the catchment resulting from past application of lime to adjacent land, according to anecdotal reports. Acid-sensitivity in the NAR catchment with only 2.0% woodland cover was attributed to a combination of high S deposition and the low soil buffering capacity of the predominantly podzolic catchment soils. It was not possible to directly test the effect of the 30% woodland cover threshold value on streamwater chemistry indicators of acidification from the study results because the number of study catchments with woodland covers above 30% was smaller than required for statistical analysis (i.e. Chi-square tests).

The results indicated that streamwater chemistry and critical loads exceedance were also influenced by local conditions, mainly soil buffering capacity and deposition inputs. Thus it is possible that catchments with woodland covers above 30% but relatively high soil buffering capacity could buffer acidic inputs while, conversely, catchments with low woodland cover, such as NAR, but with past acidification and low soil buffering capacity could be acid-sensitive under current deposition inputs despite the absence of any woodland effect.

The Forests and Water Guidelines use the 30% woodland cover threshold for all types of broadleaf trees planted in the UK. The results suggested that there were no apparent effects of the different tree species present in the study catchments, oak, birch and alder, on streamwater chemistry, apart from the clear influence of alder on streamwater NO_3 concentrations. The potential for dry pollutant deposition on woodland canopies depends on the structure of different woodland types and in the study catchments pollutant scavenging was probably lower by the open birchwoods than by the denser oak and alder woods. However, there was no significant association between mean streamwater SO_4 and xSO_4 concentrations and percentage broadleaf woodland cover. Base cation uptake is expected to be similar by most broadleaf species and soil conditions under broadleaf trees are generally less acidic than under conifers (Hagen-Thorn et al., 2004). Transpiration rates are also expected to be similar for most broadleaf tree species, especially during winter when no leaves are present (Oltchev et al., 2006). Therefore, the most marked effect of different tree species on streamwater chemistry was the particularly high NO_3 streamwater concentrations in the UL1 and UL2 catchments, which were covered with alder, although the effect could have been exaggerated by the high woodland cover in these catchments.

Woodland effects on NO_3 leaching, for example due to N fixation by alder, are quite important due to the changing deposition climate in the UK, with N, especially reduced N, exceeding S deposition inputs (NEGTAP, 2001). The response to increasing atmospheric N deposition inputs depends on the N status of each site, but the presence of alder was associated with NO_3 leaching and could lead to soil acidification in the long term by depletion of base cations through the mobile effect, and consequently streamwater acidification. However, it is highly unlikely that alder will comprise the sole and principal tree cover because future woodlands in the UK will comprise mixtures of different tree species, both conifer and broadleaf, of different ages, due to the shift of forest management towards Continuous Cover Forestry (CCF) (Reynolds, 2004). Pollutant deposition is expected to be more spatially variable in CCF woodlands than in even-aged plantation forests due to the presence of more woodland gaps and different tree heights. Therefore, the influence of individual broadleaf tree species on streamwater chemistry will be masked by the forest effect related to the combined canopy and physiological properties of different tree species. In this case, the 30% broadleaf woodland cover is considered acceptable, and there should be no need to identify effects of individual tree species on streamwater chemistry as long as large-scale monocultures are not established.

7.3.2 Effects of number of streamwater samples and timing of collection

The number of streamwater samples and timing of collection are key components of the Forests and Water Guidelines methodology for the assessment of streamwater risk to acidification. The Guidelines require the collection of one or more, usually up to three, samples from the main watercourse receiving drainage from the area proposed for new woodland at high flow, when streamwater conditions are considered more acidic (Forestry Commission, 2003). The study results support the Guidelines' recommendations for the number and timing of collection of samples. Mean streamwater chemistry determined from three samples was considered to be representative of high flow conditions in the Loch Katrine area catchments because variability in the mean streamwater concentrations of most solutes decreased substantially when three samples or more were used to calculate mean streamwater chemistry. This was further supported by the small variability in calculated critical load values for the Loch Katrine area catchments when runs of three randomly selected high flow samples were used, and the close agreement of these critical load values with those calculated using mean high flow streamwater chemistry from a larger number of samples. In addition, results from the Loch Katrine catchments verified that streamwater chemistry was more acidic at high flow because mean streamwater pH values, alkalinity, base cation (apart from K) and calculated ANC concentrations were lower while streamwater soluble Al concentrations were higher for samples collected at high rather than low flow during winter, spring and autumn periods.

In order to overcome the lack of available flow data for the majority of catchments in the UK, in the Forests and Water Guidelines catchment runoff is estimated from the most recent annual rainfall data by assuming that 15% of incoming rainfall is lost to evapotranspiration. However, evapotranspiration rates are considered to be much higher than 15% in high rainfall, upland catchments in the UK, especially those with high conifer woodland cover (Heal et al., 2004). The sensitivity analysis of the critical load calculation results (see Section 5.2.1) showed overestimation and underestimation of critical load values in the study catchments when high and low runoff estimates were used, respectively. Furthermore, measured streamflow in LK1 was much higher than expected from rainfall data, probably due to orographic enhancement of rainfall and contributions from subsurface flow, and critical loads calculation with the measured flow led to the highest critical load value for LK1.

These results suggest that the calculation of critical loads and assessment of catchment risk to acidification using the Forests and Water Guidelines is sensitive to the flow estimate used. Since it would be difficult to obtain annual flow data for each catchment where a streamwater chemistry assessment is conducted, the use of different evapotranspiration rates depending on levels of rainfall inputs, mean catchment altitude and maybe longitude might provide a more realistic runoff estimate. An alternative is the measurement of flow during streamwater sampling and the calculation of critical loads using flow weighted-chemistry, which could provide more accurate predictions of critical loads. Accurate critical loads prediction may be more important in forested catchments with high rainfall and altitude which receive higher wet pollutant deposition. However, the dangers of sampling at high flow levels to staff need to be assessed before including flow measurements in the Guidelines methodology. In addition, the Guidelines could adopt more recent formulations of the SSWC model (UBA, 2004) which use the F-term as a flux instead as a concentration and are expected to improve the prediction of freshwater critical load values.

7.3.3 Suitability of the critical loads methodology

The Forests and Water Guidelines methodology uses the critical loads approach for identifying freshwaters at risk of acidification. The critical loads methodology was successful in determining acid-sensitivity in most of the study catchments, apart from the Glen Arnisdale catchments. The problem in the Glen Arnisdale catchments was the effect of high seasalt inputs on streamwater chemistry which led to pre-industrial acid anion concentrations calculated by the SSWC model being higher than current streamwater acid anion concentrations. This led to an overestimation of critical load values and consequently underestimation of critical loads exceedance for both the critical load models and the deposition datasets used. The critical loads approach also failed to identify the risk of episodic acidification from seasalt events in the Glen Arnisdale catchments, but the streamwater chemistry data showed no indications of acidification through increases in acidity and increased Al leaching, apart from in GA3 which was the least buffered catchment in Glen Arnisdale. Therefore, it is possible that the critical loads approach used in the Forests and Water Guidelines methodology may not be suitable for coastal catchments, especially for sites in north-west Scotland, which are susceptible to high seasalt inputs. Although proximity to the coast seems to be a more important factor than percentage broadleaf woodland cover in influencing streamwater chemistry in catchments similar to those in Glen Arnisdale, higher woodland covers in catchments at intermediate distance from the coast could enhance the impact of seasalt events due to increased Cl scavenging and increase the frequency and intensity of seasalt acidification episodes.

7.3.4 Uncertainty in the identification of catchments at risk of acidification due to scaling factors

The Forests and Water Guidelines use the provisional critical load exceedance map for 1995-97 at a 10 km^2 scale. For the construction of this dataset, water samples were collected in each 10 km x 10 km grid square from the most sensitive freshwater as ascertained from available geological and soil data, with lakes preferred to rivers. However, it was recognised that due to the indicative nature of the 10 km^2 scale critical loads exceedance dataset, catchment-based assessments of risk to acidification from a scavenging effect were necessary within both exceeded and adjacent critical loads squares. The spatial variability of acid-sensitivity within each 10 km^2 square was demonstrated by the high acid-sensitivity of catchment UL1, which was lying in a not-exceeded adjacent square. However, geological and soil data from BGS (1995) and NSRI (1984), respectively, showed that the area of this adjacent square was covered predominantly by acidic parent materials and soil types. There is a possibility that scaling factors, caused by the different resolution of geological and soil datasets used, could have led to the characterisation of the critical loads square where the Ullswater area catchments were lying as a not-exceeded square because it is located next to the large area of Carboniferous limestone which begins just east to Penrith and covers a large area of central and eastern north England (Matthews, 1977). Furthermore, it should be noted that the critical load calculated from sampling of the most sensitive freshwater in the grid square may not be representative of the influence of all soil types in the grid square, since not all soil types may be present in the catchment area of the water body samples. Thus, freshwaters are only protected from acidification if all soils in a catchment have sufficient buffering capacity and are protected from acidic inputs (Cresser, 2000). Therefore, the results of the critical loads assessment for UL1 indicate the necessity for conducting streamwater assessments in catchments lying adjacent to exceeded critical loads squares.

Results of the chemical analysis of water samples from predominantly lakes in each 10 km^2 square have been used to calculate the critical loads exceedance dataset used by the Forests and Water Guidelines. However, ANC in lakes is buffered to some extent compared to upland rivers in which ANC and critical load values can vary considerably over time, falling sharply in heavy storms or snowmelt events (Smart et al., 1998). It has been suggested that the critical loads concept is not suitable for rivers, since streamwater critical load values may be considered as sample specific and do not adequately represent streamwater conditions at longer time scales. However, Cresser (2000) points out that there is no real alternative to the critical loads methodology at the moment for risk assessment of acidification in rivers.

However, any underestimation of the risk to acidification for rivers and streams inherent in the Forests and Water Guidelines is partially compensated for by the use of the 1995-97 deposition dataset. Furthermore, the SSWC model is overprotective of water quality with its assumption that all incoming atmospheric acidic deposition can reach surface waters, although the degree to which this will occur depends on the distribution of parent materials and soils in catchment areas and plant N, S and base cation biogeochemical cycling (Cresser et al., 2000). Nevertheless, Curtis et al. (1995) found that in SSWC model applications to the UK freshwaters mapping dataset, the most sensitive site in a 10 km^2 grid square was correctly identified in only one third of cases. The implication of this uncertainty is that in around two thirds of mapped grid squares where critical loads are exceeded there may be water bodies with an even greater critical loads exceedance than the mapped site. However, this uncertainty did not affect the results for the study catchments because the actual extent of critical loads exceedance was found to be less than indicated in the critical loads exceedance dataset, apart from catchments UL1 and YAR where critical loads exceedance was higher than suggested and in NAR where critical loads exceedance fell in the same critical load exceedance class as the dataset.

7.3.5 Uncertainty in pollutant deposition estimates

The Forests and Water Guidelines methodology use the 1995-97 modelled S deposition and N leaching to streamwater to quantify critical loads exceedance and construct the critical loads exceedance map (Forestry Commission, 2003). Since S deposition is currently declining and expected to decline further by 2010 (Fowler et al., 2005), the use of this map to identify areas at risk of acidification allows for a margin of safety. However, there are several potential sources of uncertainty associated with the deposition data used, including interpolation (kriging) error, uncertainties in dry deposition velocity and precipitation amount and uncertainties associated with seeder-feeder enhancement of wet S deposition at scales smaller than the 5 km x 5 km grid employed (Curtis et al., 2000). Nevertheless, the present resolution of the deposition dataset is generally considered satisfactory for S and oxidised N, but more uncertainty could exist for reduced N deposition (NEGTAP, 2001).

A further uncertainty is that modelled deposition used for calculating critical loads exceedance in the study catchments is deposition onto the area of a chosen grid square and, in particular for dry deposition, a grid average of deposition estimates over several land cover classes (Henriksen and Posch, 2001). Wet deposition is assumed to be uniform over the grid square but, due to the spatial variability in deposition within the 5 km x 5 km grid squares and the small sizes of the study catchment areas, variations may be expected in total pollutant deposition to catchments lying even within the same grid square which could lead to different responses in streamwater chemistry. Therefore, these uncertainties in pollutant deposition estimates need to be considered in the interpretation of the critical loads exceedance results.

7.3.6 Effects of changes in the pollution climate on the Guidelines' methodology

The Forests and Water Guidelines methodology for protecting freshwaters from acidification has been developed primarily for assessing acidification risks posed by S deposition and the SSWC model is considered to accurately determine critical loads of acidity caused by S deposition inputs (Wilander, 2001). However, the pollution climate has changed substantially in the UK in the past decade, with significant declines in S deposition, while N deposition, especially for reduced N, is expected to dominate acidic deposition in the future (Fowler et al., 2005). The SSWC model has been modified to take account of N deposition by estimating N leaching from measured NO_3 in water. However the FAB model seems to provide a more appropriate modelling framework because it explicitly models N processes in catchment soils and also takes account of N removal by forest harvesting, where applicable (Curtis et al., 2000). Nevertheless, the FAB model is much more data demanding than the SSWC model because, apart from water chemistry, it also requires forest and soil chemistry data. Therefore, while the adoption of the FAB model by the Forests and Water Guidelines should be advantageous in providing more accurate critical load predictions, its application would depend on the availability of mainly soil chemistry data for a large area of the UK.

The advantages of the FAB model are now widely recognised and it is currently used to produce the UK critical loads mapping dataset (UK National Focal Centre, 2004). In this study streamwater critical loads exceedance was identified in the same catchments by both the SSWC and FAB models. However the extent of calculated critical loads exceedance differed between the two models due to the different treatment of N deposition and to uncertainties in the application of FAB related to the quantification of N processes in catchment soils. Mean catchment N retention is calculated using default values of denitrification and N immobilisation for each soil type present in the study catchments (Hall et al., 1998). However, the default denitrification and N immobilisation terms used for UK soil types are literature-based estimates and there is a need for more measurements of denitrification and N immobilisation rates in the field and the laboratory, especially for moorland soils (Curtis et al., 2000).

In the study catchments there were discrepancies between N leaching derived from NO_3 concentrations in streamwater and modelled N leaching using the FAB model. Modelled N leaching to streamwater with the FAB model was higher than the estimated streamwater NO_3 fluxes in the study catchments, apart from in UL1 and UL2 where the presence of alderwood enhanced nitrification and NO_3 leaching (see Figure 5.4). Overestimation of N removal in the Glen Arnisdale catchments, combined with the low N deposition, led to negative predicted N leaching using the FAB model. The presence of woodland can further affect N soil processes because NO_3 leaching in forested ecosystems normally increases with forest age (Emmett et al., 1993). Therefore, a better quantification of the rates of denitrification and N immobilisation in UK soils is necessary to reduce uncertainties in the predictions of critical deposition loads for N and total exceedance of acidity using the FAB model.

7.3.7 Evaluation of the long-term impacts of acidification

According to the critical loads concept, a state of critical loads exceedance does not necessarily mean that the affected water body has already been acidified or even significantly affected as yet by excess acid anion deposition, but the critical chemical threshold for the protection of the site, defined by ANC, will be crossed at some unspecified point in the future (Curtis et al., 2000). Therefore, critical loads exceedance calculated by both SSWC and FAB models in UL1, YAR and NAR indicates potential damage, assuming that pollutant deposition levels remain the same as deposition in 1995-97 used by the Forests and Water Guidelines methodology or 2002 deposition generated with FRAME.

Only dynamic models such as MAGIC can be used to predict the timing of acidification to a given chemical state (Jenkins et al., 1998). Provided that emission reductions agreed under the Gothenburg Protocol for 2010 are achieved, MAGIC predictions for 12 AWMN sites indicated that recovery of water ANC will occur in these sites by 2020 (Jenkins and Cullen, 2001). For the same time scales, the results of a modelling approach with the integration of MAGIC to predict future changes in streamwater Gran alkalinity in the River Dee sub-catchments under conditions of declining S and constant N deposition indicated that low-intensity Scots pine planting is unlikely to contribute significantly to streamwater acidification in acid-sensitive sub-catchments (Wade et al., 2001). The structure of most broadleaf woodland types is similar to Scots pine woodland and new broadleaf woodland planting is expected to resemble present Scots pine afforestation. Therefore, low-intensity new broadleaf woodland planting could also be expected not to cause further streamwater acidification in acid-sensitive catchments in the future.

However, predictions of acid-sensitivity depend on the critical chemical criterion chosen to represent the actual risk to acidification. A critical ANC value of either 0 or 20 μeq l^{-1} has been used in UK critical loads applications depending on the desired level of protection of brown trout populations from acidification. Streams may require an ANC_{crit} value above 0 μeq l^{-1} to provide the same level of protection for lakes, due to the greater impacts of acid episodes in streams (UK National Focal Centre, 2004). An adoption of an ANC value of 20 instead of 0 μeq l^{-1} by the Forests and Water Guidelines methodology would have meant that critical loads were exceeded in two more study catchments, LK2 and LK3, using the 1995-97 deposition data.

However, the selected level of protection to target organisms depends on the level of knowledge of the impacts of acidification on these organisms. The critical ANC values used for UK freshwaters are based on data for brown trout from dose-response functions between water chemistry and fish populations in Norwegian lakes but there have not been many similar surveys for UK freshwaters (UK National Focal Centre, 2004). In addition, organisms of great importance, such as salmon and macrophyte communities in naturally acidic upland lakes, are considered more acid-sensitive than brown trout and their populations may be reduced even in waters with ANC above 0 μeq l^{-1}. According to the critical loads concept, severe declines in the performance or abundance of target biological receptors are expected to begin precisely at the exceedance threshold, but there is no real evidence of this happening in most acid-sensitive freshwaters (Cresser, 2000). Thus, the link between water critical load exceedance and its impact on acid-sensitive organisms needs to be more firmly established to further validate the efficacy of the critical loads concept. This is particularly important for the Forests and Water Guidelines methodology, since a better understanding of acidification effects on freshwater biota would enable a more accurate prediction of potential effects of new broadleaf woodland planting on target biota in acid-sensitive areas and variable critical ANC values could be used depending on the target species and the desired level of protection. Knowledge of land-use change effects on water ecological quality are also necessary for implementing the EU Water Framework Directive (WFD) and could contribute to the target of the EU WFD to achieve good ecological status in UK freshwaters by 2015.

7.4 Summary

Chapter 7 presented an assessment of the effectiveness of the Forests and Water Guidelines for identifying catchments at risk of acidification, based on analysis of the more intensively sampled Loch Katrine area catchments. The results indicated that streamwater chemistry from three samples collected at high flow should ensure that calculated critical loads are representative of streamwater conditions in the study catchments, but comparison of critical loads calculated using measured and estimated runoff showed that the risk of acidification may be overestimated in high altitude and rainfall catchments. An evaluation of the critical loads results presented in this chapter and Chapter 5 suggested that the Forests and Water Guidelines should be able to identify catchments most at risk of acidification where broadleaf woodland is expanding and that the 30% broadleaf woodland cover is a sensible threshold for use within the context of the Guidelines. Uncertainties in the Guidelines' methodology were related to the suitability of the SSWC model for calculating critical loads, the spatial resolution of the provisional critical loads exceedance map used to identify acid-sensitive freshwaters and of the modelled deposition estimates used to calculate critical exceedance, and to the debate on the most suitable critical ANC value for ensuring good water ecological quality in acid-sensitive catchments. It was recommended that the use of the FAB model for the calculation of critical loads, provided necessary soil chemistry data are available for most acid-sensitive areas in the UK, would improve the effectiveness of risk assessments using the Guidelines' methodology. In addition, it was highlighted that more research is necessary to quantify N processes in catchment soils and also identify the critical ANC values at which visible impacts occur on a range of acid-sensitive freshwater organisms in the UK.

Chapter 8 Conclusions

The aim of this research was to investigate the effects of broadleaf woodland cover on streamwater chemistry indicators of acidification and assess the risk of acidification in acid-sensitive catchments in the UK. Within this chapter the research findings are summarised and the implications for the effect of broadleaf woodland expansion on streamwater acidification are discussed. In addition, topics for future research and improvements in methodologies aiming to protect freshwaters in sensitive areas from acidification are suggested.

8.1 Summary of research findings

Most research in the UK has focused on the effects of conifer afforestation on surface water acidification and little attention has been given to the possible effects of broadleaf woodland expansion on water chemistry. The Forests and Water Guidelines use the critical loads approach to identify freshwaters at risk of acidification from the expansion of broadleaf woodlands in the UK. In order to investigate the effects of broadleaf woodland cover in streamwater chemistry in acid-sensitive catchments, 10 catchments with proportions of woodland cover from 10.3 to 78.7% were selected in representative acid-sensitive areas of the UK in Scotland (Glen Arnisdale and Loch Katrine area) and England (Ullswater area and Devon), along with four non-forested (control) catchments located adjacent or nearby to the forested ones. The main broadleaf tree species present in the study catchments were birch, oak and alder. Streamwater samples were collected at high flow during winter/spring months and chemical parameters were determined in them using standard methods.

Results of multivariate analyses using mean streamwater chemistry revealed clear catchment groupings which generally corresponded to their geographical locations. Most study catchments had low streamwater alkalinity values, indicating low soil buffering capacity, apart from catchments UL2 and ULCON which had relatively high streamwater alkalinity and Ca concentrations. Streamwater acid anion (SO_4 and

NO_3) concentrations were higher in the English catchments, probably because they were closer to pollutant sources and had higher woodland covers resulting in more dry deposition of atmospheric S and N pollutants. Correlation analysis showed significant positive associations between percentage broadleaf woodland cover and mean high flow streamwater NO_3 and Al concentrations and NO_3 index values in the study catchments. Streamwater NO_3 concentrations were higher in the higher forested catchments YAR, UL1 and UL2 probably due to increased N pollutant scavenging by oak and alder canopies and enhanced NO_3 leaching caused by N fixation by symbiotic bacteria in alder root nodules in UL1 and UL2. The high mean acid anion concentrations in the higher forested catchments YAR and UL1 probably led to the mobilisation of Al due to ion-exchange processes in YAR and UL1, but not in UL2 which appeared to have high soil buffering capacity. NO_3 index values indicated that NO_3 was becoming, or was already, the dominant excess acid anion in streamwater in catchments YAR, UL1 and UL2 with woodland covers ≥ 50%. No significant associations were found between percentage broadleaf woodland cover and mean streamwater high flow SO_4 and xSO_4 concentrations, probably because wet non-marine S deposition, which is unaffected by the presence of vegetation, dominated total S deposition in the study catchments. Overall, variability in atmospheric pollutant deposition and soil type composition seemed to largely influence streamwater chemistry and masked, to a certain extent, the woodland effect in the study catchments. In addition, seasalt inputs seemed to influence streamwater chemistry more than woodland cover in the maritime Glen Arnisdale catchments.

The risk of acidification in the study catchments was assessed by calculating critical loads exceedance using the SSWC and FAB models and modelled pollutant deposition estimates. Critical loads were exceeded by 1995-97 and 2002 FRAME pollutant deposition in three study catchments (NAR, YAR and UL1) for both the SSWC and FAB models. Exceedance of critical loads in catchments YAR and UL1 was mainly attributed to the relatively high streamwater concentrations of NO_3 which seemed to be influenced by the presence of broadleaf woodland through enhanced N pollutant scavenging by woodland canopies and nitrification by alder in UL1. Critical load exceedance in NAR was mainly caused by the high streamwater xSO_4

concentrations, probably due to past soil acidification and high current non-marine S deposition. Overall, the three catchments where critical loads were exceeded appeared to have low soil buffering capacity, which resulted in low critical load values, and relatively high pollutant inputs. Calculations with the FAB model showed that initial reductions in N deposition were necessary, followed by reductions in either N or S deposition, to protect catchments YAR and NAR from acid deposition, while reductions in both S and N deposition were necessary to protect catchment UL1 from acid deposition.

The Glen Arnisdale and Loch Katrine area catchments and UL2 and ULCON had the capacity to buffer acid inputs from pollutant deposition and consequently critical loads were not exceeded, and non-exceedance resulted in positive streamwater ANC values in most not-exceeded catchments. However, streamwater ANC was negative in three not-exceeded catchments in Glen Arnisdale, suggesting that they could suffer from seasalt induced episodic acidification. Macroinvertebrate data showed that streamwater ecological quality was good in most catchments where critical loads were not exceeded, and predictions of acid-sensitivity made with the Rutt model using macroinvertebrate data generally agreed with the assessments of acid-sensitivity made with the critical loads methodology.

In order to explore the mechanisms of tree cover effects in more detail, critical loads exceedance was re-assessed in the Loch Katrine area catchments using modelled dry pollutant deposition onto birch canopies using the FRAME model and woodland-specific roughness length values. The results showed that pollutant inputs from birchwood scavenging were very small compared to inputs from wet pollutant deposition and critical loads exceedance remained at the same levels in the Loch Katrine catchments. Using this approach it was shown that plans for new broadleaf woodland planting in the Loch Katrine area would not pose a risk of streamwater acidification, but pollutant scavenging by broadleaf canopies could be more important for streamwater acidification in highly forested areas where the contribution of dry deposition and pollutant loadings are higher than in the Loch Katrine area.

The results of a sensitivity analysis of the critical load calculations, using different input parameters related to ANC values, runoff estimates and least and most acidic streamwater samples, and of an uncertainty assessment of the variability of mean streamwater chemistry and critical load values in the more intensively sampled Loch Katrine area catchments showed overall that the Forests and Water Guidelines should be effective at identifying catchments at risk of acidification. Some uncertainty was found related to possible overestimation of critical loads exceedance in high altitude and rainfall catchments. There were also small changes in the number of catchments identified at risk of acidification depending on the choice of the critical ANC value, 0 or 20 μeq l^{-1}. The finding that critical loads in all study catchments with broadleaf woodland cover below 30%, apart from NAR, were not exceeded, indicating that these catchments were buffered to acid deposition, suggests that the 30% broadleaf woodland cover threshold value is a sensible one for use within the Forests and Water Guidelines framework.

8.2 Implications

Possible adverse impacts of broadleaf woodland expansion on streamwater chemistry, related to delays in chemical or biological recovery from acidification or even further acidification in the most sensitive areas, will depend on the planning of woodland expansion and on climatic changes affecting the pollution climate in the UK. Continuous Cover Forestry (CCF) in the UK will include the integration of existing conifer forests with new broadleaf woodland planting. Therefore, the effect of broadleaves on streamwater chemistry will depend on the extent of new woodland cover and the effect of individual tree species on base cation uptake, N cycling and pollutant scavenging by canopies of different height and aerodynamic roughness. However, surface water acidification would be expected to decline if CCF replaces conifer plantations with broadleaf woodlands. This research did not examine the effect of practices used to expand broadleaf woodland cover, for example ground preparation for planting, on streamwater chemistry, but best management practices currently used in the UK should ensure that new planting will have limited effects on surface water chemistry.

Since deposition of anthropogenic S is expected to decline in the future, the relative importance of N deposition for surface water acidification will increase. However, there is quite a lot of uncertainty in the prediction of the effect that climate change may have on the recovery of acidified waters or on further acidification, especially for processes influencing the fate of N deposition inputs. In particular, it is not known whether possible increases in air and soil temperature will increase or decrease the net retention of N in forest ecosystems, since increased forest growth may increase the uptake of N in vegetation but increased temperature could also enhance the mineralisation of soil organic matter leading to release of N to waters (Wright et al., 2006). In addition, there is still a lot of debate about the causes of increasing DOC trends in surface waters in almost all acid-sensitive areas in Europe and America, and whether these trends are climate-induced or are occurring in response to declining acid deposition, representing a transition to “natural”, pre-acidification water conditions (Skjelkvåle et al., 2005). It is still uncertain how a shift from mineral to organic acidity may affect surface water acidification and also whether there is any interaction between DOC concentrations in runoff and land-use change, such as the broadleaf woodland expansion in the UK. Therefore, any attempts to predict the impact that broadleaf woodland expansion may have on acid-sensitive freshwaters, for example in assessing compliance with the EU Water Framework Directive, need to address the uncertainties identified above.

8.3 Recommendations for future research

Ideally, further research on the effect of broadleaf woodland cover on streamwater chemistry in acid-sensitive catchments should include a larger number of catchments with a wider range of woodland covers, especially in the range of 30 to 50% which could not be investigated here. Furthermore, more catchments with different proportions of woodland cover should be located in each acid-sensitive region so that locational effects (e.g. pollution climate) could be disentangled from the effect of trees. Alternatively, it is recommended that a small number of one to three catchments with high broadleaf woodland covers, preferably above 30 or 50%, and located in representative acid-sensitive areas in the UK should be included in the UK

Acid Waters Monitoring Network (AWMN). Monitoring of streamwater chemistry under different flow conditions would provide valuable information on the effect of broadleaf woodland cover on streamwater chemistry and also enable comparison with streamwater chemistry in moorland and conifer forest acid-sensitive catchments. The assemblage of a streamwater chemistry dataset over a number of years could also enable the investigation of how streamwater chemistry in catchments covered with broadleaf woodland responds to long-term trends in acid deposition in the UK. The monitoring programme should include determination of a number of streamwater chemistry parameters, particularly inorganic labile Al, DOC and possibly dissolved organic nitrogen (DON), which are important parameters for assessing mineral and organic acidity in water, and also macroinvertebrate sampling to assess ecological status.

It is further recommended that the catchments included in the AWMN are located within Special Areas of Conservation (SACs), such as the study catchment YAR, where native broadleaf woodland is of particular importance to biodiversity. Research on freshwater acidification has so far focused on the impacts on recreational fisheries, but organisms, such as macrophyte communities within SACs, are considered more sensitive to acidification than brown trout and possible effects of broadleaf woodland expansion on these organisms are of particular importance, especially in the context of the EU Habitats Directive. A review of the acceptable level of protection, with the possible adoption of variable critical ANC values, may also be necessary to protect a variety of acid-sensitive organisms in areas of conservation interest.

Results of current research suggest that some improvements could be made in the Forests and Water Guidelines to increase the protection of freshwaters at risk of acidification from broadleaf woodland expansion. It is recommended that the FAB model is adopted because it treats N processes in soil in more detail than the SSWC model, and more recent modelled pollutant deposition datasets are used to calculate critical loads exceedance for providing more certainty in the identification of catchments at risk of acidification where broadleaf woodland is expanding.

Moreover, a better understanding of denitrification and N immobilisation processes and quantification of N immobilisation rates in UK upland soils is essential for increasing the accuracy of FAB model calculations. The FAB critical loads methodology would also benefit from modelled pollutant deposition datasets with a higher spatial resolution, for example at 1 km x 1 km grid squares, especially for reduced N. In order to provide more certainty in the identification of freshwaters at risk of acidification, it is recommended that the Guidelines consider updating the provisional critical loads exceedance map to a 5 km x 5 km grid square resolution, which will make it consistent with the spatial resolution of the outputs of most atmospheric pollutant deposition models used in the UK. Finally, it is highlighted that there is need for comprehensive UK datasets to determine critical ANC values for target organisms other than brown trout or salmonids in general, and recommended that research should focus on linking critical loads exceedance with evidence of ecological damage, for a range of freshwater organisms. This is essential for policy making and will ensure that methodologies aiming to protect sensitive freshwater ecosystems from acidification actually do so.

8.4 Conclusions

Broadleaf woodland appears to exert a significant influence on streamwater chemistry in acid-sensitive catchments, mainly due to pollutant scavenging and NO_3 leaching, but only when woodland covers a large proportion ($\geq$ 50%) of the catchment area. Critical loads were not exceeded in most of the study catchments because buffering capacity outweighed acidic anthropogenic inputs. However, atmospheric N deposition is of concern in very poorly buffered catchments with high woodland cover, where NO_3 was the principal acidifying ion and contributed to critical load exceedance, while acid-sensitivity may be underestimated in catchments with high seasalt inputs. Almost all study catchments with woodland cover less than 30% were well protected from acidification, suggesting that this is a sensible threshold value for risk assessments of the effects of broadleaf woodland expansion, as recommended by the Forests and Water Guidelines, to ensure protection of acid-sensitive freshwater biota.

It is recommended that future work should concentrate on monitoring the effect of broadleaf woodland on streamwater chemistry and identifying links between broadleaf woodland cover effects and streamwater acidification, primarily focusing on sensitive freshwater organisms in areas of high conservation importance. Outputs from this research would help forest authorities and environmental agencies in the UK to protect and enhance the biodiversity of freshwater ecosystems and meet the requirements of current European and national environmental legislation, whilst at the same time enabling the expansion of broadleaf woodland cover in the UK.

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Appendix A Sampling and laboratory analytical methods

A.1 Streamwater sampling

Tables A1 to A5 present the dates and flow conditions of the streamwater samples collected from the study catchments.

Table A.1 Streamwater samples and flow conditions from the Glen Arnisdale (GA) catchments. Rule readings (cm) are given in brackets

Sample No.	Date (dd/mm/yy)	Flow conditions			
		GA1	GA2	GA3	GACON
1	16/04/05	-	Low (15)	Low (8)	Low (16.5)
2	17/04/05	-	Low (12)	Low (8.5)	Low (14)
3	22/06/05	Low (3)	Low (6)	Low (6)	Low (6)
4	23/06/05	Low (3)	Low (6)	Low (6)	Low (6)
5	07/11/05	High (11)	High (24.5)	High (12)	High (17)
6	08/11/05	High (15)	High (26)	High (15)	High (25)

Table A.2 Streamwater samples and flow conditions from the Loch Katrine area (LK) catchments. Rule readings (cm) are given in brackets

Sample No.	Date (dd/mm/yy)	Flow conditions				
		LK1	LK2	LK3	LK4	LKCON
1	11/02/05	High (-)	High (-)	High (-)	High (-)	-
2	08/03/05	Low (-)	Low (-)	Low (-)	Low (-)	-
3	14/03/05	Low (10.9)	Low (9)	Low (-)	Low (11.5)	Low (-)
4	17/03/05	High (26)	High (28)	High (26.8)	High (20)	High (20)
5	22/03/05	High (24)	High (27)	High (25)	High (19.5)	High (20)
6	24/03/05	High (23)	High (27)	High (25)	High (19)	High (19.5)
7	01/04/05	Low (15)	Low (23.5)	Low (22.2)	Low (16)	Low (16.5)
8	05/04/05	High (19.5)	High (27.5)	High (26.5)	High (18)	High (18)
9	07/04/05	High (19.5)	High (25.5)	High (24.5)	High (28)	High (19.5)
10	12/04/05	High (18.3)	High (25.5)	High (24.5)	High (28)	High (19.5)
11	18/05/05	Low (8)	Low (17)	Low (15.8)	Low (7.5)	Low (9.5)
12	18/06/05	Low (13)	Low (21.5)	Low (20)	Low (13)	Low (12.5)
13	12/10/05	High (41)	High (31)	High (32)	High (-)	High (23)
14	02/11/06	High (19.5)	High (25)	High (26)	High (-)	High (18.5)
15	15/02/06	High (31)	High (-)	High (31)	High (-)	High (24)
16	23/03/06	Low (13)	Low (-)	Low (9.5)	Low (-)	Low (15.5)

Table A.3 Streamwater samples and flow conditions from the catchments near Ullswater (UL). Rule readings (cm) are given in brackets

Sample No.	Date (dd/mm/yy)	Flow conditions		
		UL1	UL2	ULCON
1	16/03/05	High (16.5)	High (11)	High (4.5)
2	14/04/05	High (16.5)	High (10.5)	High (4.7)
3	18/05/05	High (12.8)	High (8.3)	High (4)
4	22/06/05	Low (5.5)	Low (2)	Low (0)
5	08/02/06	High (13.2)	High (16.5)	High (4)
6	09/03/06	High (13)	High (16.5)	High (4.5)

Table A.4 Streamwater samples and flow conditions from the Yarner Wood (YAR) catchment. Rule readings (cm) are given in brackets

Sample No.	Date (dd/mm/yy)	Flow conditions
		YAR
1	18/02/05	High (15)
2	16/03/05	High (13.5)
3	22/03/05	High (12.5)
4	30/03/05	High (14.5)
5	02/11/05	High (23)
6	02/12/05	High (17)
7	08/03/06	High (15)
8	16/03/06	High (16)

Table A.5 Streamwater samples and flow conditions from the Narrator Brook (NAR) catchment

Sample No.	Date (dd/mm/yy)	Flow conditions
		NAR
1	04/01/05	High
2	02/02/05	High
3	01/03/05	High

A.2 Laboratory analytical methods

A.2.1 pH

Streamwater pH was measured in the field using a portable Hanna Instruments 9025 Microcomputer pH meter equipped with a low ionic strength Gelplas reference electrode with ambient temperature compensation and calibrated with low ionic strength buffer solutions (pH values of 4.10, 6.97 and 9.15). Streamwater at high flow for the study catchments had low conductivity values below 100 $\mu S\ cm^{-1}$ which can reduce the accuracy of pH determination. Field measurements of pH were restricted to the catchments in Glen Arnisdale and the Loch Katrine area because Forest Research and Eden Rivers Trust staff did not have suitable equipment for pH measurements. As an alternative, 100 ml borosilicate glass bottles were filled to the brim with streamwater to avoid degassing of carbon dioxide which interferes with the determination by increasing pH (Neal et al., 1999), and were sent to Edinburgh along with the other samples. On arrival at Edinburgh the pH of these samples was measured using a Thermo Russell RC150 pH meter with a low ionic strength reference probe. However, since streamwater pH needs to be measured in-situ, these pH values were only used as reference and were not included in the data analysis.

A.2.2 Gran alkalinity

Alkalinity is a standard water parameter measurement which provides information on the total carbonate system in a water body and the ability of a water body to buffer the effects of acidic pollution (Neal, 2001). Alkalinity can be perceived as a measure of the water's acid neutralising capacity. Alkalinity is usually expressed as the difference of two components:

a) acid buffers in solution, which are usually dominated by bicarbonate, carbonate and hydroxide ions under very alkaline conditions, or by organic acid anions, such as humates and fulvates, particularly under acidic conditions. Less common buffers, such as sulphides, occasionally provide additional buffering capacity;

b) hydrogen ion concentration.

Alkalinity is determined electrometrically using acidimetric titrations in pre-selected pH ranges. In circum-neutral to alkaline water systems (alkalinity > 200 μeq l^{-1} and pH 6-10), alkalinity is considered to be made up almost completely of bicarbonate and a single acidimetric titration to pH 4.5 is needed to determine bicarbonate alkalinity. In this case alkalinity can be considered as:

$$Alkalinity \cong [HCO_3^-] - [H^+] + [OH^-] = Bicarbonate\,Alkalinity - [H^+] + [OH^-]$$

(Equation A.1)

However, in acidic waters buffers other than bicarbonate, in particular organic acids, become important and not all the buffering components are neutralised at single titration endpoints. In this case, Equation A.1 takes the form:

$$Alkalinity = [HCO_3^-] + 2 * [CO_3^{2-}] + \Sigma n * [H_m Org^{-n}] - [H^+] + [OH^-] \quad \text{(Equation A.2)}$$

where the term $\Sigma n * [H_m Org^{-n}]$ represents the sum of the organic anion buffers.

For more acidic conditions, a method of alkalinity determination developed by Gran has been used within freshwater acidification research. In the Gran method, acidimetric titration is undertaken first to an endpoint where the buffering components are neutralised and then to higher hydrogen concentrations where the increase in acidity is directly proportional to the amount of acid added (Neal, 2001). By measuring accurately the pH (and hence the hydrogen ion concentration) at various points in the titration, the alkalinity can be directly determined. This is done by plotting the amount of hydrogen ions in the solution (*Y* axis) against the amount of acid added (*X* axis); the alkalinity is calculated using the intercept of this straight line with the *X* axis (the “equivalence point”).

As titrations of test streamwater samples showed acidic conditions (alkalinity < 200 μeq l^{-1}), the Gran method was used for alkalinity determination. Initially, 0.05 M hydrochloric acid (HCl) was used for the titrations, but, due to the low alkalinity values of most streamwater samples, it was difficult to measure accurately the titration equivalence point. Thus the molarity of the acid was reduced to 0.01 M HCl, resulting in smaller pH reductions during titration and more sensitive detection of the equivalence point. The procedure followed for determination of Gran alkalinity was based on Neal (2001) and an example of the alkalinity calculation for one water sample is given in Table A.6 and Figure A.1.

A.2.2.1 Procedure for determining Gran alkalinity

Procedure:

(i) The pH meter was calibrated using low ionic strength buffers (pH values 4.10, 6.97 and 9.15);

(ii) A 12.5 ml burette was filled with the HCl solution;

(iii) 100 ml (V_0) of filtered water sample were measured into a conical flask. The flask was placed on the magnetic stirrer and a magnetic stirring bar was put into the sample;

(iv) The pH and temperature probe were rinsed with deionised water and were placed in the flask so as not to touch the flask bottom or sides. The sample depth in the flask had to be sufficient to cover the junction of the reference electrode, the electrode bulb and the temperature sensor;

(v) Titration was initiated while the sample was stirred slowly and continuously. Sample pH was measured after each addition of titrant and after acid and sample were mixed homogeneously;

(vi) The alkalinity equivalence point was around a pH of 4.5 and the most sensitive part of the titration process was usually between pH 4.8 and pH 4.3. Enough acid was added from the burette until pH was around 4.5.

The volume of acid added (V_t) and the exact pH of the solution (to 2 decimal places) was recorded. Titration continued by cautiously adding acid drop by drop in 0.02-0.1 ml increments from pH 4.5 to 4.0 and in 0.1-0.5 ml increments to pH 3.5 to ensure that both bicarbonate and organic acid alkalinity were titrated.

Calculation of alkalinity: Gran plot

1) From the pH recorded for each step in the titration, hydrogen ion concentration was calculated by using the equation:

$$[H^+] = 10^{-pH}$$

2) For each step the Gran parameter (G) was calculated, where:

$$G = (V_0 + V_t) \cdot [H^+]$$

3) Values of G were plotted against values of V_t for titration points below pH 4.5 only and a best-fit line was fitted through the points by linear regression. From this plot the true equivalence point (V_e) was determined as the volume (V_t) where the line crossed the x-axis. The Gran alkalinity (in units of milliequivalents per litre and reported to three significant figures) of the sample was calculated from the following equation:

$$Gran\ Alkalinity = Molarity\ of\ HCl \cdot V_e \cdot 10$$

An example of the determination of the Gran alkalinity of sample 16 from catchment LK1 is shown in Table A.6 and Figure A.1. The molarity of HCl was 0.01M and V_e was 0.581. Therefore, Gran alkalinity of the sample was 0.0581 meq l^{-1} or 58.1 μeq l^{-1}.

Table A.6 pH values, titrant volumes and calculated factors for the calculation of Gran alkalinity for sample no.16 from catchment LK1

pH	H^+	V_t (ml)	$V_0 + V_t$ (ml)	G
4.5	0.0000331	1.4	101.4	0.003358
4.4	0.0000380	1.5	101.5	0.003859
4.4	0.0000417	1.6	101.6	0.004235
4.3	0.0000479	1.7	101.7	0.004868
4.3	0.0000513	1.8	101.8	0.005221
4.3	0.0000550	1.9	101.9	0.005600
4.2	0.0000617	2.0	102.0	0.006289
4.2	0.0000708	2.2	102.2	0.007235
4.1	0.0000871	2.7	102.7	0.008945
4.0	0.0001072	3.2	103.2	0.011058
3.9	0.0001318	3.7	103.7	0.013670
3.8	0.0001514	4.2	104.2	0.015771
3.7	0.0001905	5.2	105.2	0.020045
3.6	0.0002291	6.2	106.2	0.024329
3.6	0.0002818	7.7	107.7	0.030354
3.5	0.0003388	9.2	109.2	0.037002

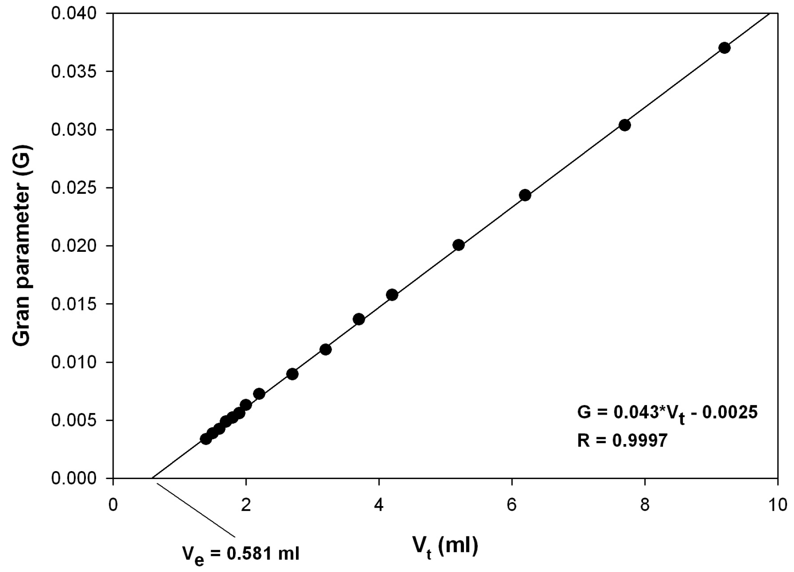

Figure A.1 Gran alkalinity plot for sample no.16 from catchment LK1

A.2.3 Base cations

Base cations (Ca, Mg, Na and K) were analysed using flame atomic absorption spectrometry (FAAS). AAS is a common and well-established technique for detecting metals and metalloids and is very reliable and simple to use with little interference. The method is based on the principle that when metal ions are converted to their atomic state by means of a heat source, light of the appropriate wavelength is absorbed and the amount of absorption can be compared against calibration curves to determine concentration (Patnaik, 1997). In FAAS the heat source is a flame. The sample is aspirated into the flame and atomised.

Water samples were kept cool at temperature < 4 ºC and were analysed within 7 days of collection. The analysis was performed using a Unicam AA M Series flame atomic absorption spectrometer with Solaar System software for control and data collection. The heat source used by the spectrometer was an air-acetylene flame. The temperature of the flame may not be enough for Ca to dissociate to its atoms and interference is possible from phosphate. To minimise phosphate interference, lanthanum (La) was added to the samples analysed for Ca to act as a releasing agent in excess and form lanthanum phosphate. Concentrations of standard solutions used during the determination of Ca, Mg, Na and K are given in Table A.7.

Table A.7 Concentrations of standard solutions (mg l^{-1}) and wavelengths (nm) used for the determination of base cations

Elements	Standard 1	Standard 2	Standard 3	Standard 4	Wavelength
Ca	5.0	10	15	20	422.7
Mg	5.0	10	15	20	285.2
Na	5.0	10	15	20	589.0
K	1.0	2.0	3.0	4.0	766.5

A.2.4 Chloride and sulphate

Water samples were analysed for chloride (Cl) and sulphate (SO_4) using ion chromatography, a method widely used for sequential determination of many common anions in wet analysis. The main advantages of the ion chromatography technique are: a) several anions can be determined in a single analysis, b) it distinguishes halides and anions in different oxidation states; such anions often interfere with each other in wet analysis and c) it is a simple and rapid technique (Patnaik, 1997).

The water samples were kept cool at < 4 ºC and were analysed within 7 days of collection. The method used for the determination of sulphate and chloride involved chromatographic separation of water soluble analytes and detection of separated anions by a conductivity detector. The analysis was performed using a DX-500 ion chromatograph (DIONEX, CA, USA). Separation was achieved using an IonPac AS4A-5C analytical column and a mobile phase composed of 1.7 mM sodium bicarbonate / 1.8 mM sodium carbonate delivered at a flow rate of 2 ml min^{-1}. Post-column eluent suppression was achieved using an anion self-regenerating suppressor (ASRS-1) operated at a current of 50 mA. Detection was via a ED40 electrochemical detector set at an output range of 30 µS cm^{-1}. Instrument control and data collection were accomplished using PeakNet software. Concentrations of standard solutions used during the determination of Cl and SO_4 are given in Table A.8.

Table A.8 Concentrations of standard solutions (mg l^{-1}) used for the determination of chloride and sulphate

	Standard 1	Standard 2	Standard 3	Standard 4
Cl	1.0	5.0	10	25
SO_4	1.0	5.0	10	25

For quality control two random duplicate samples were analysed in every run. The relative difference (d_r) between the concentrations of the duplicate samples X_1 and X_2 was calculated using the formula:

$$d_r = \frac{100 * d}{\left(\frac{(X_1 + X_2)}{2}\right)} \qquad \text{(Equation A.3)}$$

where $d = X_1 - X_2$ (Patnaik, 1997), and d_r values were subtracted from 100 to get % precision values. For Cl concentrations, the mean precision of analysis was 96.3% (s.d = 5.9) and for SO_4 the mean precision was 96.4% (s.d = 3.4) indicating in both cases high precision of analysis and good reproducibility.

A.2.5 Nitrate and ammonium

Nitrate and ammonium were measured using automated colorimetry which is a fast and cost effective technique. The method however can be unreliable for dirty and coloured samples and the presence of certain substances in samples can interfere with the test (Bartram and Ballance, 1996). Therefore, portions of the sample (200 ml) were vacuum filtered on return to the laboratory through 0.45 μm cellulose nitrate membrane filters to remove any particulate matter present in the sample. The first 50 ml of the filtrate were discarded and the succeeding filtrate was frozen to prevent degradation and was analysed within 30 days.

Analysis of water samples for nitrate and ammonium was performed using a Bran & Luebbe AA3 continuous flow analyser. Nitrate was determined by the Bran & Luebbe G-109-94 Rev.3 (Multitest MT7/MT8) method. Nitrate was reduced to nitrite by hydrazine in alkaline solution with a copper catalyst after which it was reacted with sulphanilamide and *N*-(1-naphthyl)- ethylenediamine dihydrochloride (NEDD) to form a pink compound measured at 550 nm. Phosphoric acid was added in the final stage to reduce pH, thus avoiding precipitation of calcium and manganese hydroxide. The addition of zinc to the reducing agent suppressed the complexing of copper by organic material. Determination of ammonium was achieved using method Bran & Luebbe G-102-93 Rev. 1 (Multitest MT7/MT8). The sample was reacted with salicylate and dichloro-isocyanuric acid to produce a blue compound was measured at 660 nm. Nitroprusside was used as a catalyst. Concentrations of standard solutions used during the determination of NO_3 and NH_4 are given in Table A.9.

Table A.9 Concentrations (mg l^{-1}) of standard solutions used for the determination of nitrate (NO_3) and ammonium (NH_4)

	Standard 1	Standard 2	Standard 3	Standard 4
NO_3	2.0	4.0	6.0	8.0
NH_4	1.0	2.0	4.0	8.0

A.2.6 Trace metals

Metals (Al, Mn, Fe, Pb and Zn) were analysed using optical emission spectroscopy using inductively coupled plasma (ICP-OES). The main advantage of ICP-OES is that several metals can be determined simultaneously and rapidly. Optical emission spectroscopy is the same as AAS except that emission is measured instead of absorbance. In ICP-OES, inductively coupled plasma is used as the source for atomic emission (Patnaik, 1997). The wavelengths of light that are emitted are specific to the elements present in the sample. The measured emission intensities are compared to the intensities of standards of known concentration to obtain the unknown elemental concentrations in the samples.

To prepare streamwater samples for the determination of soluble Al, Mn, Fe, Pb and Zn, a portion of the water sample (200 ml) was vacuum filtered through a 0.45 µm cellulose nitrate membrane filter. The first 50 ml of filtrate was discarded and the succeeding filtrate was then used for the determination. To avoid loss of Al from solution via precipitation on the walls of the sample containers the filtered samples were acidified with 2 ml of concentrated nitric acid (HNO_3) per litre of sample before storage in biotite vials (Bartram and Ballance, 1996). This acid addition was adequate in all cases to depress water pH below 2 and suppress Al precipitation. The maximum permissible storage time was six months, but all water samples were analysed for metal concentrations within one to three months after collection. Untreated water samples (unfiltered and not acidified/filtered samples) were also analysed along with the filtered and acidified samples for quality control. The highest metal concentrations were measured in samples that were filtered and acidified probably because filtration and acidification ensured that metals were not lost by complexation to particulate matter or adsorption during storage. Only concentrations from the filtered and acidified samples were included in the data analysis.

The analysis of samples for soluble Al, Mn, Fe, Pb and Zn was performed using a PerkinElmer Optima 5300 ICP-OES with WinLab 32 software for control and data collection. The apparatus consists of an ICP source and a spectrometer. The ICP source consists of a radio frequency generator, torch, coil, nebuliser, spray chamber and drain. A flowing stream of argon gas is ionised by an applied oscillating radio frequency field, which is inductively coupled to the ionised gas by a water-cooled coil. A sample aerosol is generated in the nebuliser and spray chamber and injected into the ICP, at a high plasma temperature of 6000 to 8000 K. These high temperatures ionise atoms producing emission spectra. Also, at this temperature, compounds completely dissociate, thus reducing any interferences. Axial viewing of the light emitted from the ICP was used because it provides better detection limits than those obtained via radial viewing. The light emitted is focused on a monochromator that is used to separate the individual wavelengths of light and focus the desired wavelengths onto the detector.

Multi-element standard solutions were prepared on the day of the analysis and were acidified with 5% HNO_3 to minimise precipitation and also adsorption of elements onto container walls. Six standard solutions were prepared for each analysis (Table A.10). A certified surface water SPS-SW-1 reference material (Spectrapure Standards AS) for the five analytes was also used for quality control during the analysis. The reference material solution contained HNO_3. Spectral interferences from ion-atom recombination, spectral line overlaps, molecular band emission, or stray light can occur that may alter the net signal intensity. These interferences were compensated for by the selection of alternate analytical wavelengths and by making background corrections. Up to five different wavelengths were used for metal determination (Table A.11). At the end of the analysis the spectra were investigated and corrected if there were deviations from the net signal intensity. In this case, the results were re-processed using the WinLab 32 software and corrected concentration values were generated. Selection of the suitable wavelength for determining the concentrations of each analyte was based on the strength of the correlation coefficients of each analyte calibration line, the magnitude of the signal peaks produced and the proximity of the concentrations determined for the standard solutions and reference material to the expected concentrations. In most cases, wavelengths that produced the highest peaks gave results that were in close agreement with the standard solution and reference material concentrations.

Table A.10 Concentrations (µg l^{-1}) of standard solutions used for the determination of Al, Mn, Fe, Pb and Zn

Elements	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6
Al	10.0	20.0	50.0	100	200	500
Mn	10.0	20.0	50.0	100	200	500
Fe	10.0	20.0	50.0	100	200	500
Pb	5.00	10.0	20.0	50.0	80.0	100
Zn	5.00	10.0	20.0	50.0	80.0	100

Table A.11 Main wavelengths (nm) used in ICP-OES analysis for the determination of Al, Mn, Fe, Pb and Zn and their approximate detection limits (µg l^{-1}) from the instrument specifications (PerkinElmer)

Elements	Wavelength 1	Wavelength 2	Wavelength 3	Approximate detection limit
Al	396.2	308.2	237.3	1.0
Mn	257.6	294.9	259.4	0.1
Fe	259.9	238.2	234.8	0.1
Pb	220.4	217.0	238.9	1.0
Zn	206.2	213.9	202.6	0.2

For quality control, standard checks were performed after every 10 samples in each instrument run using standard solution no.3 (Table A.10) and also three replicates of the reference materials were run at the beginning of each analysis. Mean concentration values of standard checks and reference materials measured for the five elements are given in Tables A.12 and A.13 for all water samples analysed. For the standard solution repeatability was good for Al, Mn and Fe, but Al had a high standard deviation. Fe and also Zn concentrations were consistently lower than the reference material concentrations.

Table A.12 Mean concentrations and standard deviation (SD) (µg l^{-1}) of standard checks (standard no.3, N= 35) made during the analysis of Al, Mn, Fe, Pb and Zn

Elements	Standard 3 concentration	Mean measured concentrations	SD
Al	50.0	54.8	11.2
Mn	50.0	48.0	3.70
Fe	50.0	50.0	8.00
Pb	20.0	19.7	3.70
Zn	20.0	19.6	4.10

Table A.13 Mean concentrations and standard deviation (SD) (µg l^{-1}) of certified reference materials (N=21) analysed during the determination of Al, Mn, Fe, Pb and Zn

Elements	Certified reference material concentrations	Mean measured concentrations	SD
Al	50.0 ± 1.0	49.5	2.90
Mn	10.0 ± 0.1	9.90	1.00
Fe	20.0 ± 1.0	15.6	3.20
Pb	5.0 ± 0.1	7.30	3.60
Zn	20 ± 1.0	16.6	2.70

For Pb and Zn, repeatability of standard solution and reference material concentrations was generally acceptable. Mean streamwater concentrations were very low for both Pb (range: 0-1.67 μg l^{-1}) and Zn (range: 0.3-5.5 μg l^{-1}) and were close to the instrument's detection limits.