ISSN 1362-9301

ECRC

ENVIRONMENTAL CHANGE RESEARCH CENTRE

University College London

RESEARCH PAPERS

No. 18

Spatial variability of nitrate concentration in lakes in Snowdonia, North Wales

Kernan, M. and Allott, T.E.H.

August 1998

Environmental Change Research Centre
University College London
26 Bedford Way
London
WC1H 0AP

Spatial variability of nitrate concentration in lakes in Snowdonia, North Wales.

M.R Kernan and T.E.H. Allott

Environmental Change Research Centre, Department of Geography, University College London, 26 Bedford Way, London WC1H 0AP.

Abstract: At a regional scale, high nitrate (NO_3^-) concentrations in upland surface waters generally occur in tandem with high nitrogen (N) deposition levels. However, significant differences in the patterns of surface water NO_3^- concentration have been observed within areas of similar N deposition yet relatively few studies have been undertaken which examine within-region variation of NO_3^- concentrations. A study of 76 lakes in Snowdonia, north Wales, an area of high deposition and sensitive catchments, was undertaken to assess variation in lake-water NO_3^- concentration across a 20 x 20 km grid square and to identify catchments vulnerable to NO_3^- leaching. Nitrate concentration varies considerably, particularly during winter when values range between 0.7 and 70 μeq l^{-1}. Retention by vegetation and soil microbes in summer reduces the amount of NO_3^- reaching the lakes but nevertheless 37% of sites are characterised by NO_3^- concentrations greater than 4 μeq l^{-1}. The elevated concentrations occurring in summer suggests that N breakthrough has occurred. By examining the ratio of NO_3^- to total strong acid anions it is shown that NO_3^- contributes significantly to freshwater acidity, particularly during the winter. Redundancy analysis shows that the highest NO_3^- leaching levels both in winter and summer occur in catchments where soil and vegetation cover is limited. Nitrogen cycling in these catchments, generally at higher altitudes, may no longer be governed by seasonal biological controls. They are likely to be saturated with respect to nitrogen as a result of the elevated deposition levels in the area. The contribution of NO_3^- to acidity is also greatest at these sites. In winter positive significant relationships are also evident between NO_3^- concentration and soil pH and coniferous woodland. The study demonstrates the importance of catchment factors in modifying the relationship between N deposition and N leaching in upland catchments.

Key words: Nitrate, catchment characteristics, redundancy analysis, acidification, lakes, Snowdonia

1. Introduction

Until recently, most assessments of the effects of acidification on surface waters have focussed on the role of sulphur (S) deposition (e.g. Harriman and Wells, 1985; Henriksen *et al.*, 1990; Forsius *et al.*, 1992; CLAG, 1995; Battarbee *et al.*, 1996). However, across Europe, S emissions have declined substantially and are expected to continue doing so in future (RGAR, 1997). Over the same period, emissions of oxidised nitrogen (NO_x) have remained relatively stable with slight increases in some areas (RGAR, 1997; Vincent *et al.*, 1997). Trends in reduced N are more difficult to quantify as sources are much more diffuse (RGAR. 1997). The contribution of N to total acid deposition is thus becoming more important (RGAR, 1997). Coincident with this has been evidence of increasing levels of nitrate (NO_3^-) in upland waters (e.g. UKAWMN, 1997; Henriksen *et al.*, 1997) and predictions of further increases in future (Curtis *et al.*, 1998).

The pattern of surface water NO_3^- concentrations across the UK indicates that waters in upland areas of England and Wales and SW Scotland are vulnerable to acidification due to NO_3^- leaching (Allott *et al.*, 1995; Harriman *et al.*, 1995). Many freshwater sites in these areas currently exhibit NO_3^- leaching in runoff (Jenkins *et al.*, 1997) and in a number of high deposition areas of Great Britain (e.g. North Wales, Lake District, Pennines) the contribution of NO_3^- to the sum of strong acid anions can reach 40% (Jenkins *et al.*, 1996; Curtis *et al.*, 1998).

Although it has been demonstrated that, at a regional scale, patterns of NO_3^- concentration in surface waters are broadly consistent with N deposition levels (INDITE, 1994; Allott *et al.*, 1995; Jenkins *et al.*, 1996), nitrate leaching can vary significantly between proximal catchments (Stevens *et al.*, 1993) and between areas which have similar N deposition levels (Reynolds *et al.*, 1992; Emmett *et al.*, 1993; Curtis *et al.*, 1998). There is, however, relatively little information relating to within-region variation in N leaching.

This paper describes the results of a case study of lake catchments within a 20 x 20 km area of North Wales, UK. Initially, variation in the NO_3^- concentration of lakes in the study area is examined to identify those with high surface water NO_3^- concentrations (i.e. where N breakthrough has occurred). The contribution of nitrogen to the acidity of the study lakes is also considered.

Secondly, catchment types that are currently most vulnerable to acidification from atmospheric N deposition are identified. The processes and mechanisms which determine the nature of the impact of N deposition on surface waters are more complex than those governing response to S alone. Although concentrations of NO_3^- in upland surface waters tend to be greater in areas of high N deposition (Allott *et al.*, 1995; Jenkins *et al.*, 1996), there is little direct evidence linking the two (Stoddard, 1994). The extent and timing of NO_3^- leaching and the precise factors controlling N breakthrough on a catchment scale are poorly understood (INDITE, 1994; Reynolds *et al.*, 1994) due to the complex process interactions governing catchment response to N deposition. It is known that the N flux within a catchment is regulated by a number of key processes including fixation, mineralisation, immobilisation, nitrification, denitrification, and assimilation by plants and soil microbes (see Reynolds *et al.*, 1992; Van Miegroet and Johnson, 1993; Reynolds and Edwards, 1995; Stoddard, 1994). These processes are mediated by the soil, biota and hydrological pathways within the contributing catchment which in turn are largely determined by the physical characteristics of the catchment. The nature and rate of N transformation in the soil is influenced by soil type, temperature, moisture and chemical composition (e.g. Reynolds *et al.*, 1992; Cresser *et al.*, 1993; Stoddard, 1994; Dise and Wright, 1995). Vegetation type and maturity govern seasonal uptake rates (Emmett *et al.*, 1993). Additionally, the hydrological controls on N cycling in the catchment which determine flow pathways and residence time can also have a significant impact on streamwater NO_3^- concentration (Reynolds and Edwards, 1995; Kaste *et al.*, 1997).

To evaluate the relationships between the spatial variation in nitrate observed in the study area and catchment characteristics, a series of variables derived from national databases are empirically related to the chemistry data using multivariate statistical techniques. In the absence of explicit, catchment specific data relating to the processes and attributes outlined above, national soil and land cover datasets were employed to act as surrogates for soil and vegetation characteristics. These data include variables reflecting the physical and chemical status of the soil, the nature of the vegetation in the catchment, the physical characteristics of the catchment together with values relating to specific processes (i.e. denitrification and immobilisation) . A fuller description is provided below.

2. Study area

The study area comprises a 20 x 20 km grid square in North Wales within the Snowdonia National Park, with Snowdon situated to the north-west (Figure 1). This is an area of high rainfall with the highest levels at the summit of Snowdon, diminishing towards the less elevated areas to the east. Annual rainfall in the Upper Glaslyn catchment has been measured at approximately 2800 mm (Edwards et al., 1990). Deposited acidity in Wales is closely related to patterns of rainfall and in the study area generally exceeds 0.6 kg H^+ ha^{-1} yr^{-1} (Donald *et al.,* 1990). Maps of mean annual wet deposition (interpolated from a monitoring network) at 20 km resolution assign the study area with modelled values for non-seasalt sulphate, nitrate and ammonium of >16 kg S ha^{-1} yr^{-1}, >8 kg N ha^{-1} yr^{-1} and >8 kg N ha^{-1} yr^{-1}, respectively (RGAR, 1997). These are among the highest deposition values in the UK.

The study area is geologically complex. Generally, Ordovician sedimentary formations (predominantly shales and slates) are dominant. Snowdon itself is mainly comprised of layered pyroclastic rocks, basaltic tuffs and rhyolitic lavas (the Snowdon Volcanic Series) which are underlain by grits and graptolitic slates of Llandeilo and Llanvirn age (Williams and Ramsay, 1959). These layered volcanics and the sedimentary formations are interspersed with acid doleritic dykes, rhyolitic tuff extrusions and granophyre intrusions (Williams and Ramsay, 1959). Ordovician volcanic and other igneous rocks characterise the higher ground in the study area as these are much more resistant to denudation than the softer sedimentary formations (Smith and George, 1948). Towards the south, Cambrian shales, slates and mudstones dominate, intruded by doleritic dykes and a large granitic mass near Blaenau Ffestiniog. Much of the study area is underlain by geology which is sensitive to acidic deposition offering little or no buffering capacity (e.g. the acid igneous rocks) although some of the intermediate igneous rocks and the Ordovician shales are less sensitive (Edmunds and Kinniburgh, 1986).

Soils vary throughout the study area. Raw oligo-amorphous peat soils (Crowdy 1 and 2 associations) are dominant in the south-east and central areas. To the north-east and south-west, the grid square is characterised primarily by brown podzolic soil cover (Malvern and Manod series, respectively), interspersed with areas of humic rankers (Bangor series) which tend to overlie the rhyolitic geology of the more elevated topography. Other soils occurring include ferric stagnopodzols to the north and in the south-east (Hafren series) and humic brown podzols to the north east (Moor Gate series). Soils in the wetter, high altitude areas tend to be intensely leached and, as a consequence, more acidic (Thompson and Loveland, 1985). Detailed descriptions of these soil associations are provided by Rudeforth *et al.,* (1984) while Ball *et al.,* (1969) discuss the structure and chemistry of soils in Snowdonia.

Land cover varies from the bare ground found at the higher altitudes to areas of improved grassland in the valley bottoms. Generally the area is dominated by upland and lowland moor. There are large areas of plantation forestry to the north west and, in a discontinuous belt, across the southern extent of the study area. A band of high relief, from the mountainous Glyder Fach/Fawr and Snowdon systems (bisected by the Pass of Llanberis) to the elevated semi-natural moorland centred on Cnicht and Moel-ry-hydd (separated from Snowdon by the Glaslyn valley) runs longitudinally along the eastern half of the study area. The east of the study area is characterised by semi-natural moorland and blanket bog with the deeper, raw acid peats of the Migneint Plateau to the south east. In the central area around Blaenau Ffestiniog slate mining is evident in a number of catchments.

3. Sampling strategy and methodology

3.1 Sites and sampling methodology

Nitrate concentrations in surface waters are typically characterised by strong seasonality (Stoddard, 1994). Each lake (76 sites) in the study area was sampled for water chemistry both in February 1996 (to target minimum N retention by the soil and biota and therefore potential maximum leaching conditions) and July 1996 (to target maximum N retention and thus minimum leaching conditions) using a single spot sample on both occasions. Table 1 provides a list of the lakes used in the study together with the altitude of the sample site and the maximum catchment altitude. The location of sites sampled in the study area is shown in Fig. 1. Water samples were refrigerated following collection and delivered to the Freshwater Fisheries Laboratory, Pitlochry within three days of sampling. The samples were analysed for a suite of chemical determinands (including base cations, major anions, nutrients, pH and alkalinity) according to the methods described in Harriman *et al.*, 1990, although only NO_3^- and NH_4^+ are considered explicitly here.

3.2 Secondary data

Catchment boundaries were digitised from 1:25,000 Ordnance Survey (OS) maps using the Geographical Information System, ARC/INFO. For each catchment, land cover data were obtained from the 25 m resolution LANDSAT TM database held at ITE Monks Wood (Fuller *et al.*, 1994). The digitised catchment boundaries were superimposed onto this using ARC/INFO and the percentage of each land class in each catchment was derived. The original 25 class dataset was combined into series of aggregated variables, shown in Table 2.

Each catchment was characterised according to a number of physical and chemical soil attributes (see Table 2). These were derived by overlaying digital catchment boundaries onto the 1:250,000 soil map of England and Wales to obtain the proportion of each soil association therein. The soil series in each association were estimated by staff at the Soil Survey and Land Research Centre (SSLRC). A range of values for the physical and chemical attributes (SSLRC derivation in Table 2) for each soil series was obtained, on an inidividual horizon basis, from soil profile data held at SSLRC (Bradley, pers. comm). Single values for each profile were derived by weighting according to horizon thickness. A series value was produced by averaging the profile values across each series. Averaged values for each catchment were calculated, the averages being weighted by the percentage occurrence within the catchment. Series with missing data were excluded from the weighting procedure.

Immobilisation and denitrification values have been estimated for UK soil types ranging between 1-3 and 1-4 kg ha^{-1} yr^{-1}, respectively (Hall *et al.*, 1997). Fixation is incorporated into the immobilisation term (Posch *et al.*, 1997). Using the weighting approach outlined above, single immobilisation and denitrification values were allocated to each of the study catchments.

Measured rainfall and runoff data were not available for individual catchments. Area weighted values for these variables were derived from the 1 km square resolution national databases held at the Institute of Hydrology. OS maps were used to provide information on altitude, catchment and lake size.

Table 1
List of Snowdonia study sites with grid references, site altitude and maximum catchment altitude

Site name	Site Code	Easting	Northing	Site altitude (m)	Maximum catchment altitude (m)	Site name	Site Code	Easting	Northing	Site altitude (m)	Maximum catchment altitude (m)
Llyn y Cwn	AR26A	263700	358500	711	999	Llyn Dinas	SNSH6427	261600	349600	60	1085
Llyn Cwmffynnon	CFYN	265000	356400	390	999	Quarry 1	SNSH6501	260100	352100	490	747
Llyn Conwy	CON	278000	346300	450	527	Level	SNSH6502	260400	352600	580	704
Llyn Glas	CZSH65	261800	355700	640	1001	Llyn Glas	SNSH6503	261100	355700	530	1050
Llyn Foel	CZSH75	271400	354800	560	872	Llyn Clyd	SNSH6504	263500	359700	610	947
Llynau Diwaunydd	DIWA	268500	353700	370	872	Llyn y Dywarchen	SNSH7401	276300	342000	500	513
Glaslyn	DW24B	261700	354600	464	1085	Llyn Morwynion	SNSH7403	273700	342500	400	552
Llyn Edno	EDNO	266300	349700	500	607	Llyn Serw	SNSH7404	277900	342800	450	460
Llynnau Gamallt 1	GAM	274800	344300	460	580	Llynnau Gamallt 2	SNSH7405	274600	344400	460	500
Llyn Idwal	IDWA	264500	359600	380	999	Un-named 2	SNSH7406	274100	345700	420	500
Llyn Llagi	LAG	264800	348300	380	672	Llyn Dubach	SNSH7407	274500	342400	400	410
Llyn Mair	MAIR	265300	341300	80	258	Llyn Bowydd	SNSH7409	272500	346700	480	658
Llyn Ffridd-y-bwlch	SNSH6401	269500	348100	320	698	Llyn Newydd	SNSH7410	272300	347200	480	586
Llyn Drynogydd	SNSH6402	269300	348800	440	524	Llyn Barlwyd 1	SNSH7411	271000	348400	450	620
Tanygrisiau	SNSH6403	268000	344100	180	770	Llyn Barlwyd 2	SNSH7412	271300	348600	450	620
Llyn Stwlan	SNSH6404	266400	344500	510	770	Llyn Manod	SNSH7413	271700	344700	400	661
Llyn y-Garnedd-uchaf	SNSH6405	265800	342400	250	710	Llyn Cefn	SNSH7414	271500	341900	300	310
Llyn y Garnedd	SNSH6406	265700	342000	230	710	Llyn u-bach	SNSH7415	272000	346000	440	648
Llyn Hafod-y-llyn	SNSH6407	264500	341400	130	234	Llynnau Mymbyr	SNSH7501	271000	357500	184	872
Llyn Hafod-y-llyn	SNSH6408	260000	344700	30	56	Reservoir 3	SNSH7502	272300	355900	380	750
Llyn Iwerddon	SNSH6409	268500	347800	480	698	Reservoir 4	SNSH7503	273200	355400	350	550
Llyn Cwmorthin	SNSH6410	267700	346400	330	698	Reservoir 5	SNSH7504	274800	354300	230	342
Llyn Conglog	SNSH6411	267400	347500	610	698	Llyn Bychan	SNSH7505	275200	359400	270	405
Llyn Coch	SNSH6412	266800	347700	630	676	Llyn Bodgynydd	SNSH7506	276000	359400	250	320
Llyn Croesor	SNSH6413	266100	345700	520	648	Llyn Goddionduon	SNSH7507	275400	358500	250	310
Llyn Clogwyn-brith	SNSH6414	266500	346700	530	550	Reservoir 1	SNSH7508	276500	359700	260	320
Llyn Cwm-corsiog	SNSH6415	266400	347000	530	676	Reservoir 2	SNSH7510	277400	359100	260	332
Llynnau 'r Cwn 1	SNSH6416	266400	348700	640	670	Llyn Parc	SNSH7513	279400	358600	214	298
Llynnau 'r Cwn 2	SNSH6417	266200	348800	610	670	Llyn Teryn	TEYR	264200	354700	380	550
Llynnau 'r Cwn 3	SNSH6418	266200	348600	630	660	Llyn Llydaw	VSH6502	263000	354400	440	1085
Llynnau Diffwys 1	SNSH6419	265900	346800	520	553	Quarry 2	VSH6504	260400	352200	500	704
Llynnau Diffwys 2	SNSH6420	265800	346600	520	553	Ceunant-y-Carnedd	VSH6505	269700	353100	360	872
Llyn Cwm-y-foel	SNSH6421	265500	346700	450	672	Llyn 'r Arrdu	VSH6506	260100	355700	580	1065
Llyn y Biswail	SNSH6422	264900	347400	550	689	Llyn Bochlywd	VSH6508	265500	359300	510	994
Un-named 1	SNSH6423	263500	346600	360	458	Llyn Lockwood	VSH6511	266300	355800	270	360
Llynnau Carrig-y-myllt 1	SNSH6424	263300	347200	420	463	Llyn Gwynant	VSH6513	264500	351800	170	1085
Llynnau Carrig-y-myllt 2	SNSH6425	263200	347400	420	463	Llyn Elsi	WSH7501	278400	355400	240	262
Llyn yr Ardd	SNSH6426	262800	346600	350	463	Llyn yr Adar	YRAD	265500	348000	580	672

Table 2
Summary of catchment variables used in the statistical analyses

Code	Variable	Derivation	Explanation
BD	Bulk density	SSLRC	▣ Catchment weighted soil bulk density
CEC	Cation exchange capacity	SSLRC	▣ Catchment weighted soil cation exchange capacity
Ca_soil	Ca in soil	SSLRC	▣ Catchment weighted soil Ca
Mg_soil	Mg in soil	SSLRC	▣ Catchment weighted soil Mg
K_soil	K in soil	SSLRC	▣ Catchment weighted soil K
Na_soil	Na in soil	SSLRC	▣ Catchment weighted soil Na
pH_soil	Soil pH	SSLRC	▣ Catchment weighted soil pH
Soil_OC	Organic carbon in soil	SSLRC	▣ Catchment weighted soil organic carbon
Top_OC	OC in top soil horizons	SSLRC	▣ Catchment weighted soil OC in upper horizons
Sub_OC	OC in sub-surface horizons	SSLRC	▣ Catchment weighted soil OC in lower horizons
Porosity	Soil porosity	SSLRC	▣ Catchment weighted soil porosity
Depth	Depth of soil	SSLRC	▣ Catchment weighted soil depth
N_imm	Nitrogen immobilisation	Hall *et al.*, 1997	▣ Catchment weighted Nitrogen immobilisation
N_den	Nitrogen denitrification	Hall *et al.*, 1997	▣ Catchment weighted Nitrogen denitrification
Rain	Rainfall (mm/yr)	ITE Monks Wood	Catchment weighted rainfall
Runoff	Runoff (mm/yr)	ITE Monks Wood	Catchment weighted runoff
L_area	Lake area (m^2)	GIS - OS Map	Lake area
C_area	Catchment area (km^2)	GIS - OS Map	Catchment area
L:C	Lake to catchment ratio	GIS	
Alt_s	Site altitude (m)	OS Map	Altitude of lake
Alt_m	Maximum altitude (m)	OS Map	Highest point in catchment
Unclass	% unclassified	ITE Monks Wood	Land cover type 'Not classified'
G_moor	% Grass/moorland	ITE Monks Wood	Lowland semi - natural grass / moor
G_m_upl	% Upland grass/moorland	ITE Monks Wood	Upland semi - natural grass moor
Agric_g	% Agricultural grassland	ITE Monks Wood	Arable and agricultural grassland
Wood_dec	% Deciduous woodland	ITE Monks Wood	Deciduous woodland
Wood_con	% Coniferous woodland	ITE Monks Wood	Coniferous woodland
Bare	% Bare ground	ITE Monks Wood	Bare ground

▣ Weighted averaging equation - $[x]_c = \sum A_s [x]_s / \sum A_s$ where $[x]_c$ is a value for some physical or physical soil attribute for the catchment. A_s is the area of soil map series s and $[x]_s$ is the value for this attribute for soil map series s. The denominator $\sum$ is taken over soil map series $s_1 \ldots\ldots s_n$.

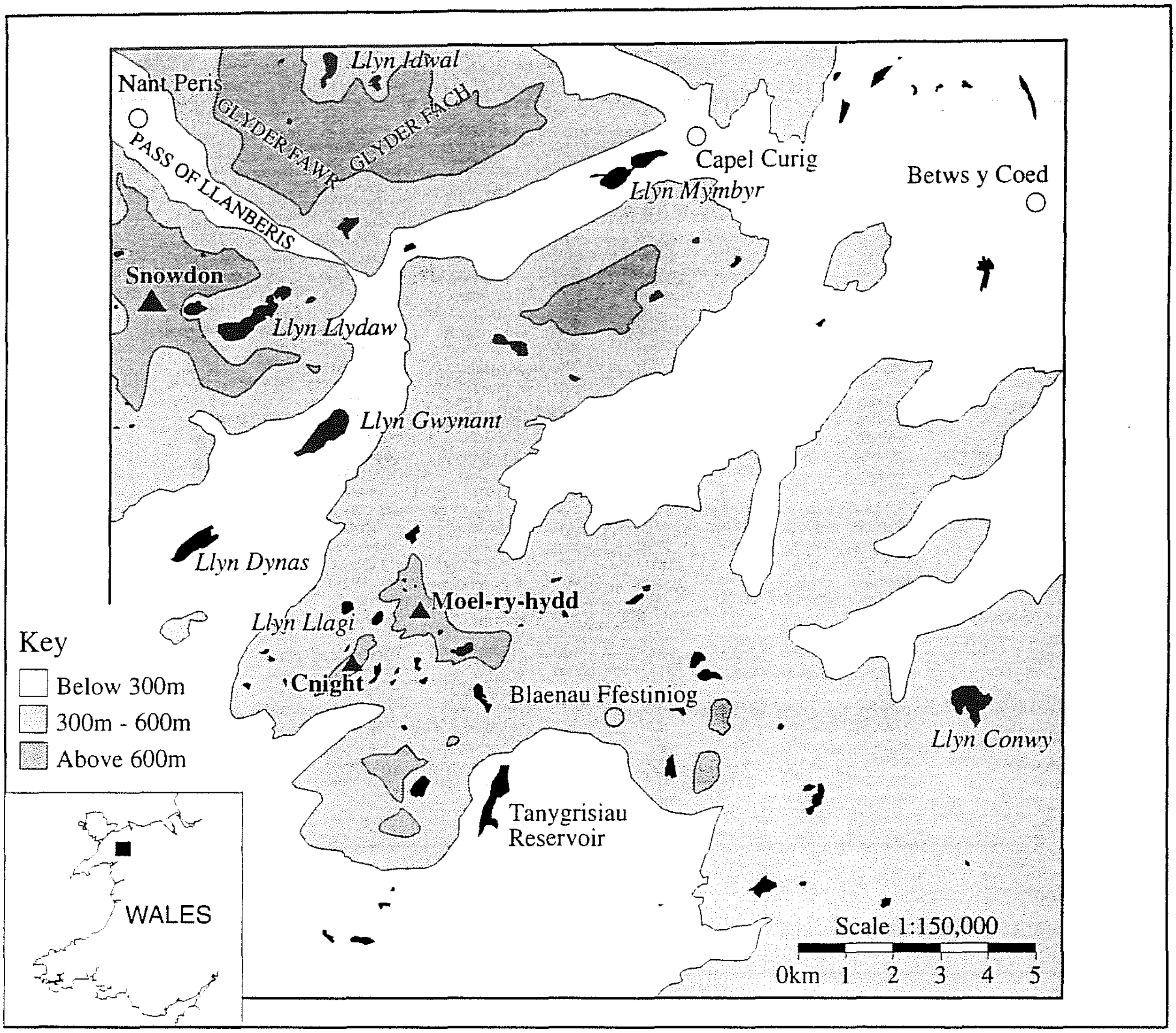


Fig. 1: Map of study area indicating location of lakes and patterns of relief.

3.3. Analytical techniques

To examine the relationships between catchment attributes and NO_3^-, concentration redundancy analysis (RDA) (Van den Wollenburg, 1977) was undertaken. This technique allows the extent to which the catchment attributes explain variation in NO_3^- concentration to be quantified. RDA models response data as a function of the explanatory data (ter Braak, 1994). RDA was implemented using CANOCO Version 3.10 (ter Braak, 1987) and the results were plotted using CALIBRATE (Juggins and ter Braak, 1993)

4. Results

4.1 Variation in nitrate and ammonium concentration

Lake-water NO_3^- concentration varied considerably throughout the study area in both seasons (Table 3). The distribution of NO_3^- values in surface waters across the study area is shown for winter and summer by Figure 2, a scatterplot with histograms, which highlights the different distributions between the two seasons. In winter, mean NO_3^- across all lakes was 24 μeq l^{-1} with a standard deviation (S.D.) of 12.3 and minimum and maximum values of 0.7 and 70 μeq l^{-1}, respectively. In summer, with more N cycled through the biomass, NO_3^- concentrations were lower. The mean value was 5.5 μeq l^{-1} (S.D. 7.7) with minimum and maximum values below detection limit and 34 μeq l^{-1}, respectively. Comparison with studies from stream sites in central and north Wales reveal similar patterns of winter mean nitrate values, although summer means in the study sites are comparatively lower (Reynolds *et al.*, 1994; Stevens *et al.*, 1997). Concentrations of surface water NO_3^- in upland

Table 3
Summary statistics: NO_3^- and NH_4^+ concentration in the 76 study lakes

		Valid N	Min.	Max.	Mean	Range	Variance	Std. Dev.
NO_3^-	Winter	76	0.7	70.0	24.3	69.3	152.4	12.3
	Summer	76	BD	34.0	5.5	34.0	60.21	7.8
NH_4^+	Winter	76	BD	7.0	1.7	7.0	2.7	1.7
	Summer	76	BD	13.0	2.3	13.0	7.4	2.7

BD = Below detection limit   All units in microequivalents per litre

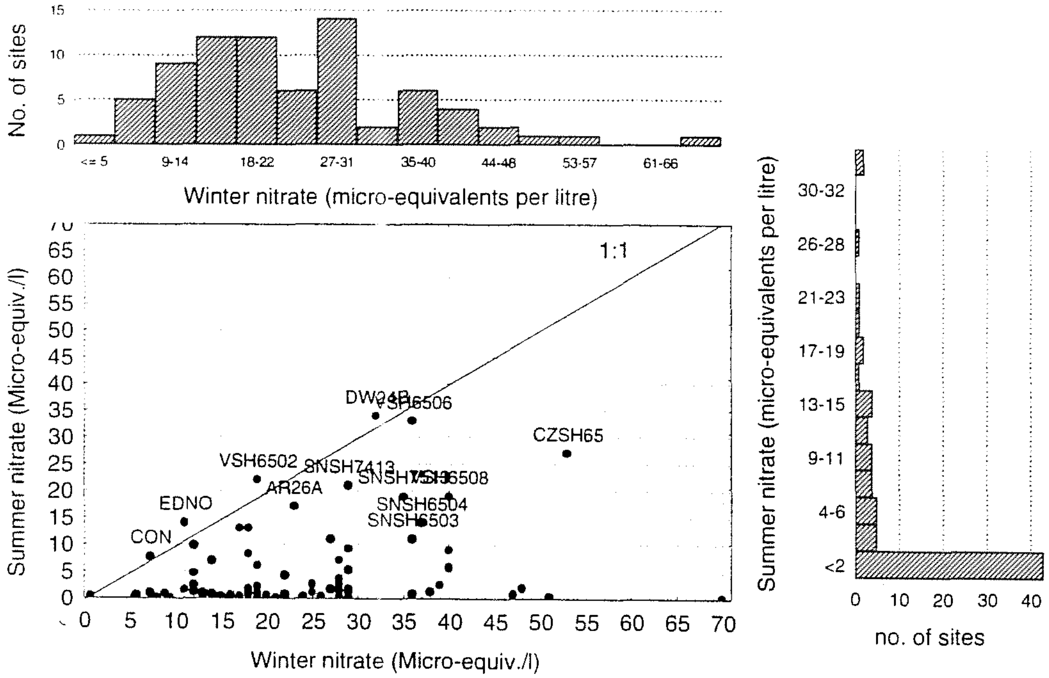


Fig 2: Distribution of NO_3^- values in summer and winter sample

grass/moorland catchments often exhibit summer minima and winter maxima (Edwards *et al.*, 1985; Reynolds *et al.*, 1992). This pattern is also observed in upland afforested catchments (Roberts *et al.*, 1984; Reynolds *et al.*, 1989) although summer maxima have also been noted in forest streams (Stevens et al., 1993). N cycling in pristine environments is dominated by plant and microbial uptake with measurable concentrations of oxidised and reduced N only occurring following snowmelt or storm conditions (Stoddard, 1994). At nearly all study sites, nitrate levels are higher during the winter when biological activity in the catchments is reduced. However, there are a number of lakes on or around the 1:1 line where summer and winter NO_3^- concentrations are similar. Most of these sites (e.g. AR26A, DW24B, VSH6506) are among the highest altitude lakes in the study area. With one exception, all study lakes here have winter NO_3^- values greater than the 4 eq l^{-1} adopted by Kämäri *et al.*, (1992) as a background level (although it should be noted that surface waters in low deposition areas of northern Scotland have NO_3^- concentrations < 1 µeq l^{-1}). Even during the growing season, 37% of lakes exceed this value, indicating incomplete assimilation of N into the terrestrial biomass. Where NH_4^+ has been detected (at about half the lakes) concentrations are generally low although maximum values of 13 µeq l^{-1} and 7 µeq l^{-1} were observed in summer and winter, respectively (Table 3).

4.2 Contribution of NO_3^- to mineral acidity

The contribution of NO_3^- to total non-marine acid anions can be assessed by examining NO_3^- as a proportion of mineral acidity (NO_3^- / NO_3^- + non-marine SO_4^{2-}). This has been termed the N-acidification ratio (Henriksen *et al.*, 1997). Figure 3 shows cumulative frequency curves for the N-acidification ratio (NAR) for the winter and summer samples. In winter, NAR varies between just above zero to 0.5 and at almost 50% of the lakes NO_3^- contributes over 25% of total mineral acidity. Comparison with the cumulative frequency curve of NAR for the July samples highlights the effect of seasonality on the relative contribution of NO_3^- to strong anion concentration. The summer samples have a much more skewed NAR distribution relative to winter NAR, (which approximates a normal distribution). Almost 75% of lakes have summer NAR values of less than 0.1 suggesting that the biomass utilisation of N species is buffering the surface waters against N derived acidity in summer, reducing its importance relative to the contribution of SO_4^{2-}.

4.3 Relationship between NO_3^-, NH_4^+, NAR and catchment attributes

Redundancy analysis (RDA) was undertaken using NO_3^-, NAR and NH_4^+ from both the winter and summer samples as response variables and the variables representing catchment attributes (described above) as explanatory variables. The purpose was to produce a correlation biplot (Fig. 4) which allows the structure of the relationships between the chemical determinands and catchment variables to be explored synoptically. Chemical and catchment variables are plotted, together with sites, relative to ordination axes. These axes represent the primary gradients of variation within the structure of the data, both in terms of the chemistry and the catchment variables, the former constrained to be linear combinations of the latter. The vectors point in the direction of maximum variation, the length being proportional to this variation. Where the angle between vectors is acute the variables are inferred to be positively correlated, the correlation increasing proportionally with the length of the vector. Obtuse angles signify negative correlations. The angles described between variable vectors and the axes can be interpreted similarly so that a variable with a long vector describing an acute angle with Axis 1 is highly correlated with it. The position of the sites in the biplot initially depends on chemical composition. Sites are arranged so that the distance between them reflects their dissimilarity. The position of a site relative to the arrowhead of a chemical or catchment vector indicates approximately where that site lies along the range of that variable.

Figure 4 shows that the main chemical gradient is associated with variation in NO_3^- and NAR, both in winter and summer. Sites vary positively along this axis so that lakes with high values for these variables (e.g. AR26A, CZSH65) are positioned to the right of the biplot. Axis 2 is associated with summer and winter NH_4^+ with the latter exhibiting the greater variance. The key catchment variables driving the variation along Axis 1 are rainfall, percentage bare ground (Bare) and maximum catchment altitude (Alt_m). Inter-set correlations between Axis 1 and all other variables have moduli of <0.5 indicating that they do not contribute substantially to variation in NO_3^- and NAR (ter Braak, 1990). Axis 2 is associated mostly with variation in site altitude (Alt_s), lake to catchment ratio (L:C), soil pH (pH_soil) and deciduous woodland (Wood_dec). However, none of these variables have interset correlations with a modulus >0.5 suggesting that factors outside those represented by the variables used are responsible for variation in NH_4^+. It may be that local, catchment specific mechanisms (e.g. clearfelling or upland pasture improvement) may be more important here. The majority of land cover and soil variables do not appear influential in the analysis. The empirical study by Dise and Wright (1995) was also characterised by a large number of catchment variables (including many of the soil chemistry variables used here) which were not significantly correlated with N leaching and concluded that either the importance of these were overshadowed by N deposition or that there were insufficient data to assess their importance.

To assess the level of explanation offered by the catchment attributes a series of RDAs was undertaken using NO_3^-, NH_4^+, and NAR as individual response variables. This approach results in a single constrained axis (ter Braak, 1987) and is akin to multiple regression with the eigenvalue for this axis indicating how much of the variation in the response variable can be explained by the catchment attributes. To eliminate collinearity and reduce the likelihood of spurious explanation often associated with large numbers of predictors (Økland and Eilertson, 1994) forward selection was implemented in CANOCO. This allows a minimum set of statistically significant variables to be identified that explain the chemistry data almost as well as the full set (ter Braak, 1990). Variables are selected iteratively and the significance of each is tested using Monte Carlo permutations (ter Braak, 1990). Table 4 summarises the results of these analyses. The catchment data account for much more of the variation in NAR than NO_3^- in both the winter and summer samples. The greatest difference in NO_3^- concentration appears to be between vegetated and non-vegetated catchments as evidenced by the importance of percentage bare ground which accounts for 25% and 28% of the NO_3^- variation in the winter and summer samples, respectively. Catchments dominated by bare ground (with limited vegetation and little soil cover) are associated with high NO_3^- concentrations. Whereas percentage bare ground is the only explanatory variable identified following forward selection of the summer data, soil pH and percentage coniferous woodland also explains a small but statistically significant amount of variation in NO_3^- in the winter sample. In summer, bare ground is also the dominant explanatory variable in terms of NAR values, accounting for over half the variance. Rainfall is also significant during

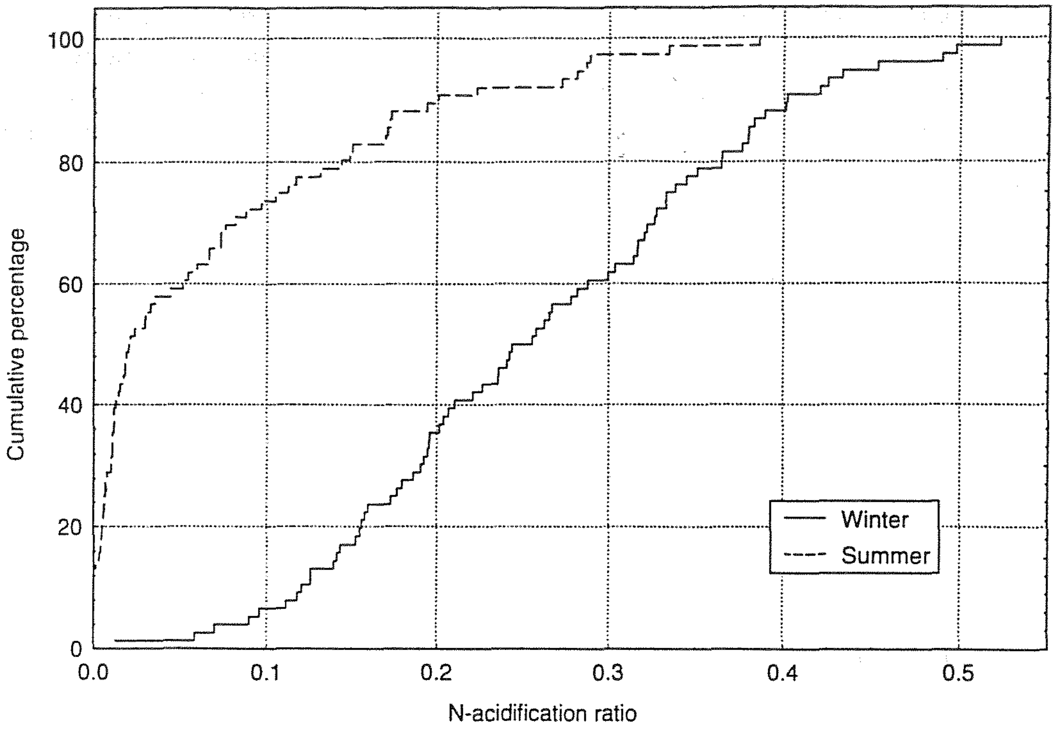


Figure 3: Cumulative frequency curves for N-acidification ratio (winter and summer)

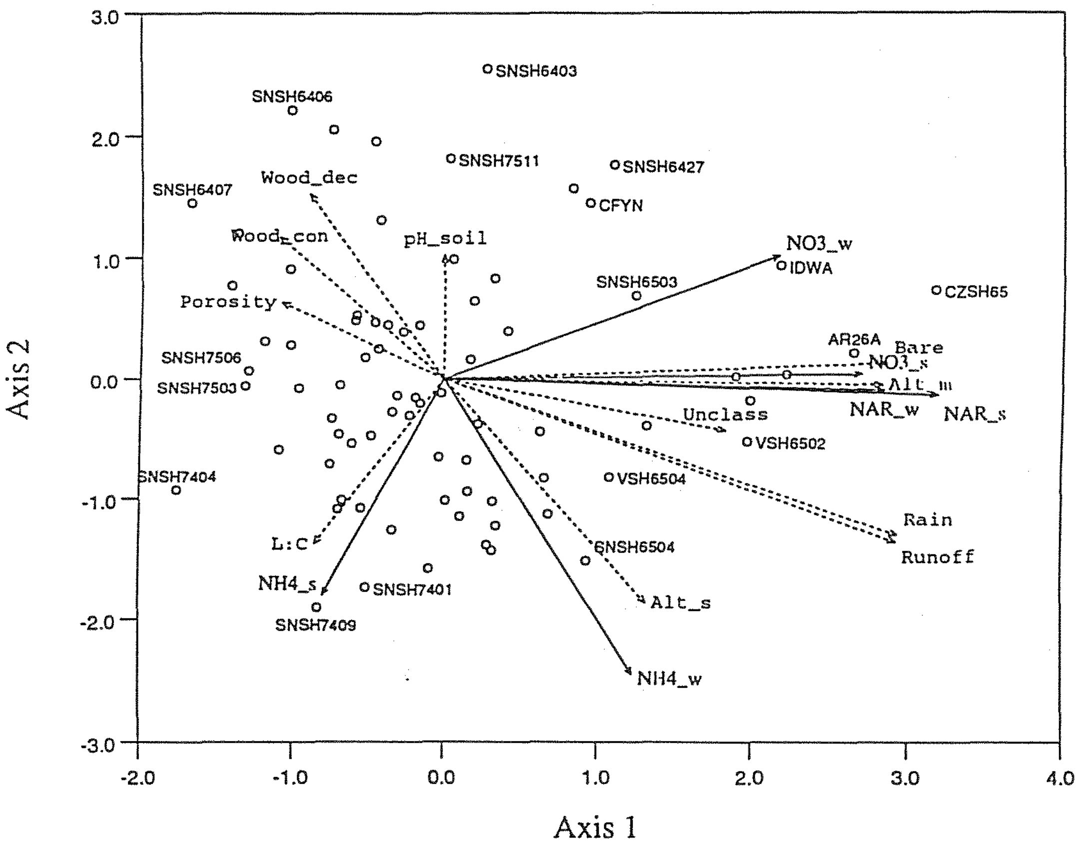


Figure 4: Redundancy analysis correlation biplot of chemistry (solid vectors) and catchment (broken vectors) variables (Plotted using CALIBRATE – Juggins and ter Braak, 1993). Sites are represented by open circles. The chemistry and catchment variable vectors have been multiplied x 4 for clarity. Variables with very short vectors have been omitted. Response variables have been centred and standardised See Table 2 for variable codings.

Table 4
Catchment attributes identified as significantly explaining variation in NO_3^-, NH_4^+ and NAR. Monte Carlo Permutation tests were used to determine significance, initially at the 5% level. Thereafter, Bonferroni adjustment was used to prevent too many variables being judged significant (Manly, 1992)

Response Variable	Total Variance Explained	Significant explanatory variables (with cumulative extra fit). - see table 2 for definitions - signs indicate positive (+) or negative (-) relationships
NO_3^- (winter)	24.6%	Bare (13%)+, pH_soil (20%)+, Wood_con (25%)+
NO_3^- (summer)	27.7%	Bare (28%)+
NH_4^+ (winter)	19.0%	Alt_s (19%) -
NH_4^+ (summer)	7.0%	G_m_upl (7%) -
NAR (winter)	51.6%	Runoff (48%)+, L:C (52%)+
NAR (summer)	46.2%	Bare (39%)+, Rainfall (46%)+

NB: Inferred correlations in Fig 4 area based on multivariate relationships between explanatory and response variables across more than one gradient. In RDA with a single response variable there is only gradient and this may explain why the vectors plotted in Fig 4 suggests a negative relationship between coniferous woodland and NO_3^- concentration whereas the forward selection procedure indicates the converse.

summer. In the winter sample, variation in NAR is predominantly explained by runoff (48%) with an additional 4% accounted for by lake to catchment ratio. Catchment variables are relatively poor predictors of NH_4^+. In summer, only percentage upland grass/moor (G_m_upl) emerged from the forward selection procedure explaining 7% of the variation in NH_4^+. Maximum catchment altitude accounts for 19% of NH_4^+ variation in winter.

5. Discussion

A key concern with regard to selection of the study area was to focus on catchment response to atmospheric deposition of N. However, with the data used, it is not possible to determine whether enhanced NO_3^- concentrations in these lakes has resulted from the effects of upland agricultural improvement as has been observed elsewhere in Wales (Roberts *et al.*, 1984, 1986; Hornung *et al.*, 1986). Nevertheless, most of these catchments contain no agricultural grassland or arable farming thus minimising the potential N loading from these sources. Additionally, most coniferous forestry is of mature age and does not require application of fertiliser. It is assumed here therefore that NO_3^- concentration reflects elevated N inputs from atmospheric rather than terrestrial sources.

Nitrate concentrations varied significantly across the study area. In summer these ranged from below detection limit to 34 μeq l^{-1} although most sites exhibited concentrations considerably lower than this upper limit. Similar levels occur in stream sites throughout upland Wales (Reynolds et al., 1994). For the winter sample the range extends to 70 μeq l^{-1} which is very high for upland areas where, typically, concentrations are <8 μeq l^{-1} (Reynolds and Edwards, 1995) Most of the study lakes show a high degree of seasonality with lower NO_3^- concentrations during the growing season. Seasonal variation of N deposition may be a factor with higher levels reported during winter months (Donald *et al.*, 1990; Reynolds *et al.*, 1992; INDITE, 1994). However, it is clear that NO_3^- is also leaching in summer from a large number of sites and at some the seasonal signal is absent (see Fig. 2). Elevated NO_3^- concentrations during the growing season suggest a dampening of the seasonal pattern in N cycling and may indicate that catchments are saturated according to the scheme proposed by Stoddard (1994). The saturation stage criteria for sites with infrequent samples (Stoddard and Traaen, 1995) proposes that sites with more than two samples where $NO_3^- > 5$ µeq l^{-1} should be classed as Stage 2. N retention in these catchments is reduced as biological demand no longer controls N cycling and under these circumstances mineralisation and nitrification, in combination with deposition can modify catchments so that they become a net source of N rather than a sink (Stoddard, 1994). If this classification is applied to these data, approximately one third of the catchments are likely to be classed at Stage 2.

The presence of NH_4^+ in some lakes may also be indicative of N saturation as microbial demand, vegetation uptake and ion exchange usually limit leaching of NH_4^+ (Stoddard, 1994). However, it is also possible that nitrification in some catchments is inhibited by site specific factors (e.g. C:N ratios, soil moisture and temperature) or that NH_4^+ is being produced within the lakes.

At many sites NO_3^- contributes significantly to acidity as measured by the N-acidification ratio (NAR). This ratio also exhibits a strong seasonality. At 50% of sites winter NAR is above 0.25 whereas in summer at 75% of sites it is less than 0.1 (Fig. 3). Nitrate is making a significant contribution to the acidification of runoff primarily during the winter months. However, at a number of sites NO_3^- is also a significant contributor to acidity during the growing season (NAR > 0.2 at 10% of sites). Similar ranges for NAR have been noted at upland sites throughout the UK (Jenkins *et al.*, 1996), in heavily impacted areas in Europe (Henriksen and Brakke, 1989; Henriksen *et al.*, 1997) and in North America (Stoddard, 1994). With continued N loading onto these catchments it is probable that the number of lakes where N makes a significant contribution to acidity in summer will increase. If sites become N saturated, the biological control on N cycling is removed and the potential for acidification is greater.

The multivariate statistical analyses sought to characterise the catchments currently leaching N. At a simplistic level NO_3^- leaching is equal to the sum of N deposition, nitrification and external addition less uptake and denitrification (Ferrier *et al.*, 1995). Although the empirical relationships described here are not based on explicit parameterisation of these terms, the use of surrogates based on soil physical and chemical attributes and land cover is intended to represent these key processes.

The key variable driving variation in lake-water NO_3^- concentration is percentage bare ground in the catchment. Catchments with a high proportion of bare ground tend to exhibit elevated lake NO_3^- levels. These catchments have little or no soil or vegetation and therefore lack the N retention capabilities of forest and moorland catchments where N is taken up during the growing season. It may be that there is no biological or microbial uptake during the growing season either due to a lack of soils and vegetation in the catchments or because these catchments are N saturated in excess of biological demand. At higher altitudes where thin soils, steep slopes and high precipitation levels combine to produce high runoff the role of soil and vegetation in N retention is superseded by hydrological controls (Kaste *et al.*, 1997). In small upland catchments characterised by rapid storm flow the interaction between the N in soil solution and the soil and biota is reduced which will influence the impact on surface water NO_3^- concentration of the N cycling processes described above. However, without more detailed, catchment specific, soil and deposition data it is not possible to determine whether leaching at these sites is due to hydrological factors or as a result of N saturation (or some combination of both).

In the summer sample, percentage bare ground accounts for all explained variation (28%) in lake-water NO_3^- concentration. During the growing season, catchments with extensive vegetation and soil cover, where biological demands and edaphic controls dominate N cycling, retain all or most deposited N. These contrast with those catchments with thin soils and sparse vegetation, with limited biological demand, or where N leaching is in steady state with respect to deposition, which are leaching most or all atmospheric N inputs.

In the winter sample percentage bare ground is less important in comparison with the summer sample and a combination of percentage coniferous woodland and soil pH are responsible for almost half the explained NO_3^- variation. Both vary positively with NO_3^- concentration. The amount of plantation forestry in the catchment explains an extra 5% of the variation. The role of forestry in N cycling and deposition scavenging is well documented (Fowler *et al.,* 1989; Reynolds *et al.,* 1989). Increased NO_3^- leaching from forested catchments has been observed in mid and north Wales where N inputs exceed tree and microbial requirements (Stevens *et al.,* 1994). Stand age has been found to be of particular significance with NO_3^- concentrations increasing with plantation age (Reynolds *et al.,* 1994; Stevens *et al.,* 1992). Although data relating specifically to stand age were not available for this study, observations in the field confirmed that most forestry in the catchments sampled is relatively mature, suggesting that the effects of N deposition onto the forest canopy are of more significance than uptake. Additionally, there are other processes impacted by forestry which may influence N leaching including mineralisation and nitrification in forest floor soils beneath mature trees (Emmett *et al.,* 1993; Reynolds *et al.,* 1994). Seasonality in NO_3^- concentrations has been observed in older forests where the large amounts of mineral N in the soil accumulated in the summer are leached out following autumn rains (Reynolds *et al.,* 1994) which is in keeping with the positive relationships identified between coniferous woodland and NO_3^- concentration in the winter sample.

The significance of soil pH in the winter sample is not clear. The positive relationship between this variable and lake water NO_3^- concentration in winter indicates that catchments where soil pH is relatively high are associated with elevated NO_3^- concentrations . Traditionally, production of NO_3^- through nitrification was thought to be favoured by high soil pH (e.g. Aber et al., 1989) although it is now believed that nitrification does occur in very acid soils (Gundersen and Rassmussen, 1990) assuming the supply of NH_4^+ is adequate (Stoddard, 1994). In areas of high N deposition, catchments with deep soils and gentle slopes are characterised by longer soil water residence times which can lead to increased pools of soil N and enhanced nitrification (Dise and Wright, 1995). Conversely, increased runoff from thin acid soils overlying steep slopes can bypass the biological controls on N cycling and raise NO_3^- levels in surface waters (Kaste et al., 1997). Indeed, nitrate leaching to surface waters may be associated with high or low soil pH (Dise and Wright, 1995). In the study area, the catchments with the lowest pH values occur on the acid raw peats in the south east whereas higher soil pH is found in catchments with high proportions of coniferous forestry planted on deeper mineral soils. It may be that the significance of soil pH in this analysis is an artefact, reflecting the mechanisms which give rise to elevated NO_3^- concentrations in forested catchments.

Redundancy analysis with the nitrate acidification ratio (NAR) as a sole response variable reveals that, with regard to the summer sample, bare ground is once again the most important variable. Catchments with large areas of bare ground exhibit higher lake NAR values. Thus NO_3^- contributes proportionally more to the acidity of these lakes than those in catchments where the soil and vegetation cover, and consequently, microbial and vegetation requirements are more extensive. Rainfall accouts for an additional 7% of the NO_3^- variation in the summer sample. Higher lake-water NO_3^- levels are found in catchments with higher rainfall. Rainfall data used here represents a yearly value and reflects altitude, with orographic enhancement increasing precipitation levels. High altitude lakes will also tend to be characterised by poor soil and vegetation coverage.

In summer, 48% of NAR variation is explained by runoff alone with high runoff values being associated with high NAR values. The runoff data employed represent mean annual totals thus no seasonal patterns are imposed on the analysis. The importance of runoff may be due to the coincidence of high runoff, thin soils and steep slopes at elevated altitudes, coupled with orographically enhanced precipitation levels. As with the summer sample, NO_3^- contributes relatively more to lake acidity where the paucity of soil and vegetation coverage limits catchment N retention. The amount of bare ground in the catchment is less important in winter because the reduced biological processes outside the growing season means there is less contrast between catchments with little soil and vegetation and those where soils are deeper and vegetation more abundant. It may be that N leaching to surface waters is driven by catchment hydrology during winter whereas biological controls are more important during the growing season.

Lake to catchment ratio (L:C) is also statistically significant in the winter sample explaining an extra 4% extra of the variation in NAR with catchments with high NAR values characterised by low lake to catchment ratios. This relationship is primarily driven by high altitude lakes with low L:C values but high proportions of bare ground. In lake catchments where soil and vegetation cover are minimal it has been suggested that the most important sink for N is the lake itself (Kelly *et al.*, 1987). In-lake retention of N is a function of runoff and lake to catchment area ratio (Kelly *et al.*, 1987). Thus the increased contribution of NO_3^- to acidity in these lakes may be due to a combination of thin soils and sparse vegetation in the catchment and the greater N retention in systems with low lake to catchment ratios (e.g. Henriksen, 1994).

A key consideration is whether the strong relationships between NO_3^- and bare ground reflect different deposition inputs due to altitudinal enhancements (Fowler *et al.*, 1988) as catchments with thin soils and sparse vegetation tend to occur at higher altitudes. UK N deposition levels are available on a 20 x 20 km grid square basis (RGAR, 1997) and the study area is characterised by a single mapped deposition value for each of the mapped species. This value does not account for the catchment scale variations in altitude, aspect and vegetation cover which are important in deposition processes (Ross and Linberg, 1994). The highest lake-water NO_3^- concentrations in winter occur to the north-east of the study area, in catchments above 600 m and in forested catchments in the north and south. Elevated nitrate levels in the summer are also associated with the higher altitude catchments. However, bare ground is the single most important variable explaining variation in both NO_3^- and NAR suggesting that these relationships are not exclusively deposition driven because S deposition is also enhanced at altitude (RGAR, 1997). Thus if deposition alone was responsible for elevated NO_3^- concentrations at higher altitudes, there would be no relationship between NAR and altitude.

The variables used in these analyses do not represent several important mechanisms and attributes which have been identified as key modifiers of N cycling in catchments. The N status of soils can impact on catchment loss of N (Stoddard and Traaen, 1995). The existence of large N pools within the soil means that microbial processes will not be N limited and consequently, may contribute to N leaching (Johnson, 1992) and % soil N has been correlated with N leaching in empirical studies (Dise and Wright, 1995). C:N ratios are also important with low ratios favouring nitrification (Dise and Wright, 1995). These data were not available from soil survey datasets. With regard to vegetation, data relating to stand age (for forestry) and vegetation type would be useful. More generally, the use of catchment specific data (e.g. soil samples) would be preferable to the averaged profile data used to characterise the catchment soils. It would also be useful to examine sites where more frequent sampling has been undertaken so that the response data can approximate mean conditions. The use of spot samples in this respect may lead to the modelling of unrepresentative responses. High density deposition monitoring data would also be useful to allow for variation in deposition data.

6. Conclusions

There is clear evidence of elevated NO_3^- concentrations due to N deposition within the study area. Similar levels in upland catchments have also been observed at regional and national scales (Allott *et al.*, 1995; Reynolds *et al.*, 1994). A significant contribution by NO_3^- to surface water acidity is apparent. Currently this impact is greater outside the growing season, reflecting the seasonal dynamics of N cycling. Elevated N deposition levels may lead, initially, to increased NO_3^- concentrations outside the growing season when N uptake is lower and precipitation levels (and snowmelt) are more important (Mulder *et al.*, 1997). However, a number of sites in the study area are also impacted during the summer and if N loadings to these continue it may be that summer breakthrough will become more widespread should deposition (and catchment N generation) exceed biological demand. Currently the catchments where N breakthrough appears to have occurred tend to be those at high altitude with limited soil and vegetation. These may already be in steady state with respect to N deposition and leaching. However at some future steady state, with continued orographic N loading, high altitude moorland catchments with relatively limited N retention capacities and catchments with maturing forestry or where clearfelling has occurred may be vulnerable to N leaching. Nitrogen saturation may occur in these catchments once the N sinks can no longer assimilate elevated deposition levels. Lakes may be particularly susceptible to acidification in catchments where these conditions are coupled with poorly buffered soils and geology.

Acknowledgements

This work was funded by the UK Department of Environment, Transport and the Regions as part of the critical loads research programme (Contract EPG1351). Additional support was provided by the NERC Environmental Diagnostics Freshwater Critical Loads Programme. The authors thank FFL for analytical chemistry, the Institute of Hydrology for rainfall and runoff data, the Institute of Terrestrial Ecology for the use of the Land Cover Database, OS for permission to digitise topographical maps and SSLRC for the use of soils data. We are indebted to colleagues at ECRC for assistance with fieldwork.

References

Aber, J.D., Nadelhoffer, K.J., Streudler, P. and Melillo, J. (1989) Nitrogen saturation in northern forest ecosystems. *Bioscience* **39**, 378-386

Allott, T.E.H., Curtis, C.J., Hall, J., Harriman, R. & Battarbee, R.W. (1995) The impact of Nitrogen Deposition on Upland Surface Waters in Great Britain: A Regional Assessment of Nitrate Leaching. *Water, Air and Soil Pollution* **85**: 297-302

Ball, D.F., Mew, G. and MacPhee, W.S.G. (1969) *Soils of Snowdon*. Field Studies 3, 69-107.

Battarbee, R.W., Allott, T.E.H., Juggins, S.J., Kreiser, A.M., Curtis, C. and Harriman, R. (1986) Critical loads of acidity to surface waters - an empirical diatom-based palaeolimnological model. *Ambio* **25**, 366-369.

CLAG Freshwaters (1995) *Critical Loads of Acid Deposition for UK Freshwaters.* Report to the UK DoE by the Critical Loads Advisory Group, Sub-group on Freshwaters.

Curtis, C., Allott, T.E.H., Reynolds, B. & Harriman, R. (1998) The Prediction of Nitrate Leaching with the First-Order Acidity Balance (FAB) Model for Upland Catchments in Great Britain. *Water, Air and Soil Pollution* **105**, 205-215

Cresser, M., Killham, T.E. Edwards, T. (1993) *Soil chemistry and its applications.* Cambridge University Press, Cambridge, UK.

De Vries, W., Posch, M., Reinds, G.J. and Norton S.A. (1990) *Critical loads and their exceedance on forest soils in Europe.* Report 58 (revised version), DLO The Winand Staring Centre for International Land Soil and Water Research, Wageningen, The Netherlands.

Dillon, P.J. & Molot, L.A. (1990) The role of ammonium and nitrate retention in the acidification of lakes and forested catchments. *Biogeochemistry* **11**: 23-43

Dise, N.B. and Wright, R.F. (1995) Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management.* **71**, 153-161

Donald, A.P., Stoner, J.H., Reynolds, B., Oldfield, F., Rippey, B. and Natkanski, J. (1990) Atmospheric Deposition. In R.W. Edwards, A.S. Gee and R.W. Stoner (eds.) *Acid Waters in Wales.* Klewer Academic Publishers, London.

Edmunds, W.M. and Kinniburgh, D.J. (1986) The susceptibility of UK groundwaters to acidic deposition. *The Journal of the Geological Society* **143**, 707-720

Edwards, A.C., Creasey, J. and Cresser, M.S. (1985) Factors influencing nitrogen inputs and outputs in two Scottish upland catchments. *Soil Use Management* **1**, 83-87

Edwards, R.W., Gee, A.S. and Stoner, R.W. (1990) *Acid Waters in Wales.* Klewer Academic Publishers, London.

Emmett, B.A., Reynolds, B., Stevens, P.A., Norris, D.A., Hughes, S., Görres, J. and Lubrecht, I. (1993) Nitrate Leaching from Afforested Welsh Catchments - Interactions between Stand Age and Nitrogen Deposition. *Ambio* **22**, 386-394.

Ferrier, R.C., de Vries, W. and Warfvinge, P. (1995 The use of Dynamic Models for the Determination of Critical Loads for Nitrogen – Developments since Lökeberg. In M. Hornung, M.A. Sutton and R.B. Wilson (Eds.) *Mapping and modelling of critical loads for nitrogen – workshop report.* Report of a workshop held at Grange-over-sands, Cumbria on 24-26 October 1994.

Forsius, M., Kämäri. J. and Posch, M. (1992) Critical Loads for Finnish lakes: Comparison of three steady-state models. *Environmental Pollution* **77**, 185-193

Fowler, D., Cape, J.N., Leith, I.D., Choularton, T.W., Gay, M.J. & Jones, A. (1988) The influence of altitude on rainfall composition at Great Dun Fell. *Atmospheric Environment, 22,* 1355-1381

Fowler, D., Cape, J.N., & Unsworth, M.H. (1989) Deposition of atmospheric pollutants on forests. *Philosophical Transactions of the Royal Society* ***B234,*** 247-265

Fuller, R.M., Groom, G.B and Jones, A.R. (1994) The Land Cover Map of Great Britain; An Automated Classification of LANDSAT Thematic Mapper Data. *Photogrammatic Engineering and Remote Sensing* **60**, 553-562

Gosz, J.R. (1981) Nitrogen cycling in coniferous forests. In F.E. Clarke and T. Roswell (Eds.) Terrestrial Nitrogen Cycles. *Ecological Bulletin* **33**, 405-426.

Gundersen, P. and Rasmussen, L. (1990) Nitrification in forest soils: Effects from nitrogen deposition on soil acidification and aluminium release. *Review of Environmental Contamination and Toxicology* 113, 1-45

Hall, J., Hornung, M., Freer-Smith, P., Loveland, P., Bradley, I., Langan, S., Dyke, H., Gascoigne, J. & Bull, K. (1997) *Current status of UK critical loads data - December 1996.* Report to the Department of Environment, ITE Monks Wood, UK.

Harriman, R., Gillespie, E., King, D., Watt, A.W., Christie, A.E.G., Cowan A.A. and Edwards, T. (1990) Short-term ionic reponses as indicators of hydrochemical processes in the Allt a'Mharcaidh catchment, western Cairngorms. *Journal of Hydrology* **116**, 267-285

Harriman, R. and Wells, D.E. (1985) Causes and Effects of Surface Water Acidification in Scotland. *Journal of Water Pollution Control* **84**, 215-224

Harriman, R., Allott, T.E.H., Battarbee, R.W., Curtis, C., Jenkins, A. and Hall, J. (1995) Critical Loads of Nitrogen and their Exceedance in UK Freshwaters. In M. Hornung, M.A. Sutton and R.B. Wilson (Eds.) *Mapping and modelling of critical loads for nitrogen – workshop report.* Report of a workshop held at Grange-over-sands, Cumbria on 24-26 October 1994.

Henriksen A. (1994) Nitrogen "saturation" - partly a hydrological effect? *Nitrogen from Mountains to Fjords* - Newsletter 2/1994.

Henriksen, A. and Brakke, D.F. (1989) Increasing contribution of nitrogen to the acidity of surface waters in Norway. *Water, Air and Soil Pollution* **42**, 183-201

Henriksen, A., Kämäri., J., Posch, M., Lövblad, G., Forsius, M. and Wilander, A. (1990) *Critical Loads to Surface Waters in Fennoscandia – Intra- and Inter-grid Variability of Critical Loads and their Exceedance* Miljörapport 1990:17, Nordic Council of Ministers, Copenhagen 1990

Henriksen, A., Hindar, A., Hessen, D. and Kaste, Ø. (1997) Contribution of nitrogen to acidity in the Bjerkreim River in Southwestern Norway. *Ambio* **26**, 304-311

Hornung, M., Stevens, P.A. and Reynolds, B. (1986) The impact of pasture improvement on the soil solution chemistry of some stagnopodzols in mid-Wales. *Soil Use Management* **2**, 18-26

INDITE (1994) *Impacts of Nitrogen Deposition in Terrestrial Ecosystems.* Report of the UK Review Group on Impacts of Atmospheric Nitrogen Deposition. UK Department of Environment.

Jenkins, A., Boorman, D. and Renshaw, M. (1996) The UK Acid Waters Monitoring Network: an assessment of chemistry data, 1988-93 *Freshwater Biology* **36**, 169-178

Jenkins, A., Renshaw, M., Helliwell, R., Sefton, C., Ferrier, R. and Swingewood, P. (1997) *Modelling surface water acidification in the UK.* Report No. 131, Institute of Hydrology, Wallingford, UK.

Johnson, D.W. (1992) Nitrogen retention in forest soils. *Journal of Environmental Quality* **21**, 1-12

Juggins, S.J. and ter Braak. C.J.F. (1993) *CALIBRATE v 0.52 (Beta Test) – a computer program for species – environment calibration by [weighted averaging] partial least squares regression.* ECRC, University College London.

Kämäri, J., Jeffries, D.S., Hessen, D.O., Henriksen, A., Posch, M. and Forsius, M. (1992) Nitrogen critical loads and their exceedance for surface waters. In P. Grennfelt and E. Thörnelöf (Eds.) *Critical loads for Nitrogen, NORD 1992:41* Nordic Council of Ministers, Copenhagen, Denmark.

Kaste, Ø., Henriksen, A. and Hindar, A. (1997) Retention of Atmospherically-derived Nitrogen in Subcatchments of the Bjerkreim River in Southwestern Norway. *Ambio* **26**, 296-303

Kelly, C.A., Rudd., J.W.M., Hesslein, R.H., Schindler, D.W., Dillon, P.J., Driscoll, C.T., Ghereni, S.A. and Hecky, R.E. (1987) Prediction of biological acid neutralization in acid sensitive lakes. *Biogeochemistry* **3**, 129-140

Lawrence, , G.B. (1988) Whole tree harvesting of an acid sensitive watershed. In H. Barth (ed.), *Effects of Land Use in Catchments on the Acidity and Ecology of Natural Surface Waters.* Air Pollution Research Report 13.

Manly, B.J.F. (1992) *The Design and Analysis of Research Studies.* Cambridge University Press, Cambridge.

Mulder, J., Nilsen, P., Stuanes, A.O. and Huse, M. (1997) Nitrogen Pools and Transformations in Norwegian Forest Ecosystems with Different Atmospheric Inputs. *Ambio* **26**, 273-281.

Økland, R.H. and Eilertson, O. (1994) Canonical correspondence analysis with variation partitioning: some comments and an application. *Journal of Vegetation Science* **5**, 117-126

Posch, M. (1995) Critical Loads for Aquatic Ecosystems. In M. Hornung, M.A. Sutton and R.B. Wilson (Eds.) *Mapping and modelling of critical loads for nitrogen – workshop report.* Report of a workshop held at Grange-over-sands, Cumbria on 24-26 October 1994.

Posch, M., Kämäri, J., Forsius, M., Henriksen, A. and Wilander, A. (1997) Exceedance for critical loads for lakes in Finland, Norway and Sweden: rduction requirements for acidifying nitrogen and sulphur deposition. *Environmental Management* **21(2)**, 291-304

Reynolds, B. and Edwards, A. (1995) Factors influencing dissolved organic nitrogen concentrations and loadings in upland streams of the UK. *Agricultural Water Management* **27**, 181-202.

Reynolds, B., Hornung, M. and Hughes, S. (1989) Chemistry of streams draining grassland and forest catchments at Plynlimon, mid-Wales. *Hydrological Sciences Journal* **34**, 667-686

Reynolds, B., Emmett, B.A. and Woods, C. (1992) Variations in streamwater nitrate concentrations and nitrogen budgets over 10 years in a headwater catchment in mid-Wales. *Journal of Hydrology* **136**, 155-175

Reynolds, B., Ormerod, S.J. and Gee, A.S. (1994) Spatial patterns in stream nitrate concentrations in upland Wales in relation to catchment forest cover and forest age. *Environmental Pollution* **84**, 27-33.

RGAR (1997) *Acid Deposition in the United Kingdom 1992-1994.* Fourth Report of the Review Group on Acid Rain, Department of Environment, Transport and the Regions.

Roberts, G., Hudson, J.A. and Blackie, J.R. (1984) Nutrient inputs and outputs in a forested and grassland catchment at Plynlimon, mid-Wales. *Agricultural Water Management* **9**, 177-191

Roberts, G., Hudson, J.A. and Blackie, J.R. (1986) Effect of upland pasture improvement on nutrient release in flows from a 'natural' lysimeter and a field drain. *Agricultural Water Management* **11**, 231-245

Ross, H.B. and Lindberg, S.E. (1994) Atmospheric Chemical Input to Small Catchments. In Moldan, B. and Cerný, J. *Biogeochemistry of Small Catchments: A Tool for Environmental Research.* John Wiley & Sons Ltd, Chichester, England, pp. 55-84.

Rudeforth, C.C., Hartnup, R., Lea, J.W., Thompson, T.R.E. and Wright, P.S. (1984) *Soils and their use in Wales.* Soil Survey of England and Wales Bulletin No. 11, Harpenden, UK.

Smith, B. & George, T.N. (1948) *British Regional Geology: North Wales.* HMSO, London

Stevens, P.A., Ormerod, S.J. and Reynolds, B. (1997*) Final Report on the Acid Waters Survey for Wales.* Institute of Terrestrial Ecology (NERC) Project T07072R5

Stevens, P.A., Norris, D.A., Sparks, T.H. and Hodgson, A.L. (1994) Nitrate leaching losses from Sitka Spruce forests and moorlands in Wales. Wate, *Air and Soil Pollution* **73**, 297-317.

Stevens, P.A., Williams, T.G., Norris, D.A. and Rowland, A.P. (1993) Dissolved inorganic nitrogen budget for a forested catchment at Beddgelert, North Wales. *Environmental Pollution* **80**, 1-8

Stevens, P.A., Norris, D.A., Emmett, B.A., Gomes, J., Reynolds, B., Hughes, S., Williams, T.G., Sparks, T.H. and Lubrecht, W.C. (1992) *Annual Report for 1991 of the Nitro- gen Deposition Manipulation Study, 1.* Forest Nitrogen Survey. Report to the National Power/Powergen Joint Environmental Programme, Institute of Terrestrial Ecology, Bangor.

Stoddard, J.L. (1994) Long-Term Changes in Watershed Retention of Nitrogen - Its Causes and Aquatic Consequences. In L.A. Baker (ed.), *Environmental Chemistry Of Lakes and Reservoirs*, ACS Advances in Chemistry Series No. 237, American Chemical Society, Washington D.C.

Stoddard, J.L. and Traaen, T.S. (1995) The Stages of Nitrogen Saturation: Classification of Catchments include in "ICP on Waters". In M. Hornung, M.A. Sutton and R.B. Wilson (Eds.) *Mapping and modelling of critical loads for nitrogen – workshop report.* Report of a workshop held at Grange-over-sands, Cumbria on 24-26 October 1994.

ter Braak, C.J.F. (1987) *CANOCO – a FORTRAN Program for CANOnical Community Ordination by [Partial] [Detrended] [Canonical] Correspondence Analysis, Priciple Components Analysis and redundancy Analysis (Version 3.1)* Agricultural Mathematics Group, Wageningen.

ter Braak, C.J.F. (1990) *Update notes: CANOCO Version 3.10.* Agricultural Mathematics Group, Wageningen.

ter Braak, C.J.F. (1994) Canonical community correlation. Part 1: basic theory and linear methods. *Ecoscience* **1**, 127-140.

Thompson, T.R.E. and Loveland, P.J. (1985) The acidity of Welsh soils. *Soil Use and Management* **1**, 21-24

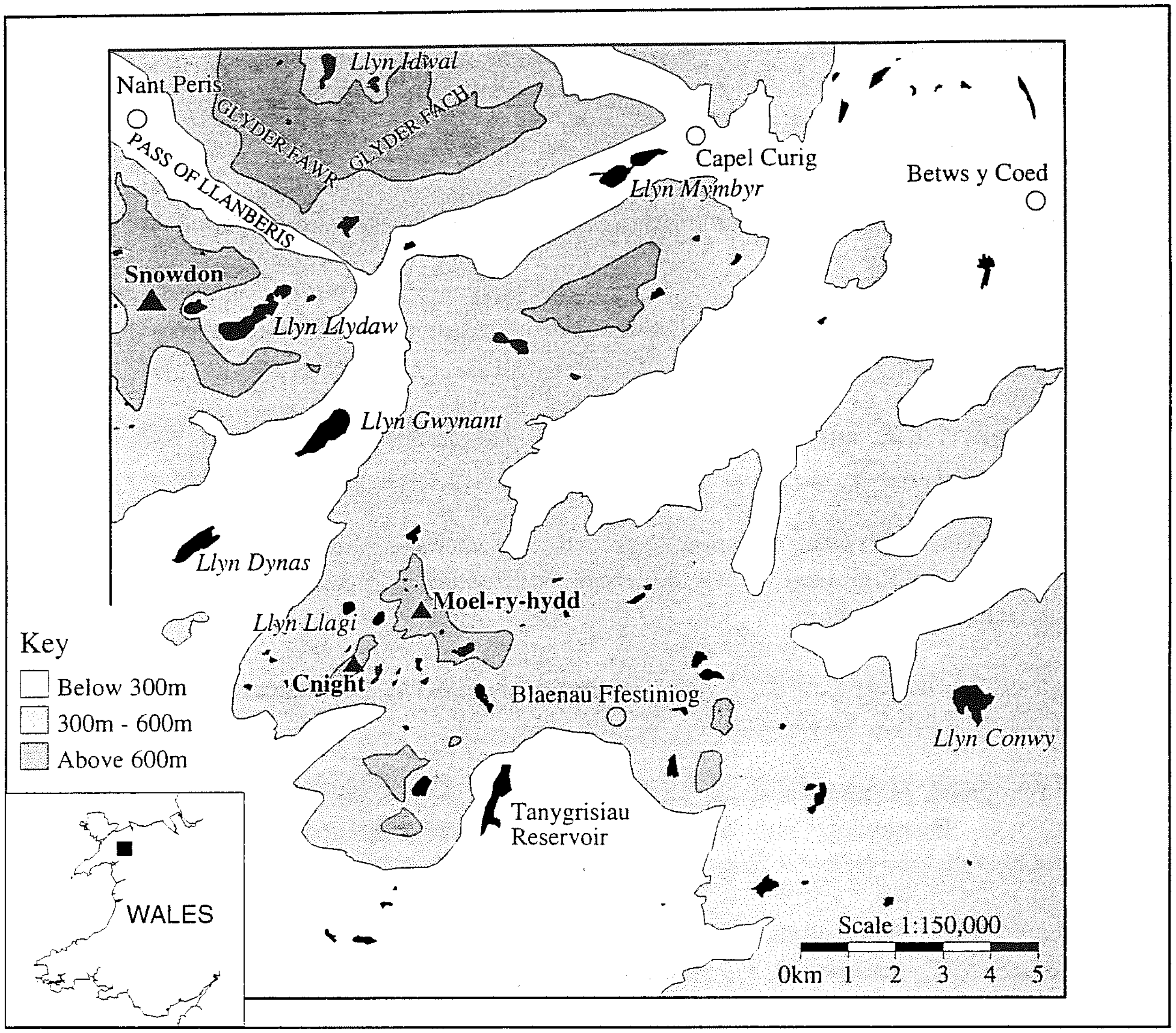
UKAWMN (1997*) United Kingdom Acid Waters Monitoring Network: summary of data for Year 9 (1996-1997).* Edited by D.T. Monteith, M.Renshaw, C.Evans and W.R.C. Beaumont. ENSIS Publishing, London.

Van den Wollenburg, A.L. (1977) Redundancy analysis. An alternative for canonical correlation analysis. *Psychometrika*, **42,** 207-219

Van Miegroet, H. and Johnson, D.W. (1993) Nitrate Dynamics in Forest Soils. In T.P. Burt, A.L. Heathwaite and S.T. Trudgill (Eds.) *Nitrate: Processes, Patterns and Management.* John Wiley & Sons Ltd., England.

Vincent, K.J., Campbell, G.W., Downing, C.E.H., Hasler, S.E., Davies, M., Stedman, J.R., Sansom, L.E., Briscombe, C. & Page, H.M. (1997) *Acid deposition monitoring in the United Kingdom: the first ten years.* Report AEAT/20017110/REMA-304. AEA Technology, Culham, UK.

Williams, D. and Ramsay, J.G. (1959) *Geology of some Classic British Areas: Snowdonia.* Geologists' Association Guides No. 28. Benham & Company Limited, Colchester.


Llyn Idwal
Nant Peris
GLYDER FAWR
GLYDER FACH
PASS OF LLANBERIS
Capel Curig
Llyn Mymbyr
Betws y Coed
Snowdon
Llyn Llydaw
Llyn Gwynant
Llyn Dynas
Moel-ry-hydd
Llyn Llagi
Cnight
Blaenau Ffestiniog
Llyn Conwy
Tanygrisiau Reservoir
Key
Below 300m
300m - 600m
Above 600m
WALES
Scale 1:150,000
0km 1 2 3 4 5