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

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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-hyd (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 individual 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

<table>
<thead>
<tr>
<th>Site name</th>
<th>Site Code</th>
<th>Easting</th>
<th>Northing</th>
<th>Site altitude (m)</th>
<th>Maximum catchment altitude (m)</th>
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<td>999</td>
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<td>354600</td>
<td>360</td>
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<td>340900</td>
<td>450</td>
<td>527</td>
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<td>355900</td>
<td>460</td>
<td>1041</td>
</tr>
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<td>CZ895B</td>
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<td>354600</td>
<td>480</td>
<td>1072</td>
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<tr>
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<td>460</td>
<td>500</td>
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Table 2
Summary of catchment variables used in the statistical analyses

<table>
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<tr>
<th>Code</th>
<th>Variable</th>
<th>Domination</th>
<th>Explanation</th>
</tr>
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<tbody>
<tr>
<td>HD</td>
<td>Bulk density</td>
<td>SS LOC</td>
<td>Catchment weighted soil bulk density</td>
</tr>
<tr>
<td>FTC</td>
<td>Carbon exchange capacity</td>
<td>SS LOC</td>
<td>Catchment weighted soil carbon exchange capacity</td>
</tr>
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<td>Ca_soil</td>
<td>Ca in soil</td>
<td>SS LOC</td>
<td>Catchment weighted soil Ca</td>
</tr>
<tr>
<td>Mg_soil</td>
<td>Mg in soil</td>
<td>SS LOC</td>
<td>Catchment weighted soil Mg</td>
</tr>
<tr>
<td>K_soil</td>
<td>K in soil</td>
<td>SS LOC</td>
<td>Catchment weighted soil K</td>
</tr>
<tr>
<td>Na_soil</td>
<td>Na in soil</td>
<td>SS LOC</td>
<td>Catchment weighted soil Na</td>
</tr>
<tr>
<td>pH_soil</td>
<td>Soil pH</td>
<td>SS LOC</td>
<td>Catchment weighted soil pH</td>
</tr>
<tr>
<td>Soil_OC</td>
<td>Organic carbon in soil</td>
<td>SS LOC</td>
<td>Catchment weighted soil organic carbon</td>
</tr>
<tr>
<td>Top_OC</td>
<td>OC in top soil horizons</td>
<td>SS LOC</td>
<td>Catchment weighted soil OC in upper horizons</td>
</tr>
<tr>
<td>Nbh_OC</td>
<td>OC in subsoil horizons</td>
<td>SS LOC</td>
<td>Catchment weighted soil OC in lower horizons</td>
</tr>
<tr>
<td>Porosity</td>
<td>Soil porosity</td>
<td>SS LOC</td>
<td>Catchment weighted soil porosity</td>
</tr>
<tr>
<td>Depth</td>
<td>Depth of soil</td>
<td>SS LOC</td>
<td>Catchment weighted soil depth</td>
</tr>
<tr>
<td>N nutrient</td>
<td>Nitrogen immobilisation</td>
<td>Hall et al., 1997</td>
<td>Catchment weighted Nitrogen immobilisation</td>
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<td>N_den</td>
<td>Nitrogen denitification</td>
<td>Hall et al., 1997</td>
<td>Catchment weighted Nitrogen denitification</td>
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<tr>
<td>Rainfall</td>
<td>Rainfall intensity</td>
<td>ITE Monks Wood</td>
<td>Catchment weighted rainfall</td>
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<tr>
<td>Runoff</td>
<td>Runoff intensity</td>
<td>ITE Monks Wood</td>
<td>Catchment weighted runoff</td>
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<tr>
<td>LA</td>
<td>Lake area (m²)</td>
<td>GIS - OS Map</td>
<td>Lake area</td>
</tr>
<tr>
<td>C catch</td>
<td>Catchment area (km²)</td>
<td>GIS - OS Map</td>
<td>Catchment area</td>
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<tr>
<td>LC</td>
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<td>GIS</td>
<td>Lake to catchment ratio</td>
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<tr>
<td>All</td>
<td>Site altitude (m)</td>
<td>OS Map</td>
<td>Site altitude</td>
</tr>
<tr>
<td>AB</td>
<td>Maximum altitude (m)</td>
<td>OS Map</td>
<td>Maximum altitude</td>
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<td>unclassified</td>
<td>ITE Monks Wood</td>
<td>Land cover type 'Not classified'</td>
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<td>Grassmoorland</td>
<td>ITE Monks Wood</td>
<td>Lowland semi - natural grass / moor</td>
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<tr>
<td>C2_gmo</td>
<td>Upland grassmoorland</td>
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<td>Upland semi - natural grass / moor</td>
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<tr>
<td>AP</td>
<td>Agricultural grassland</td>
<td>ITE Monks Wood</td>
<td>Arable and agricultural grassland</td>
</tr>
<tr>
<td>Wood</td>
<td>Deciduous woodland</td>
<td>ITE Monks Wood</td>
<td>Deciduous woodland</td>
</tr>
<tr>
<td>Wood</td>
<td>Coniferous woodland</td>
<td>ITE Monks Wood</td>
<td>Coniferous woodland</td>
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<tr>
<td>Soil</td>
<td>Bare ground</td>
<td>ITE Monks Wood</td>
<td>Bare ground</td>
</tr>
</tbody>
</table>

- [x] Weighted averaging equation: \( x = \sum \frac{A_i}{A} \times [x_i] \), where \([x_i]\) is a value for some physical or physical soil attribute for the catchment. A is the area of soil map series \( S \) and \([x]\) is the value for this attribute for soil map series \( S \). The denominator \( \sum A_i \) is taken over soil map series \( S \).
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

<table>
<thead>
<tr>
<th></th>
<th>Valid N</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Range</th>
<th>Variance</th>
<th>Std. Dev.</th>
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<td>NO$_3^-$</td>
<td>Winter</td>
<td>76</td>
<td>0.7</td>
<td>70.0</td>
<td>24.3</td>
<td>152.4</td>
<td>12.3</td>
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<tr>
<td></td>
<td>Summer</td>
<td>76</td>
<td>BD</td>
<td>34.0</td>
<td>5.5</td>
<td>60.21</td>
<td>7.8</td>
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<tr>
<td>NH$_4^+$</td>
<td>Winter</td>
<td>76</td>
<td>BD</td>
<td>7.0</td>
<td>1.7</td>
<td>2.7</td>
<td>1.7</td>
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<tr>
<td></td>
<td>Summer</td>
<td>76</td>
<td>BD</td>
<td>13.0</td>
<td>2.3</td>
<td>7.4</td>
<td>2.7</td>
</tr>
</tbody>
</table>

BD = Below detection limit All units in micro-equivalents 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$_3^-+\text{non-marine SO}_4^{2-}$). 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 inter-set 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 \( \text{NO}_3^- \), \( \text{NH}_4^+ \) 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).

<table>
<thead>
<tr>
<th>Response Variable</th>
<th>Total Variance Explained</th>
<th>Significant explanatory variables (with cumulative extra fit).</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NO}_3^- ) (winter)</td>
<td>24.6%</td>
<td>Bare (13%)+, ( \text{pH} ) <em>soil</em> (20%)+, ( \text{Wood} ) <em>con</em> (25%)+</td>
</tr>
<tr>
<td>( \text{NO}_3^- ) (summer)</td>
<td>27.7%</td>
<td>Bare (28%)+</td>
</tr>
<tr>
<td>( \text{NH}_4^+ ) (winter)</td>
<td>19.0%</td>
<td>( \text{Alt} ) <em>s</em> (19%) -</td>
</tr>
<tr>
<td>( \text{NH}_3^- ) (summer)</td>
<td>7.0%</td>
<td>( \text{G} ) <em>m_upl</em> (7%) -</td>
</tr>
<tr>
<td>NAR (winter)</td>
<td>51.6%</td>
<td>Runoff (48%)+, ( \text{L:C} ) (52%)+</td>
</tr>
<tr>
<td>NAR (summer)</td>
<td>46.2%</td>
<td>Bare (39%)+, ( \text{Rainfall} ) (46%)+</td>
</tr>
</tbody>
</table>

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 \( \text{NO}_3^- \) concentration whereas the forward selection procedure indicates the converse.

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 \( \text{NO}_3^- \) 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 \( \text{NO}_3^- \) 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 \( \text{NO}_3^- \) 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 \( \text{NO}_3^- \) is also leaching in summer from a large number of sites and at some the seasonal signal is absent (see Fig. 2). Elevated \( \text{NO}_3^- \) 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 NO₃⁻ > 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 NH₄⁺ in some lakes may also be indicative of N saturation as microbial demand, vegetation uptake and ion exchange usually limit leaching of NH₄⁺ (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 NH₄⁺ is being produced within the lakes.

At many sites NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ concentration is percentage bare ground in the catchment. Catchments with a high proportion of bare ground tend to exhibit elevated lake NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ variation. Both vary positively with NO₃⁻
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 NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ concentration in winter indicates that
catchments where soil pH is relatively high are associated with elevated NO₃⁻
concentrations. Traditionally, production of NO₃⁻ 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 NH₄⁺ 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 NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ 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 accounts for an additional 7% of the
NO₃⁻ variation in the summer sample. Higher lake-water NO₃⁻ 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.

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References


