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No. 79**

**SUMMARY OF RESEARCH UNDER DETR CONTRACT  
“ACIDIFICATION OF FRESHWATERS: THE ROLE OF  
NITROGEN AND THE PROSPECTS FOR RECOVERY”  
EPG/1/3/117**

**Work Package 1: Nitrogen**

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## Nitrogen: key points

- 1) Reviews of the recent literature have confirmed that for in-lake retention the model currently employed in FAB is appropriate for a wide range of sites within Europe as well as North America, but only for lakes where thermal stratification (winter or summer) does not develop over long periods. Site-specific evaluations should, however, be carried out where possible.
- 2) A literature review coupled with intensive field and laboratory experimentation has confirmed that the denitrification model in the UNECE Mapping Manual would lead to a significant overestimate of denitrified N fluxes in UK upland soils. It is recommended that the soil-specific, literature-derived values used in previous British FAB applications should continue to be used.
- 3) Since it has been confirmed that denitrification is only a minor sink for atmospheric N deposition, the high rates of N retention currently observed in upland catchments must be due mainly to immobilisation in soil organic matter.
- 4) Extensive regional surveys (Pennines, Wales) and intensive study within a single catchment at Lochnagar demonstrate a high degree of spatial variability in soil C and N content both between and within different soil types. It is difficult therefore to assume that the C/N ratio of a single soil sample is representative of an entire catchment.
- 5) In the moorland environments that characterise much of the UK uplands, soils are often peaty and much of the organic matter within them may be chemically inert. As a result, the whole-soil C/N ratio may be a poor predictor of catchment N immobilisation and (hence) leaching.
- 6) Results from the intensive study sites show that the surface organic horizons (top 5cm of soil profile) are the most biologically active in a variety of moorland soils and should have an important role in controlling nitrate leaching. Future work should therefore focus on this part of the soil profile.
- 7) Nitrification appears to be a key process in the active organic horizons, and may be inhibited in very acid soils, perhaps explaining the leaching of ammonium in the severely acidified Pennine region.
- 8) Soilwater nitrate concentrations do not correlate with streamwater concentrations for all the intensive study sites, but extractable soil nitrate does. This could be due to rapid nitrification in some soilwaters.
- 9) Spatial heterogeneity in the distribution of inorganic N between compartments and the key processes which control leaching occurs at several scales, with three catchments receiving rather similar inputs but having very different outputs, soil types behaving differently within catchments, and hotspots of activity occurring even within a given soil type.
- 10) Dynamic models in future must focus on adequate representation of the key factors controlling immobilisation/mineralisation/nitrification, representation of

both the active (labile) and inactive (refractory) C and N pools within the soil, and how to quantify these pools given the apparent spatial variability.

- 11) Finally, problems with catchment heterogeneity may be addressed by an alternative method of calibrating MAGIC to 'landscape types', rather than whole catchments. Since these defined landscape units should have more homogenous C and N characteristics than whole catchments, this approach has potential to provide a more accurate simulation of N leaching within MAGIC 7.
- 12) In general, the use of MAGIC 7 to derive target load functions for S and N deposition represents a significant step forward, whereby dynamic models may be used to aid the development, rather than simply assess the consequences, of emissions controls.
- 13) Revisions have been made to both the FAB model and the national mapping dataset, including the incorporation of sites previously without soils data, the inclusion of Northern Ireland, the omission of base cation deposition data, and model runs with both  $ANC_{crit} = 0$  and  $ANC_{crit} = 20 \mu eq l^{-1}$ .
- 14) A MAGIC7 model application to the Afon Gwy using changes in C/N ratio suggests that the 'steady state' condition of nitrate leaching assumed within FAB may take a very long time to attain, due to the requirement to change the N status of a very large organic pool. If correct, this result is significant in that it implies that FAB may provide a pessimistic prediction of surface water N concentrations (and therefore ANC) over shorter (e.g. < 100 year) timescales.

# Task1.1: Review values for catchment nitrogen sinks reported in the literature

C.Curtis

## **1.1 Review values for catchment nitrogen sinks reported in the literature**

The potential N sinks of greatest interest in this work programme are denitrification, the long-term immobilisation of N in soil organic matter, and in-lake retention of N. Net uptake of N in biomass is only significant if there is large scale removal of biomass from the catchment e.g. forestry. Since this work programme focuses mainly on moorland ecosystems (due to the large amount of ongoing work on forestry under the Terrestrial Umbrella programme), net N uptake is not considered further.

### **1.1.1 Denitrification**

A comprehensive review of the literature on denitrification from upland systems was carried out under Section 1.2 of this work programme (see below). Denitrification rates were found to be typically low in shallow, poorly developed upland soils (<2 kgN ha<sup>-1</sup> yr<sup>-1</sup>), rising to higher levels in deeper, poorly-drained organic soils (2-6 kgN ha<sup>-1</sup> yr<sup>-1</sup>). The literature default values used in previous national applications of the FAB model were confirmed as appropriate for British soils by this new review.

### **1.1.2 In-lake retention of acid anions and acidity**

#### **Summary**

Models of in-lake retention of acid anions have been developed from work carried out mainly in Canada. These models have since been applied elsewhere, including several countries in Europe, and found to adequately describe S and N retention in acid-sensitive lakes.

The key factors which determine the levels of S and N retention are water retention time and areal discharge. The retention processes are input-dependent, which means that retention rates (though not percentages) increase with loading. Processes which retain N tend to be more rapid than the most important S retention process of SO<sub>4</sub><sup>2-</sup> reduction and sedimentation.

For N the processes are more complex than for S. At very low inorganic N loadings, the major retention process is algal uptake and the mass-transfer coefficient is very large i.e. while absolute retention rates are small due to low availability of NO<sub>3</sub><sup>-</sup>, the proportion retained is very high. However, the process of algal uptake is often strongly P-limited in acid-sensitive lakes, so in most cases the predominant removal mechanism is denitrification. Under such circumstances the mass-transfer coefficients are smaller, since the process occurs only at the sediment-water interface rather than throughout the water column.

Likewise, where larger inputs of NO<sub>3</sub><sup>-</sup> lead to measurable concentrations in the lake all year round, the implication is that algal uptake is minimal (due either to algal N-saturation or severe P-limitation) and denitrification is the major removal mechanism, again resulting in lower mass-transfer coefficients.

The relative importance of S and N retention, in terms of acidity consumed (alkalinity produced) is determined by the relative concentrations of the two anions, but also by lake retention time. In lakes with very short retention times, the greater rapidity of N retention processes means that they are likely to be more important than S retention.

Since the key retention processes for both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  require anaerobic conditions, stratification and the formation of an anaerobic hypolimnion is a major factor. Seasonal differences in acid anion retention will therefore be determined by whether summer or winter stratification occurs, and are therefore likely to vary regionally.

In lakes where stable stratification is infrequent or short-lived, which is likely to be the case for many acid-sensitive lakes in the UK, the key factor is the contact time of water with the anaerobic sediment, hence the importance of the areal discharge rate (runoff/mean depth,  $\text{m yr}^{-1}$ ). The model of Kelly *et al.* (1987) employed in the FAB model is intended for use only in such lakes, and not in those with significant stratification.

The range of mass transfer coefficients recommended in the UNECE Mapping Manual ( $S_S = 0.2\text{-}0.8 \text{ m yr}^{-1}$  and  $S_N = 2\text{-}8 \text{ m yr}^{-1}$ ; UBA, 1996) has been found to be appropriate for lakes in European countries and not just North America. Mid-range values ( $S_S = 0.5$ ,  $S_N = 5.0 \text{ m yr}^{-1}$ ) should therefore continue to be used for UK lakes while site specific values are being derived.

## Introduction

Alkalinity generation in lakes is a natural process, which may be increased by acidic inputs in an analogous way to the increased base cation leaching from soils which can provide extra buffering of acidic deposition inputs (Norton *et al.*, 1990). Alkalinity generation per square metre of lake sediment is commonly comparable to the areal rate in the terrestrial catchment (Norton *et al.*, 1990). However, unlike the buffering provided by base cation leaching in the terrestrial part of a catchment, which is a geochemical process, alkalinity generation in lakes is largely a result of biological neutralisation processes, which tend to be more sustainable than geochemical ones (Kelly, 1994).

The processes which generate alkalinity are (by definition) processes which consume acid anions and the associated acidity, and it is the consumption or retention of acid anions which lends itself to the mass balance modelling approach. The biological processes which retain acid anions are different for sulphate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ). A further difference is introduced by the more complex processes which determine the conversion of ammonium ( $\text{NH}_4^+$ ) inputs into  $\text{NO}_3^-$  via nitrification, which consumes alkalinity, but can result in the regeneration of alkalinity if the  $\text{NO}_3^-$  is then itself retained. The processes are considered separately below for S and N retention, followed by a summary of the existing models for those processes.

## Processes retaining S

In lakes, removal of  $\text{SO}_4^{2-}$  occurs mainly by the reduction of  $\text{SO}_4^{2-}$  to sulphide in sediments, resulting in the formation of organic sulphur compounds and iron sulphides

(Rudd *et al.*, 1986a; Rudd *et al.*, 1986b; Kelly *et al.*, 1987).  $\text{SO}_4^{2-}$  reducers are ubiquitous in aquatic sediments, so S reduction is observed in most lakes (Kelly, 1994). The process occurs in hypolimnetic and epilimnetic sediments, and is limited only by  $\text{SO}_4^{2-}$  availability in appropriate anaerobic habitats.  $\text{H}^+$  is effectively consumed as long as the S remains in these forms (Rudd *et al.*, 1986a) or is lost from the system as  $\text{H}_2\text{S}$  gas (van Miegrot, 1994). Epilimnetic sediments may be very important since they can be in contact with  $\text{SO}_4^{2-}$  rich surface waters all year round, while the hypolimnetic sediments can be starved of  $\text{SO}_4^{2-}$  during stratification, causing  $\text{SO}_4^{2-}$  reduction to cease (Kelly, 1994).

Reduction of  $\text{SO}_4^{2-}$  follows a seasonal pattern, generally being lowest in winter due to less microbial oxygen consumption and therefore a lesser likelihood of anaerobic conditions (Kelly, 1994). Furthermore, in winter, increased oxygen penetration can re-oxidise stored S in sediments, releasing  $\text{SO}_4^{2-}$  back to water column. The organic form is most resistant to re-oxidation.

Using stable isotopes it has been shown that much of the reduced  $\text{SO}_4^{2-}$  is rapidly converted to organic S in the sediment and with time the end products will be dominated increasingly by organic S (Rudd *et al.*, 1986b). Most organic S in sediments comes originally from  $\text{SO}_4^{2-}$  reduction and not from the sedimentation of organic S formed in the water column by biological uptake processes (see below), which tend to be much less important than  $\text{SO}_4^{2-}$  reduction.

Alkalinity generation ( $\text{H}^+$  consumption) by S reduction is a function of thermocline depth, oxygen levels,  $\text{SO}_4^{2-}$  supply and light penetration (Schindler & Turner, 1982). A deeper thermocline causes a decreased hypolimnion and hence less  $\text{SO}_4^{2-}$  is entrapped for reduction in the hypolimnion. Completeness of overturn affects the process. If oxygen is introduced, reduction is inhibited, but if no new  $\text{SO}_4^{2-}$  is introduced it becomes depleted and causes substrate limitation. After thorough overturn, oxygen and  $\text{SO}_4^{2-}$  enter the hypolimnion, so that  $\text{SO}_4^{2-}$  reduction starts later in summer when oxygen is depleted, but there is still sufficient time to then remove all  $\text{SO}_4^{2-}$  by reduction from the hypolimnion. The total amount of alkalinity generation therefore tends to be greater after full overturn. However, in wet years when water renewal time is faster, more of the  $\text{SO}_4^{2-}$  is flushed out, with a lower proportion of inputs sedimented.

As proportion of inputs, sedimentation of reduced S is very variable, since  $\text{SO}_4^{2-}$  reduction is probably a complex function of availability of  $\text{SO}_4^{2-}$  and organic matter, temperature and oxygen. Over 5 years of experimental acidification (via sulphuric acid additions) at Lake 223 in the Experimental Lakes Area of Canada, around a third of sulphur inputs were sedimented (Schindler & Turner, 1982). In a similar study at Lake 239 in the ELA, Schindler *et al.* (1986) calculated that in-lake alkalinity generation via  $\text{SO}_4^{2-}$  removal, amounted to  $39 \text{ meq m}^{-2} \text{ yr}^{-1}$ . However, acidification of a lake in the same area from neutral to pH=5 showed  $\text{SO}_4^{2-}$  reduction increased as  $\text{SO}_4^{2-}$  concentration increased, but reduction sharply declined when pH was further reduced to 4.5 (Kelly, 1994).

Release of  $\text{SO}_4^{2-}$  from sediments may occur when there is rapid cooling and influx of oxygen into sediments. This process could produce periodic pulses of  $\text{H}^+$  with effects



analogous to snowmelt (Rudd *et al.*, 1986a). In Schwarzee, an Alpine lake, increases in lake  $\text{SO}_4^{2-}$  from 1984 to 1994 despite reduced S deposition were attributed to climate (Wögrath and Psenner, 1995), whereby warmer climate caused longer ice-free periods and less reduction / more oxidation of S in lake sediments. It cannot therefore be assumed that summer stratification is the key period for S retention in all lakes; formation of an anoxic hypolimnion under ice cover could mean that winter is the main period for  $\text{SO}_4^{2-}$  reduction in high altitude or high latitude lakes.

Winter return of  $\text{SO}_4^{2-}$  may also greatly increase at low pH due to the appearance of filamentous metaphytic algae in very acidified lakes, whose growth and decay cause the major S reduction zone to be closer to the sediment surface (sediment -water interface), thereby increasing S oxidation in winter (Kelly, 1994). The overall effect of low pH values can therefore be to reduce  $\text{SO}_4^{2-}$  retention and in-lake alkalinity generation (Kelly *et al.*, 1995).

Sulphate uptake into algae, followed by sedimentation, may also contribute to in-lake retention of  $\text{SO}_4^{2-}$  (Kelly, 1994). Bacterial and/or algal uptake in the water column and sediments can be significant when  $\text{SO}_4^{2-}$  inputs are low, but will be a relatively small proportion of sinks at high  $\text{SO}_4^{2-}$  inputs. Similarly, *Sphagnum* (usually in wetlands, but sometimes in floating mats; Thies, 1995) can take up  $\text{SO}_4^{2-}$ .

### Processes retaining N

Unlike  $\text{SO}_4^{2-}$ , N can be retained or removed by several processes, including denitrification, plankton uptake and sedimentation, and infiltration by macrophyte stands with their periphyton.

Nitrogen loading from terrestrial sources may be reduced by littoral macrophytes which can act as effective nutrient scavengers (Catalan *et al.*, 1994). Kopacek *et al.* (1995) proposed that littoral vegetation could contribute to low  $\text{NO}_3^-$  in forest lakes but not in very low productivity (low phosphorus) alpine lakes. Plant uptake is only a net retention process in the longer term if the N is not returned to the water column during decay. For example, if total macrophyte biomass were increasing over the timescales considered in modelling applications, or if incomplete decomposition led to accumulation of N in organic sediments, then an uptake term would be required for in-lake N retention models. However, this process is not easily quantified or modelled, and can only occur if littoral vegetation cover is significant. It is therefore not considered further here.

Atmospheric inputs of N may occur in reduced or oxidised forms, and usually a combination of the two. When  $\text{NO}_3^-$  is not retained within the terrestrial catchment or lake, then it is effectively the mobile anion of a strong acid, accompanied by a proton as it is exported from the lake. On the other hand,  $\text{NH}_4^+$  is a base and would not therefore lead to acidification if it remained in that form. However,  $\text{NO}_3^-$  is typically the dominant exported N species regardless of N input source. Despite potentially large atmospheric  $\text{NH}_4^+$  inputs which may exceed those of  $\text{NO}_3^-$ , measurable concentrations of  $\text{NH}_4^+$  are rarely found in acid sensitive lakes. The fate of the retained  $\text{NH}_4^+$  determines whether there has been a net generation of acidity.

Biological uptake of  $\text{NH}_4^+$  is neutral in terms of acid-base status, since the dissolution of  $\text{NH}_3$  to form  $\text{NH}_4^+$  consumes a proton, and the uptake of  $\text{NH}_4^+$  releases a proton (Reuss & Johnson, 1986). However, if the “retained”  $\text{NH}_4^+$  has actually been nitrified to  $\text{NO}_3^-$  then there has been a net release of a proton and it effectively acts as a strong acid. In either case, the net acidification effect is equivalent to the  $\text{NO}_3^-$  leached.

### Nitrification

Nitrification is the microbial oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  and is therefore an aerobic process. Aquatic nitrification is especially sensitive to  $\text{pH} < 5.4-5.6$  (Kelly, 1994). Aquatic nitrifiers require  $\text{NH}_3$  not  $\text{NH}_4^+$  and as  $\text{pH}$  declines,  $\text{NH}_3$  becomes less available. When nitrification is not inhibited,  $\text{NH}_4^+$  does not accumulate in the water column, despite being produced in sediments by decomposition in addition to atmospheric inputs. Decomposition of organic C supports both denitrification and S reduction, and is also affected at  $\text{pH} < 5$ .

Although autotrophic nitrification is inhibited by low  $\text{pH}$ , heterotrophic nitrification in forest soils is not (Lang & Jagnow, 1986), so the  $\text{NO}_3^-$  exported from forested catchments into acid lakes is not necessarily derived from atmospheric  $\text{NO}_3^-$ . Acidification was found to have little effect on  $\text{NO}_3^-$  retention by Dillon and Molot (1990). While denitrification appears to be unaffected by low  $\text{pH}$ , nitrification ceased in 2 experimentally acidified lakes.

Strauss and Lambertini (2000) found that when environmental conditions are within the physical and chemical constraints for nitrification, the C/N ratio of the environment is a critical factor regulating nitrification in stream sediments. The quality of the organic carbon substrate was also important, with more labile forms resulting in greater nitrification rates.

### *Denitrification and biological uptake/sedimentation*

For  $\text{NO}_3^-$ , both algal uptake (reduction to organic matter by photosynthesis) and bacterial denitrification are potentially the major removal mechanisms (Rudd *et al.*, 1986a; Kelly *et al.*, 1987). Both consume  $\text{H}^+$  in proportion to the nitrate consumed (Rudd *et al.*, 1986a).

Rudd *et al.* (1986a) found that  $\text{NO}_3^-$  in the porewater of sediments was depleted to background levels within 1-2cm of the sediment-water interface through denitrification, the rate of which depends on the concentration in the overlying water. Comparison of N gradients in sediments of acidified and non-acidified lakes showed that denitrifiers were not markedly affected by acidification or had adjusted to the low  $\text{pH}$ .

Molot and Dillon (1993) investigated the relative importance of denitrification as a cause of in-lake retention of N. In previous studies lake denitrification had been measured directly, or using the mass-balance approach, i.e. as the residual term in a measured mass balance. Mass balance studies typically use flux measurements of N and P plus N/P ratios in surficial sediments, which works because no P is lost via gas phase reactions. Their alternative entailed the use of  $^{210}\text{Pb}$  dating and sediment analysis to measure sediment accumulation of N, in conjunction with mass balances. Denitrification is then equal to inputs less outputs and loss to sediments (Molot &

Dillon, 1993), i.e. it is still calculated as the residual in a mass balance, but sedimentation losses are accounted for.

#### In-lake retention of S and N calculated from lake budget studies

Dillon *et al.* (1982) calculated mass balances for S and N for lakes in Canada and found that almost all  $\text{NO}_3^-$  and  $\text{NH}_4^+$  inputs to one, Harp Lake, were retained, while  $\text{SO}_4^{2-}$  outputs were greater than inputs calculated from bulk deposition, which was attributed to unmeasured dry deposition inputs.

Dillon and Molot (1990) studied lakes in the Muskoka-Haliburton area of Canada over 8 hydrologic years (1976-84) and found very little difference between years in terms of retention of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and TIN (<10%). At the subcatchment level, the minimum  $\text{NH}_4^+$  retention was 94%, while  $\text{NO}_3^-$  retention was more variable (52-98%), although in two thirds of monitored “catchment years” it was greater than 80%. For total inorganic nitrogen (TIN) the range was 70-98%. In-lake retention increased from 57% for  $\text{NO}_3^-$  to 88% for  $\text{NH}_4^+$  (overall 67% for TIN). In-lake retention of both N species was lower than in the subcatchments, i.e. the lakes were less efficient  $\text{NO}_3^-$  and  $\text{NH}_4^+$  sinks, even though water residence time in lakes was almost certainly much greater (Dillon & Molot, 1990).

In a later study of these lakes, net gain (sedimentation + denitrification) per unit area ranged from 990 to 1495  $\text{mg m}^{-2} \text{yr}^{-1}$  (Molot & Dillon, 1993). Expressed as percentage retained, the calculated ranges were 27-87% for  $\text{NO}_3^-$ , 76-88% for  $\text{NH}_4^+$ , 24-37% for total organic N (TON) and 36-73% for total N. As overall mean figures, of N inputs in bulk deposition, 67% was retained terrestrially, 12% was denitrified in lakes, 4% was stored in lake sediments and 17% was exported from lake outflows.

In ELA Lake 239 (NW Ontario), Schindler *et al.* (1986) calculated that while reduction of  $\text{NO}_3^-$  generated alkalinity (19  $\text{meq m}^{-2} \text{yr}^{-1}$ ),  $\text{NH}_4^+$  removal consumed 13  $\text{meq m}^{-2} \text{yr}^{-1}$  of alkalinity, the net effect being the generation of only 6  $\text{meq m}^{-2} \text{yr}^{-1}$ .

Jeffries *et al.* (1986) working in the Turkey Lakes watershed, also in Ontario, found no net retention of  $\text{SO}_4^{2-}$  and low retention of nitrogen due to losses in the spring melt.

Mass balance models were applied to two ultraoligotrophic lakes in the Tatra Mountains of Poland (Dlugi Staw and Zielony Staw) by Rzychon and Worsztynowicz (1995). While  $\text{SO}_4^{2-}$  retention was found to be zero in Zielony Staw and just 1% in Dlugi Staw, TIN retention was calculated as 48% and 13% in the two lakes, respectively.

Thies (1995), working on the dystrophic Huzenbacher See in the German Black Forest, measured areal alkalinity generation rates through depletion of acid anions. Over two budget years, in-lake processes removed 60 and 52% of  $\text{NO}_3^-$ , 53 and 88% of  $\text{NH}_4^+$ , and 12 and 15% of  $\text{SO}_4^{2-}$ . These processes increased alkalinity by 48 and 47%. It was speculated that a floating *Sphagnum* peat mat will have acted like a wetland and retained much  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ .

Mass balance studies of two Pyrenean lakes, Redo and Baciver, found significant in-lake retention of acid anions (Camarero and Catalan, 1994). The rate of  $\text{SO}_4^{2-}$  reduction in Redo was low ( $5.4 \mu\text{eq m}^{-2} \text{day}^{-1}$ ) and undetectable in Baciver. These figures are much lower than those found by Kelly *et al.* (1987). Denitrification rates in both lakes were comparable to those found by Kelly *et al.* (1987), at  $243 \mu\text{eq m}^{-2} \text{day}^{-1}$  (Lake Redo) and  $198 \mu\text{eq m}^{-2} \text{day}^{-1}$  (Lake Baciver), but would indicate a greater mass transfer coefficient for N.

Berge *et al.* (1997) studied N retention in gauged lakes in 2 very different Norwegian catchments. Along the mesotrophic Eikern watercourse, 5 lakes were studied, ranging from meso- to eutrophic status in agricultural areas. These lakes are shallow, with little stratification, short renewal times and vegetation cover from 19-100%. In the Bjerkreim catchment, 3 ultraoligo- to oligotrophic lakes were studied. Residence time varied from 1 day in the lowermost lake (50% of littoral vegetated with *J.bulbosus* & *Sphagnum* sp.) to 2.6 years in the uppermost (no littoral vegetation). While most Eikern lakes showed efficient N retention, Bjerkreim lakes had inflows and outlets with almost identical concentrations of N species, indicating little effect from in-lake processes. Eikern lakes showed a classic seasonal pattern in N concentrations with higher concentrations in winter, despite much higher flows, while Bjerkreim lakes showed no seasonal pattern, presumably because of short retention times and insignificant N uptake.

Of the Eikern lakes, the highest average N retention value was 28%, with values as low as 5% in the eutrophic lakes (Berge *et al.*, 1997). The year to year variation in N transport was greater than variation in per cent retention, indicating a stable lake characteristic. In the Bjerkreim lakes, retention was remarkably low; even a lake with 2.5 years retention time showed only 5% N retention. In the other 2 Bjerkreim lakes N retention was near zero. Overall, 3 years of budget studies indicated that N retention is higher in eutrophic lakes (20-30%) than in oligotrophic lakes (<5%). While there was a high correlation between mean N retention and mean P concentration, no correlation was found between N retention and water residence time. It was concluded that N retention in these lakes is linked to biological processes and not to passive sedimentation processes.

Kopacek *et al.* (1995) also found that lakes receiving more TP had lower  $\text{NO}_3^-$  concentrations. They proposed that lakes with more TP had higher primary production and therefore probably higher assimilation of N. Also, higher loads of autochthonous organic matter in lakes enhance rates of hypolimnetic oxygen depletion and denitrification.

This hypothesis is supported by the work of Findlay *et al.* (1999) at ELA Lake 302 (NW Ontario), who showed that N additions to the lake did not remedy acidification by increasing algal biomass and stimulating primary production, which was probably due to continued P deficiency. However, increased P loading did stimulate internal alkalinity generation.

### Models of in-lake retention

The most widely used model, that of Kelly *et al.* (1987), applies only to acid-sensitive lakes, which tend to be low in primary productivity and so have small/no anoxic zones during stratification. Higher productivity lakes have larger anoxic hypolimnia and require a different model. However, such lakes are less acid-sensitive and therefore of less concern here. Their hypothesis, that the contact time of the water with sediments should be a crucial factor in determining the proportion of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  removed from the water as it passes through the lake, was tested using the Vollenweider model for P removal, adapted for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . Using both mass balance methods and direct measurements at the sediment-water interface, they derived “mass transfer coefficients” for S and N.

Retention, expressed as a fraction of inputs retained, can be calculated as:

$$R = 1 - q / (q + S) = S / (q + S)$$

R is retention, “q” (areal water discharge) can be calculated as mean depth “z” (m) divided by water residence time “t” (years), or discharge ( $\text{m}^3 \text{ yr}^{-1}$ ) divided by area ( $\text{m}^2$ ), and S is the mass transfer coefficient. Areal water discharge can be visualised as the height of a  $1\text{m}^2$  column of water that is displaced by new water each year (units in  $\text{m yr}^{-1}$ ). The mass transfer coefficient S is the height of the column from which  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  is removed each year ( $\text{m yr}^{-1}$ ).

In modelling terms, net S removal is a first-order reaction, directly related to  $\text{SO}_4^{2-}$  concentration and expressed mathematically as a mass transfer coefficient or “piston velocity” (Kelly, 1994), referred to as  $S_S$ . Several methods have been used to calculate  $S_S$  producing different ranges of values; sediment  $\text{SO}_4^{2-}$  profiles (epilimnion) ( $0.17 - 0.36 \text{ m yr}^{-1}$ ), whole lake  $\text{SO}_4^{2-}$  budgets ( $0.3-0.5 \text{ m yr}^{-1}$ ) and long-term S accumulation ( $0.5-0.8 \text{ m yr}^{-1}$ ). Overall  $S_S = 0.5 \pm 0.3 \text{ m yr}^{-1}$  for a broad range of softwater lakes ( $\text{pH}>5$ ), but would be significantly higher in lakes with large anaerobic hypolimnia (Kelly, 1994).

Where measurable, removal coefficients for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were found to increase with increasing residence time (Rudd *et al.*, 1986a; Kelly *et al.*, 1987). Removal of  $\text{NO}_3^-$  ( $S_N$ :  $7.4 - 9.2 \text{ m yr}^{-1}$ ) was much greater than for  $\text{SO}_4^{2-}$  ( $S_S$ :  $0.4 - 0.54 \text{ m yr}^{-1}$ ) (Kelly *et al.*, 1987). Variations in mean depth, water residence time and mass transfer coefficient are all important mathematically, but in practice residence time explains most of the variation in  $\text{SO}_4^{2-}$  removal. Mass transfer coefficients are much larger in lakes with anoxic hypolimnia, because diffusion rates are much faster across the oxic/anoxic water interface than across the sediment /water interface.

According to the model of Kelly *et al.* (1987) the mass-transfer coefficient for N is assumed to be a constant if denitrification is the major  $\text{NO}_3^-$  removal mechanism. Nitrate removal was also related to water residence time, but there is a division between lakes with undetectable summer  $\text{NO}_3^-$  and those with detectable summer  $\text{NO}_3^-$ . In lakes with no detectable summer  $\text{NO}_3^-$  in surface water,  $S_N$  values were very high and in these lakes the dominant removal mechanism is probably algal (water column) uptake, which cannot be predicted by this model. For lakes that have excess  $\text{NO}_3^-$  in the summer epilimnion, most of the permanent removal of  $\text{NO}_3^-$  appears to be done by denitrification.

Algal uptake of  $\text{NO}_3^-$  has a very high mass transfer coefficient, but total uptake is limited by phosphorus availability (Kelly *et al.*, 1987).

In lakes with significant  $\text{NO}_3^-$  concentrations and with net  $\text{SO}_4^{2-}$  consumption in sediments,  $\text{NO}_3^-$  consumption exceeded  $\text{SO}_4^{2-}$  consumption by factors of 1.0 – 6.2, with most lakes consuming  $\text{H}^+$  by denitrification about twice as fast as by  $\text{SO}_4^{2-}$  reduction (Rudd *et al.*, 1986a).  $\text{SO}_4^{2-}$  reduction and  $\text{H}^+$  consumption were much faster, per unit volume, in inorganic sediment.

Baker and Brezonik (1988) used published lake budgets to calibrate a dynamic model of in-lake alkalinity generation and found that rate constants (mass transfer coefficients) were generally similar among soft water lakes, with  $S_S = 0.5 \text{ m yr}^{-1}$ ,  $S_{\text{NO}_3^-} = 1.3 \text{ m yr}^{-1}$  and  $S_{\text{NH}_4^+} = 1.5 \text{ m yr}^{-1}$ .

In 8 Ontario lakes the mass transfer coefficient for total inorganic N ( $S_N$ ) varied from 3.5 – 10.8. Variability of  $S_{\text{NO}_3^-}$  may reflect in situ variability in turbulence and microbial denitrification, nitrification and assimilation rates (Dillon and Molot, 1990). It is also a function of the type of biological process responsible for  $\text{NO}_3^-$  consumption;  $S_{\text{NO}_3^-}$  values are  $<11 \text{ m yr}^{-1}$  when denitrification is the major sink but  $>25 \text{ m yr}^{-1}$  when algal consumption is the primary sink. A large  $S_{\text{NO}_3^-}$  decrease in a lake in which algae dominate  $\text{NO}_3^-$  consumption can be taken as evidence that N saturation of the algal community is occurring. However, this may also be caused by high  $\text{NH}_4^+$  loading, in which case denitrification will be the major N sink and  $S_{\text{NO}_3^-}$  values will not be sensitive to changes in  $\text{NO}_3^-$  loading.

Covariance among loading and areal discharge rate and flushing rate could obscure whether retention is affected by loading or areal discharge rate. This was tested by Dillon and Molot (1990), who found that loading and/or areal discharge rate exerts a real influence on lake N retention.

Molot and Dillon (1993), working on gauged lakes in central Ontario lakes, calculated annual net gain of total nitrogen (TN) as the difference between total inputs of TN minus export, divided by lake area. They referred to the mass-transfer coefficient of Kelly *et al.* (1987) as the “apparent settling velocity”  $v$  ( $\text{m yr}^{-1}$ ). This provides a generalised rate constant for N loss by all processes other than outflow i.e. “ $v$ ” integrates burial in sediments and loss by denitrification. For central Ontario lakes, the mass transfer coefficient “ $v$ ” was calculated as 3.5-3.6  $\text{m yr}^{-1}$ .

Calculated mass transfer coefficients for nitrogen in two Tatra Mountain lakes, calculated from mass balances, were 6.5  $\text{m yr}^{-1}$  and 10.6  $\text{m yr}^{-1}$  (Dlugi Staw and Zielony Staw: Rzychon and Worsztynowicz, 1995).

## Discussion

The majority of mass-balance studies for acid anions in acid-sensitive lakes have been carried out in Canada, particularly during the 1980s and early 1990s. More recently, the approaches adopted by the Canadians have been applied elsewhere, including

Norway, the Tatra mountains and the Pyrenees. The results of published studies are summarised in Table 1.1.1.

In general, in lakes receiving close to natural inputs of N, removal is almost complete ( $S_N > 25 \text{ m yr}^{-1}$ ), while in lakes with elevated  $\text{NO}_3^-$ , removal occurs at a much slower relative rate ( $S_N < 7 \text{ m yr}^{-1}$ ) (Kelly, 1994). This difference is due to rapid algal uptake (the major N removal process at low inputs) throughout the surface water, compared with the restriction of denitrification (the major process at high inputs) to a narrow zone close to the sediment-water interface i.e. less of the water is subject to denitrification compared with algal uptake.

Kelly *et al.* (1987) suggest that in lakes with very low summer  $\text{NO}_3^-$  the absence of  $\text{NO}_3^-$  is due to high algal uptake rates, and in these lakes their in-lake retention model would require very high values of the mass-transfer coefficient  $S_N$ . However, in a British context, the absence of  $\text{NO}_3^-$  in acid-sensitive lakes during the summer is probably not due to algal uptake within the lake, but to very high uptake rates in the terrestrial catchment, as demonstrated by very similar seasonal patterns in the  $\text{NO}_3^-$  of streamwater that flows into these lakes. The dependence of algal N uptake on phosphorus availability has also been demonstrated in several studies, and acid-sensitive British lakes are generally strongly P-limited. Hence it seems likely that denitrification is the major N retention mechanism in these lakes, and that the model of Kelly *et al.* (1987) is appropriate. As lake retention times shorten, internal alkalinity generation from  $\text{NO}_3^-$  reduction by denitrification becomes relatively more important than  $\text{SO}_4^{2-}$  reduction, because of more rapid uptake processes for N (Schindler *et al.*, 1991).

In lakes which freeze over and are subjected to spring thaw inputs of surface runoff, the lower density of cold runoff waters can restrict the portion of the lake affected by snowmelt to a narrow layer just underneath the ice (Jeffries, 1990). Since snowmelt may account for a large proportion of ionic inputs to lakes, it is possible that in some lakes a significant flux of acid anions may exit the lake without much interaction with deeper waters and sediments, reducing the potential for biological retention processes. However, in the UK the proportion of the annual flux of acid anions occurring during spring snowmelt is small relative to more northerly, colder regions where the existence of a snowpack over long periods allows atmospheric deposition to accumulate in the snowpack, to be released in a short period of snowmelt. This process is therefore unlikely to be significant in the UK.

Alkalinity consumption by denitrification is assumed to be permanent but the fate of reduced  $\text{SO}_4^{2-}$  is more complex, due to the possibility of remobilisation (Rudd *et al.*, 1986a). Climatic factors are likely to be important in affecting both processes.

The range of mass transfer coefficients recommended in the UNECE Mapping Manual ( $S_S = 0.2\text{-}0.8 \text{ m yr}^{-1}$  and  $S_N = 2\text{-}8 \text{ m yr}^{-1}$ ; UBA, 1996) would seem to be broadly applicable to acid-sensitive lakes in Europe and North America, and appropriate for UK lakes. Work is, however, ongoing on the determination of site-specific estimates in-lake S and N retention in British upland lakes.

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### 1.1.3 N immobilisation

A review of N immobilisation rates in soil organic matter was carried out under the separately funded Soils Umbrella programme (see mid-term report) and is not reported here.

# Task1.2: Feasibility study for the use of HOST for characterisation of catchment soil N dynamics

R.Helliwell and R.Ferrier

## **1.2 Feasibility study for the use of the Hydrology of Soil Types (HOST) model for the characterizing of catchment soil N dynamics**

In semi-natural ecosystems the rate of denitrification is driven primarily by soil wetness and, to a lesser extent, by land use, nutrient status of the soil, soil pH and temperature. Rates of denitrification for different soil types in Scotland were calculated using an integrated approach comprising i) HOST classification, ii) Soil Wetness Classification developed by Lilly and Mathews (1994), and iii) estimates of denitrification derived from literature.

### HOST (Hydrology Of Soil Types)

HOST is a hydrologically based classification of soils whereby soil types are assigned to one of 29 HOST classes on the basis of their physical properties and the hydrogeology of the substrate (Boorman *et al.*, 1995). Scottish soils are classified into soil map units which represent soil series and HOST classes have been assigned to each of these depending on the hydrological status of soil.

### Soil Wetness Class

In the U.K. the soil water regime is often expressed as a Soil Wetness Class. Table 1 shows how the soil parameters of 'depth to a gleyed layer' and 'depth to a slowly permeable layer' can be combined with the meteorological parameter of Field Capacity Days (the number of days in which the climatic soil moisture deficit is zero) to estimate the Soil Wetness Class (Lilly and Mathews 1994). Freely draining soils with <200 field capacity days are assigned a Soil Wetness Class of one. Those soils that are almost permanently waterlogged to within 40 cm of the soil surface for >200 field capacity days i.e. gleyed and peaty soils, were assigned a wetness class of six (Table 1). The soils that are waterlogged for long periods will have greater N<sub>2</sub>O and NO emissions i.e. potentially high denitrification rates. The 'depth to gleying' and the 'depth to the slowly permeable layer' were determined for all map units in order to establish the Soil Wetness Class (Lilly, unpublished).

The strong association between the HOST class and Soil Wetness Class for each map unit resulted in a robust methodology enabling quantification of soil wetness for all soil types in Scotland. Soil wetness is the main control behind the rate of denitrification in soil systems and the combination of these methods resulted in greater confidence in soil wetness estimates.

### Rates of Denitrification derived from Literature

Denitrification rates derived from an extensive literature search of 'natural' soils were assigned to each of the six Soil Wetness Classes (Table 2). Denitrification rates at catchment scale were calculated within a geographic information system (GIS) by superimposing a digitised catchment boundary onto the Soil Map of Scotland and spatially weighting each rate identified by the area soil map unit.

Table 1. Relationship between Soil Wetness Class, Climate and Soil Attributes (Lilly and Mathews, 1994)

CLIMATE	SOILS						
	Gleyed within 70 cm depth						Not gleyed
	Depth to slowly permeable layer						
	Average FCD	Mineral soil	<40 Peaty soil	40-60 cm	60-80 cm	>80 cm Drainage outfalls	
Limited						Not Limited	
<100	II		II		II-VI	I	I
100-125	III		III	II	III-VI	I	I
125-150	III		III	II	III-VI	I	I
150-175	IV		IV	III	III-VI	I	I
175-200	IV	V	IV	III	IV-VI	I	I
200-225	V	VI	IV	III	V-VI	I-II	I
225-250	V	VI	V	IV	V-VI	II	I
250-300	V	VI	V	V	V-VI	III	I
>300	VI	VI	VI	VI	VI	IV	I

\*FCD Field Capacity Days

### Denitrification in Galloway region

A pilot study using this methodology was conducted in the Galloway region of south-west Scotland. Deep peat is widely developed in this region under the influence of high rainfall and poor drainage. These organic soils are the principal element of most soil map units and dominate the soil distribution. Under the prevailing high rainfall the soils are strongly flushed by springs and seepage from higher ground. Despite the steep slopes, gleying of varying degrees of intensity is predominant for most soils. As a result of these soil characteristics, 42 catchments in the Galloway region have high denitrification rates ( $4-5.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ). The soils of the remaining catchments are poorly developed alpine rankers and lithosols, which occur in freely drained high altitude areas. The denitrification rates of these catchments are considerably lower ( $0.8-3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) (Fig 1).

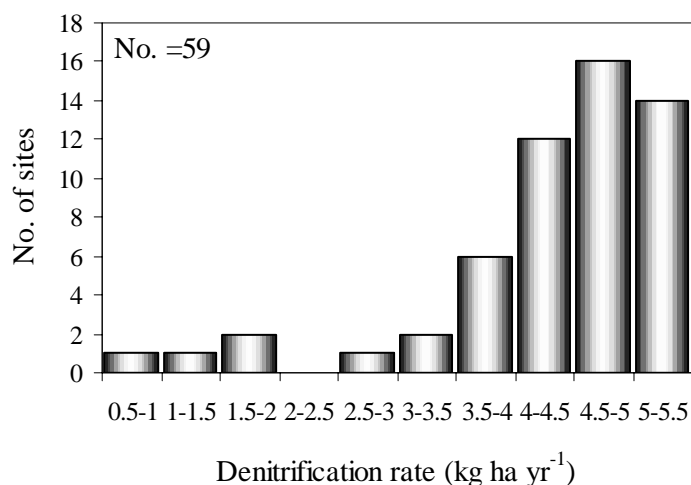
### Conclusion

It is likely that denitrification may alleviate some of the effects of excess N in catchments dominated by peat and gleyed soils. In the UK, measurements of denitrification in undisturbed, semi-natural ecosystems are rare. Work at the “Nitrogen Budget” sites (Workpackage 1.3) will address this issue and provide new denitrification data for British moorland systems. Ultimately the revised denitrification data will be used in the parameterisation of MAGIC7 in a regional application to Galloway. Subsequent work will address whether the use of surrogates based on the HOST classification can be used to characterise N immobilisation dynamics within catchments.

Table 2. Estimation of denitrification based on HOST and Wetness Class

Wetness Class	Typical soil type	Denitrification rate kg ha yr	Source
I	1. Rankers 2. Subalpine soil 3. Brown earth 4. Humus iron podsol	0-0.8	Emmett and Reynolds, 1996 (Measured: Aber, Wales)
II	1. Imperfectly drained brown earth 2. Imperfectly drained humus iron podsol	0.28	Ashby <i>et al</i> , 1998 (Well drained upland soil with low organic matter (C is the limiting factor))
III	Peaty gleyed podsol Non calcareous gley Gleyed brown earth	2-3	Emmett and Reynolds 1996
IV	Non calcareous gley	3.2	Dutch and Ineson, 1990 (Peaty gley, Kershope forest)
V	Non-calcareous gley Peaty podsol Peaty gley	4	Hall <i>et al</i> , 1997 (Gley soil)
VI	Peaty gley Basin peat Blanket peat Peaty ranker	4-6.2	Hornung <i>et al</i> 1995 (Peat with high pH) Melin and Nommik, 1983 (Mature Scotspine, Sweden) Freifelder <i>et al</i> , 1998 (Various soil types under normal moisture conditions)

Figure 1. Denitrification rates derived from the HOST model and Soil Wetness Classes for catchments in the Region of Galloway



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# Task1.3: Evaluation of N dynamics at a catchment scale for four catchments across a gradient of N leaching relative to deposition

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### 1.3 EVALUATE THE NITROGEN DYNAMICS AT A CATCHMENT SCALE FOR AT LEAST FOUR CATCHMENTS ACROSS A GRADIENT OF N LEACHING RELATIVE TO DEPOSITION

#### 1.3.1 Introduction: rationale for study and site selection

Four sites were selected for intensive N-budget study (N-budget sites) along gradients of N deposition and N saturation (Table 1.3.1, Figure 1.3.1). Total N deposition ranges from low levels at the Allt a'Mharcaidh, Cairngorms, up to levels at the River Etherow (Pennines) which are among the highest (for both S and N) in the country.

*Table 1.3.1: Deposition data (ITE annual mean data for 1992-94, catchment weighted)*

<b>Deposition (kg ha<sup>-1</sup> yr<sup>-1</sup>)</b>	<b>Allt a' Mharcaidh</b>	<b>Afon Gwy</b>	<b>Scoat Tarn</b>	<b>River Etherow</b>
<b>S (non-marine):</b>	6.4	19.0	20.3	39.7
<b>Total N:</b>	5.2	23.7	23.8	31.6
<b>Runoff (mm):</b>	1093	2476	2526	1192

The various stages of N saturation, as defined by water chemistry, are represented in these four sites (Figure 1.3.1). In the Allt a'Mharcaidh very little nitrate is seen at any time, with just occasional leakage in early spring, indicating strong N limitation in the terrestrial catchment. In the Afon Gwy (Plynlimon) elevated rates of nitrate are observed annually through the winter and spring months, but levels decline to near zero during the summer period of maximum terrestrial N demand. At Scoat Tarn in the Lake District nitrate leaching follows a distinct seasonal pattern but occurs all year round, never declining to zero and indicating strong N saturation. In the Pennine site experiencing the highest deposition levels, severe N saturation is indicated by the very high nitrate leaching year round and the breakdown of the seasonal pattern. Mean chemistry data for 1997 are shown in Table 1.3.2.

All four sites have non-forested, acid-sensitive catchments with a range of soil types in order to ensure that plot-based experiments on major N sink processes cover most major upland soil types. A separate study to compare forested and unafforested sub-catchments was carried out at Loch Grannoch.

The current formulation of the FAB model has been applied to the four N-budget sites using the mean 1997 data (Figure 1.3.2), and shows that according to the most recent deposition data (1992-94) three of the four sites exceed their critical load - only Allt a'Mharcaidh is not exceeded. At the Gwy, either S or N deposition could be reduced to prevent critical load exceedance, while at Scoat Tarn and the River Etherow both S and N deposition are sufficiently high to cause critical load exceedance on their own, so that both must be reduced significantly to protect the sites. A gradient of critical load exceedance is therefore covered by the four sites.

### Acid deposition measurements

In order to provide the best possible N input data the sites were co-located with Acid Deposition Network primary or secondary sites with, as a minimum, bulk deposition collectors within the catchments which are serviced at least 2-weekly.

### Water chemistry (leaching outputs)

The four selected sites are all included within the UK Acid Waters Monitoring Network (AWMN) which provides historical water chemistry data (at least 10 years). However, the sampling frequency was increased from monthly (streams) or quarterly (Scoat Tarn) to 2-weekly to improve surface water leaching estimates. At the River Etherow, water samples from two tributary streams (Rose Clough and Swan Clough) draining the soil plot study areas were also taken 2-weekly for chemical analysis. The two main tributaries of Scoat Tarn were sampled in the same way, to provide data on in-lake retention processes at the site.

At the Scoat Tarn outflow, the only site without flow gauging, a pressure-transducer flow gauge was installed. Stage measurements were calibrated to discharge through periodic dilution gauging. Stage data obtained indicate a high degree of temporal flow variability at both sites.

*Table 1.3.2: Selected water chemistry data (AWMN annual mean data for 1997)*

	<b>Allt a'Mharcaidh</b>	<b>Afon Gwy</b>	<b>Scoat Tarn</b>	<b>River Etherow</b>
<b>pH</b>	6.52	5.35	5.05	4.58
<b>ΣBC* (µeq/l)</b>	93	71	45	300
<b>SO4* (µeq/l)</b>	33	45	42	206
<b>NO3 (µeq/l)</b>	2	15	18	57
<b>ANC (µeq/l)</b>	58	12	-15	37
<b>Cl (µeq/l)</b>	107	149	174	323
<b>TOC (mg/l)</b>	2	2.6	0.98	8.3

\* non marine

### Experimental plots on major soil types

Best available soil maps were used to select up to four major soil types within each catchment (Figures 1.3.3a-e). Each soil type constituted a study area on which replicated experimental plots were set up (Table 1.3.3).

### Primary experimental plots

In each of the 13 soil study areas, 3 replicate experimental plots were installed (39 plots in total). Each plot (dimensions 3×1m) comprised:

1. soilwater suction sampler located below rooting zone
2. static denitrification chamber
3. <sup>15</sup>N additions area
4. adjacent grazing enclosure

Table 1.3.3: Experimental areas at N budget sites

Site	Soil code	Soil type
Allt a'Mharcaidh	M1	Peaty ranker
Allt a'Mharcaidh	M2	Valley peat
Allt a'Mharcaidh	M3	Peaty podsol
Allt a'Mharcaidh	M4	Shallow peat
Afon Gwy	G1	Hilltop peat
Afon Gwy	G2	Peaty gley
Afon Gwy	G3	Podsol
Afon Gwy	G4	Valley peat
Scoat Tarn	S1	Podsol
Scoat Tarn	S2	Peaty gley
Scoat Tarn	S3	Deep peat
River Etherow	E1	Deep peat (recently burnt <i>Calluna</i> )
River Etherow	E2	Deep peat (unburnt <i>Calluna</i> )

### *Soilwater samples*

Suction samplers were assembled at UCL during the spring and installed in June/July. After a “settling-in” period during which the samplers were emptied but the samples discarded, soilwater sampling commenced in early September 1999. Sampling was done fortnightly and the samples were analysed for NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and organic N at MLURI. The sampling programme finished at the end of October 2000.

### *Denitrification measurements*

The static denitrification chambers were constructed at UCL during the spring and installed in June/July 1999. After a “settling-in” period, sampling commenced in September 1999. They were sampled with syringes and airtight glass vials 4-weekly and analysed for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O on a GC at CEH Bangor. Sampling finished in October 2000.

Figure 1.3.1: Long-term nitrate concentrations at CLAM intensive study sites (AWMN data)

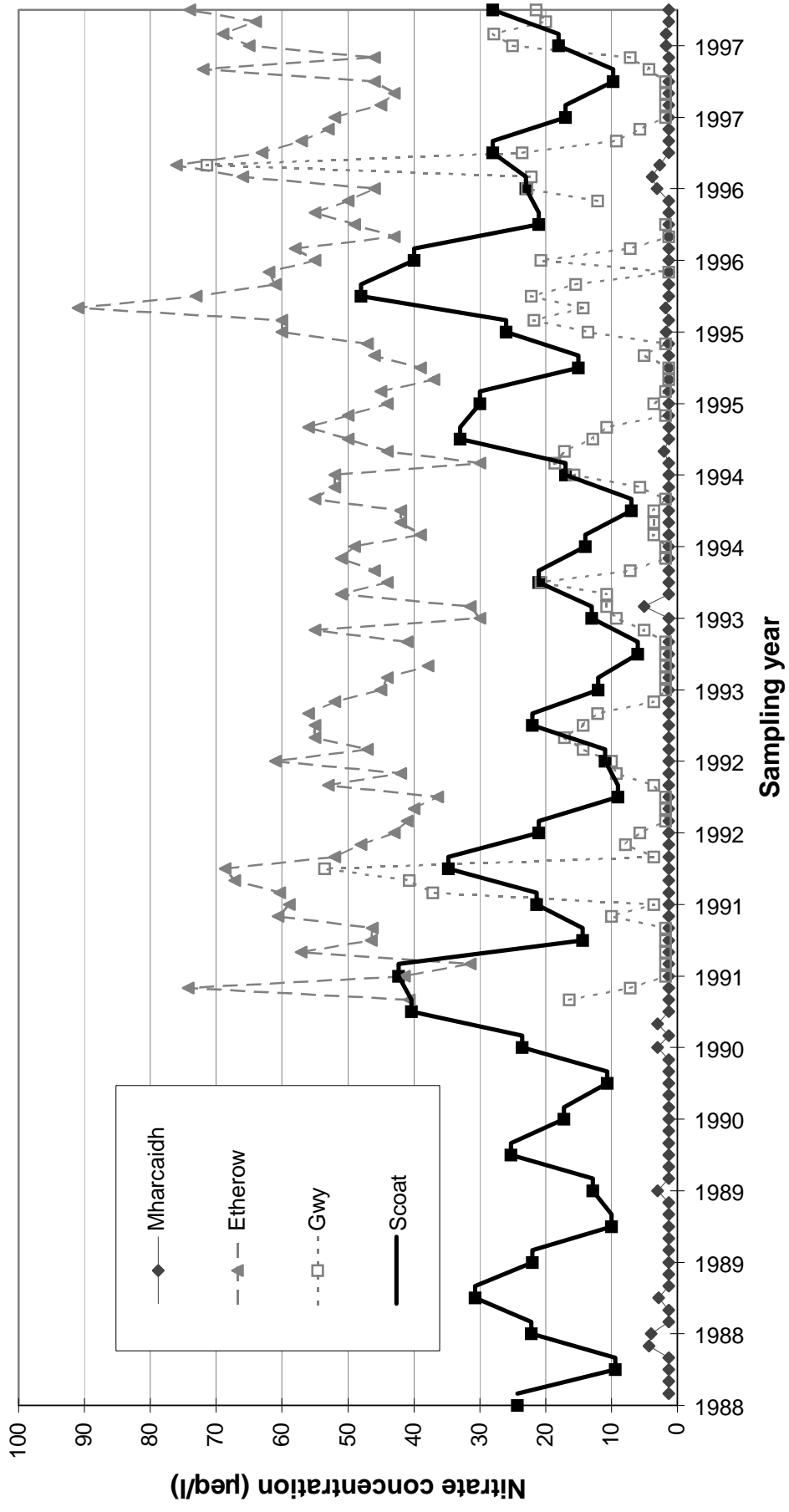
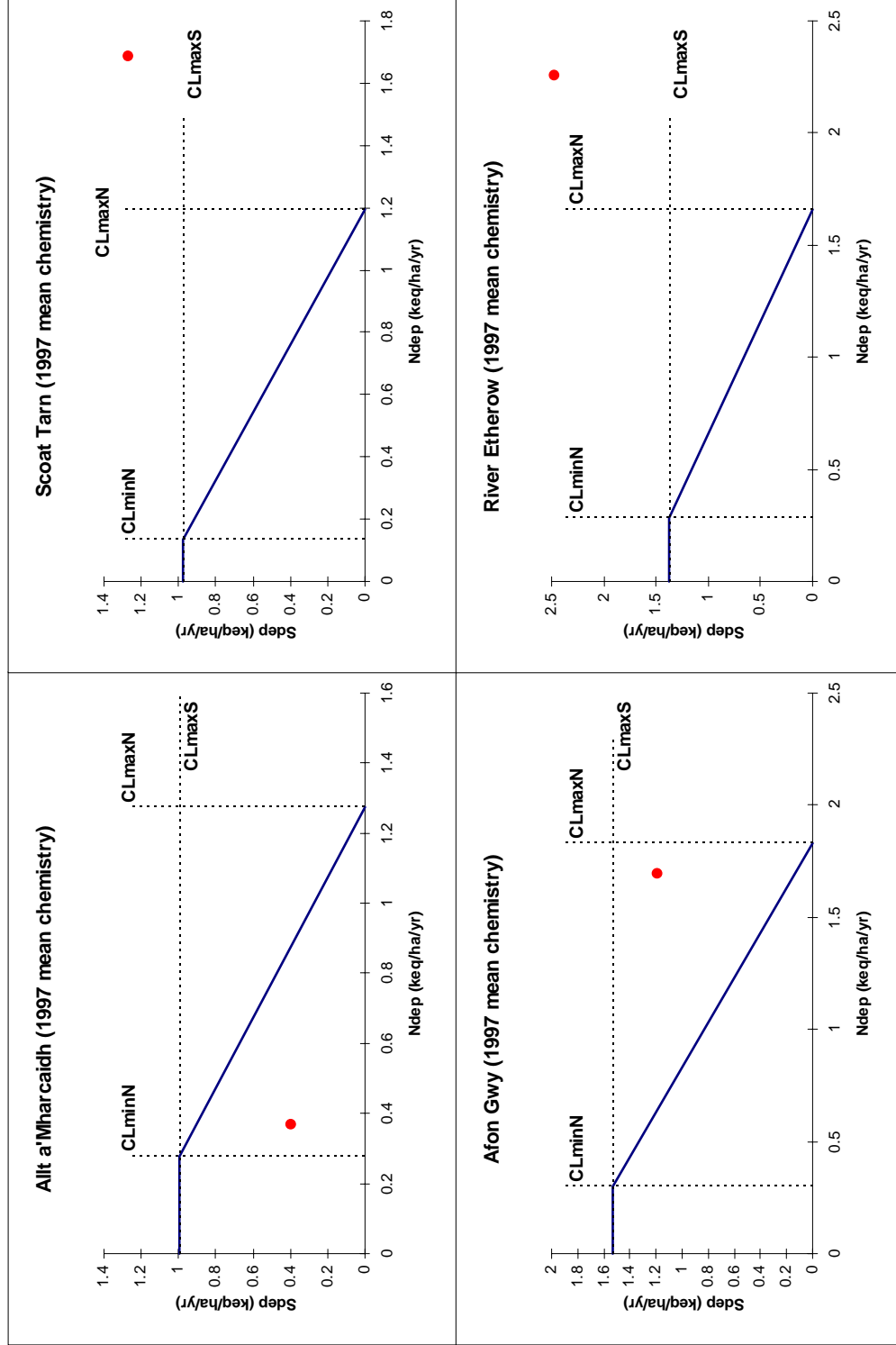


Figure 1.3.2: FAB Model Critical Load Function for N-budget sites



### *<sup>15</sup>N additions*

Funding for the <sup>15</sup>N additions work was secured from National Power in November 1999. The addition of <sup>15</sup>N labelled solution will provide data on N immobilisation and uptake through destructive sampling of soils and vegetation in the plots which was carried out at the end of the sampling period. <sup>15</sup>N additions commenced in October 1999 and was continued for a period of 12 months. The analyses for <sup>15</sup>N are currently ongoing under the National Power funded programme and are not reported here.

### *Grazing exclosures*

Grazing exclosures (1m<sup>2</sup>) were installed adjacent to the soil experimental plots in March 1999. They remained in situ throughout the 1999 growing season and were removed in September 1999. Soil and vegetation samples (0.5×0.5m plots in the centre of the 1m<sup>2</sup> fenced exclosures) were then removed from within the fenced plots and from adjacent unfenced areas. These samples were processed to provide the following information:

- wet weight - live and dead standing vegetation
- dry weight - live and dead standing vegetation
- year's growth (*Calluna* shoots)

Comparison of these data from inside and outside the fenced exclosures provides a qualitative indication of grazing intensity.

In addition, root layer samples were collected along with soil cores separated by horizon. The soil, root layer and above-ground biomass dried samples are being analysed for <sup>15</sup>N at CEH Merlewood in order to provide natural abundance figures and a baseline for comparison with post-addition values of <sup>15</sup>N. Again, since analysis is still in progress, these results are not presented here.

### *Soil moisture*

Soil moisture was measured 2-weekly at 3 points within each plot using a theta-probe. Measurements were carried out throughout the complete sampling period.

### *Soil temperature*

In each of the 13 study areas a temperature datalogger was buried at 5-10cm depth and programmed to take soil temperature measurements at 2 hour intervals. The loggers were installed in September 1999 when soilwater chemistry and denitrification measurements started and were downloaded quarterly until finally being removed in October 2000.

### Secondary experimental plots

Identical secondary experimental plots were paired with the primary plots in 7 selected soil study areas (Table 1.3.4: 3 replicates per soil type = 21 plots).

The secondary plots included soilwater suction samplers which served as emergency replacements for samplers in primary plots in case of damage or failure to collect a sample.

#### *N addition effects on denitrification rates*

The static chambers in the secondary plots were used for fertiliser addition experiments in which  $\text{NH}_4\text{NO}_3$  solution was added fortnightly at a rate equivalent to  $20 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  in 10% of annual estimated runoff (see Table 1.3.1). The fertiliser was added in identical amounts every 2 weeks directly into the static chambers after gas sampling had been carried out. The experiment provided data on the effect of N additions on denitrification rates for comparison with denitrification data from paired plots without N additions. Soil moisture was measured 2-weekly (3 replicates) by theta-probe, but no  $^{15}\text{N}$  additions were carried out at these plots.

*Table 1.3.4: Secondary experimental plots at N budget sites*

Site	Soil code	Soil type
Allt a'Mharcaidh	M3	Peaty podsol
Allt a'Mharcaidh	M4	Shallow peat
Afon Gwy	G1	Hilltop peat
Afon Gwy	G2	Peaty gley
Afon Gwy	G3	Podsol
River Etherow	E1	Deep peat (recently burnt <i>Calluna</i> )
River Etherow	E2	Deep peat (unburnt <i>Calluna</i> )

A summary of all the sampling work carried out in the N-budget study catchments is provided in Table 1.3.5.

#### **Forested non-forested comparison**

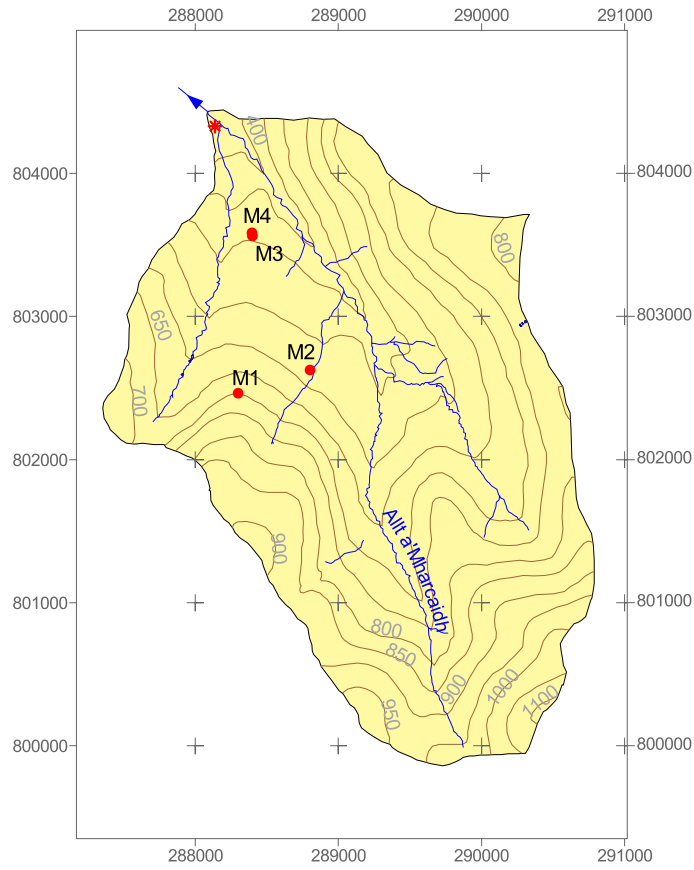
A comparison of nitrate leaching between forested and non-forested sub-catchments was undertaken in the Loch Grannoch catchment (N deposition -  $24\text{-}28 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ). Twice monthly sampling and chemical analysis of samples from six sub-catchments, at different stages of forest development, and at the Loch Grannoch outflow commenced in January 1999. Over 30 sites covering a range of soil types were selected and soils were sampled in August 1999 for C/N analysis by MLURI. A further 9 sites were selected for denitrification studies and the N- chambers installed in August 1999. Sampling of rain and mist for chemistry and carbon particles in the Grannoch catchment continued on a twice monthly basis during 1999-2000.

Table 1.3.5: Measurements at N-budget catchments

Measurement	Location	Sampling frequency	Method	Sampling dates
<b>Water chemistry</b>	Catchment outflow	At least 2-weekly	Dip sample	Mar. 1999 (ongoing)
<b>Bulk deposition</b>	Within catchment	At least 2-weekly	AEA Bulk Collector	Mar. 1999 (ongoing)
<b>Soilwater chemistry</b>	Primary plots	2-weekly	Suction sampler	Sept. 1999 – Oct. 2000
<b>Denitrification</b>	All plots	4-weekly	Static chamber + vials	Sept. 1999 – Oct. 2000
<b>Soil moisture</b>	All plots	2-weekly	Theta probe	Aug. 1999 – Oct. 2000
<b>Soil temperature</b>	Study area (soil type)	2 hourly	Tinytalk datalogger	Sept. 1999 – Oct. 2000
<b><sup>15</sup>N natural abundance</b>	Exclosures + adjacent areas	One-off	Destructive soil+vegn.	Mar. – Sept. 1999
<b><sup>15</sup>N post additions</b>	Primary plots	One-off	Destructive soil+vegn.	Sept. 1999 – Oct. 2000
<b>Grazing offtake</b>	Exclosures + adjacent areas	One-off	Veg. year's growth	Sept. 1999 – Oct. 2000
<b>N additions &amp; N<sub>2</sub>O</b>	Secondary plots	Monthly	Static chamber	Oct. 1999 – Oct. 2000
<b>Flow</b>	Catchment outflow	30 minutes	Pressure transducer	Sept. 1999 – Oct. 2000



Figure 1.3.3a: Experimental Plots at Allt a'Mharcaidh



## Allt a'Mharcaidh

- \* Bulk deposition collector
- Experimental plots

Name	Soil	Exclosure	N Budget & <sup>15</sup> N	N Additions
M1	Hillside Peat	No	Yes	No
M2	Valley Peat	Yes	Yes	No
M3	Peaty Podzol	Yes	Yes	Yes
M4	Shallow Peat	Yes	Yes	Yes

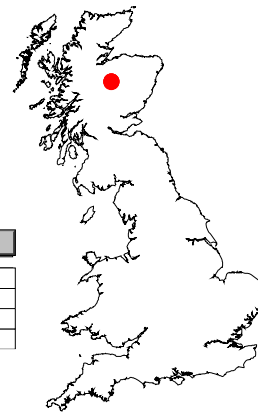
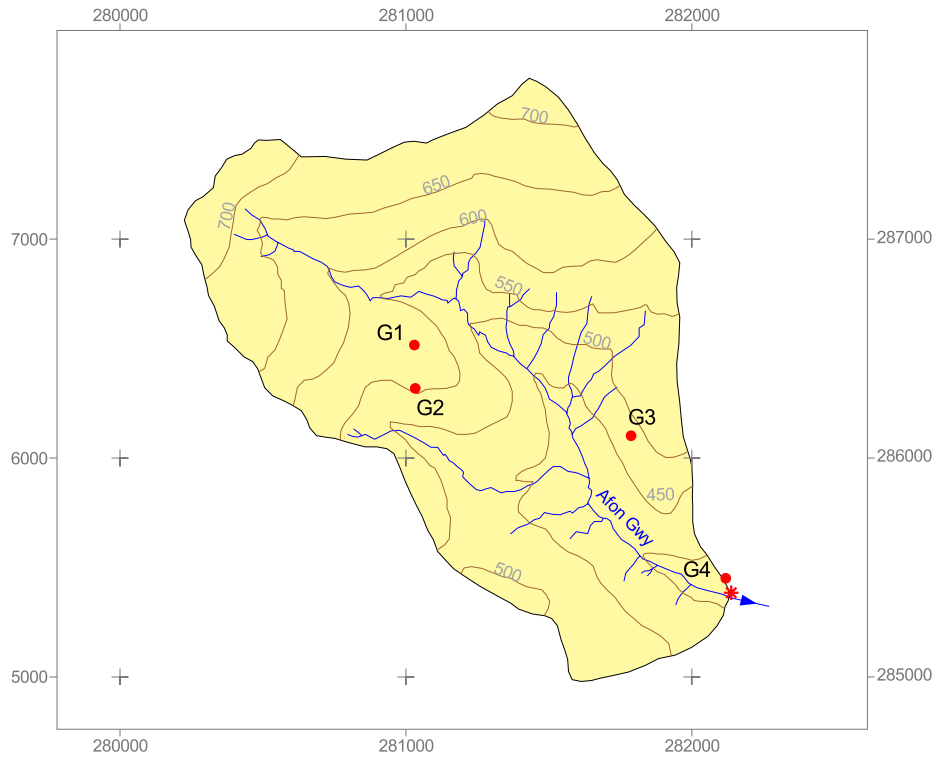


Figure 1.3.3b: Experimental Plots at Afon Gwy



## Afon Gwy, Wales

- \* Bulk deposition collector
- Experimental plots

Name	Soil	Exclosure	N Budget & <sup>15</sup> N	N Additions
G1	Hilltop Peat	Yes	Yes	Yes
G2	Peaty Gley	Yes	Yes	Yes
G3	Podzol	Yes	Yes	Yes
G4	Valley Peat	Yes	Yes	No

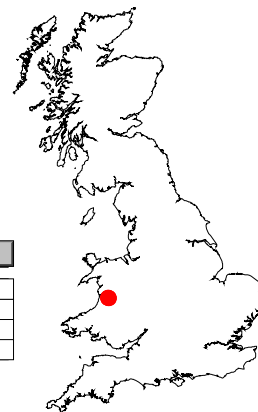
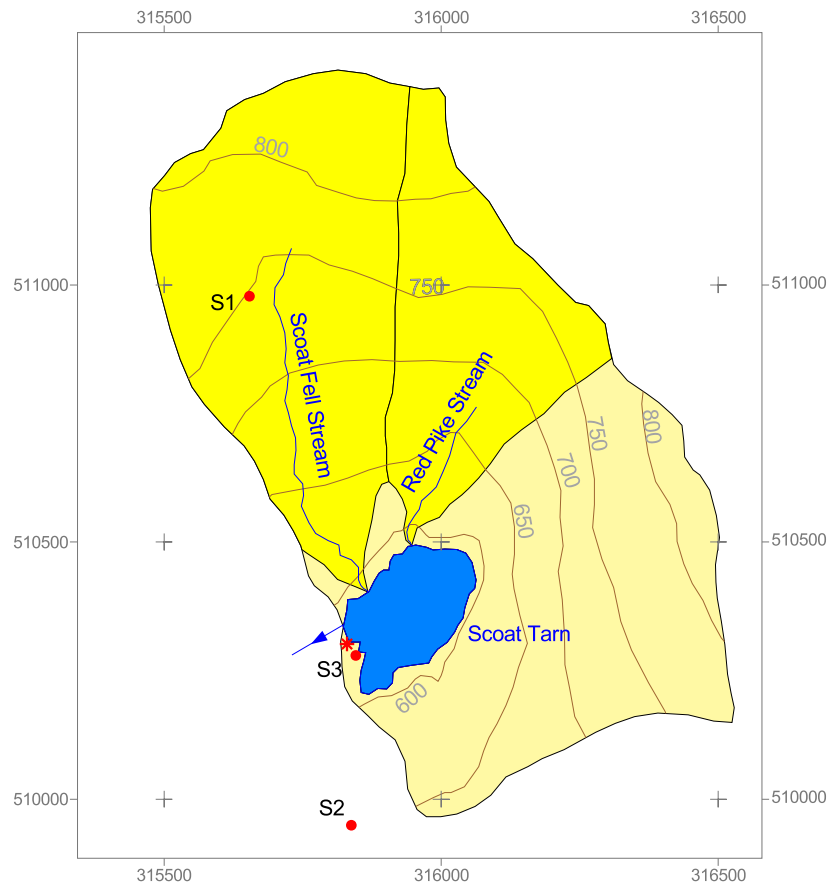


Figure 1.3.3c: Experimental Plots at Scoat Tarn



## Scoat Tarn, England

- \* Bulk deposition collector
- Experimental plots

Name	Soil	Exclosure	N Budget & <sup>15</sup> N	N Additions
S1	Podzol	Yes	Yes	No
S2	Peaty Gley	Yes	Yes	No
S3	Deep Peat	Yes	Yes	No

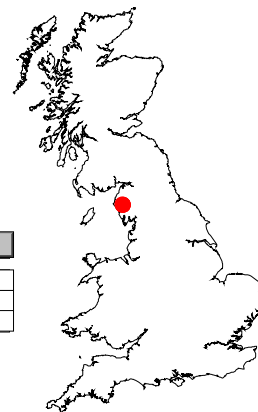
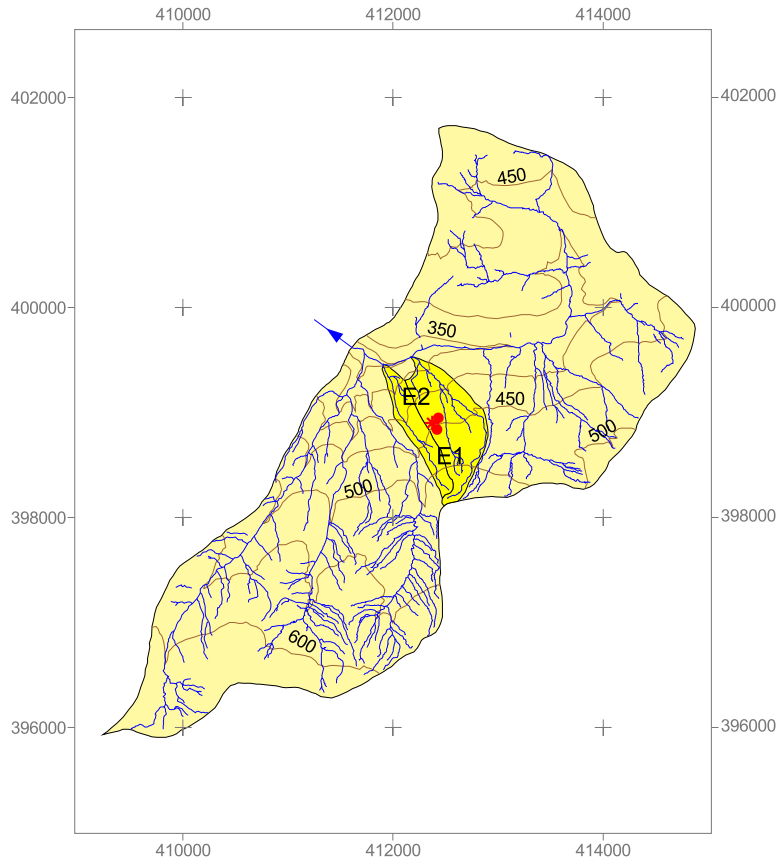


Figure 1.3.3d: Experimental Plots at River Etherow



## River Etherow, England

- \* Bulk deposition collector
- Experimental plots

Name	Soil	Exclosure	N Budget & <sup>15</sup> N	N Additions
E1	Burnt Calluna	Yes	Yes	Yes
E2	Calluna	Yes	Yes	Yes

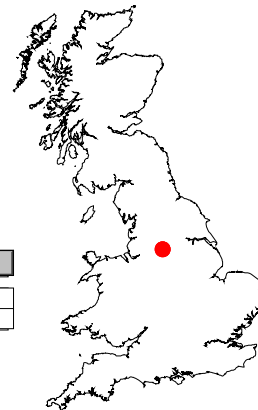
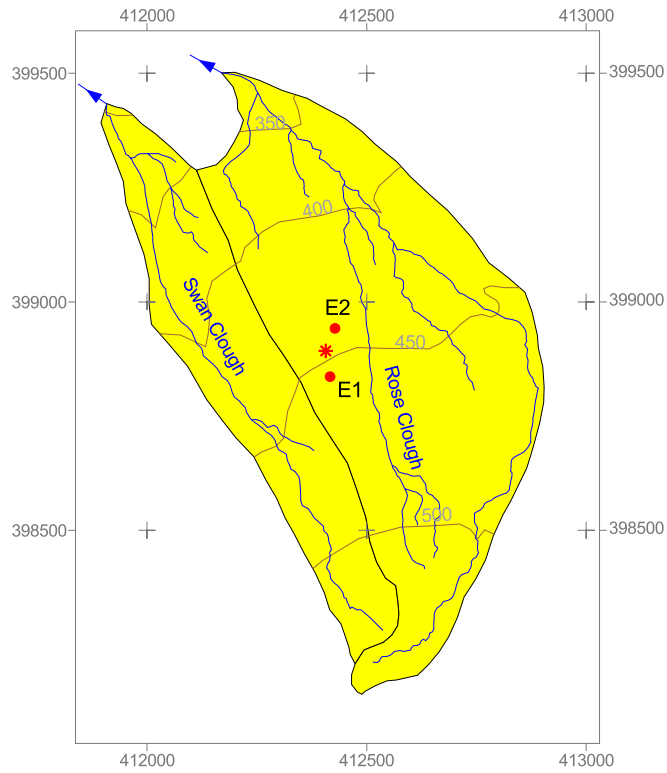


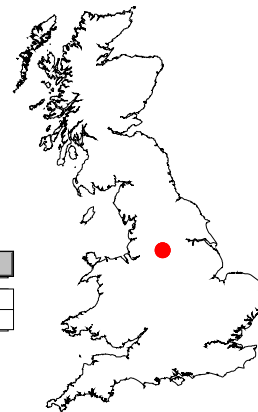
Figure 1.3.3e: Experimental Plots at River Etherow relative to Swan and Rose Clough



## River Etherow, England

- \* Bulk deposition collector
- Experimental plots

Name	Soil	Exclosure	N Budget & <sup>15</sup> N	N Additions
E1	Burnt Calluna	Yes	Yes	Yes
E2	Calluna	Yes	Yes	Yes



### 1.3.2 Acid deposition measurements

In order to provide the best possible N input data the sites were co-located with Acid Deposition Network primary or secondary sites with, as a minimum, bulk deposition collectors within the catchments which are serviced at least 2-weekly. At the Afon Gwy and Allt a'Mharcaidh, weekly samples were collected.

The acid anion, pH and rainfall data are presented in Figures 1.3.4a-d. Annual mean data, raw and volume weighted, are presented in Tables 1.3.6a-b, while budget year mean data are presented in Tables 1.3.7a-b.

Table 1.3.6a: Annual raw mean bulk deposition chemistry

SITE	Period	n	Rain		SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	K <sup>+</sup>	Cond.	H <sup>+</sup>	NMS
			mm	pH	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µScm <sup>-1</sup>	µeqL <sup>-1</sup>
MHAR	1999	39	20.5	4.92	24.0	10.8	8.2	93.6	40.2	20.5	105.0	2.7	22.8	12.1	12.6
MHAR	2000	34	19.8	4.70	21.0	12.1	5.7	68.8	21.1	9.3	79.6	2.2	21.1	19.9	12.7
<b>MHAR</b>	<b>Overall</b>	<b>73</b>	<b>20.2</b>	<b>4.80</b>	<b>22.6</b>	<b>11.4</b>	<b>7.0</b>	<b>82.1</b>	<b>31.3</b>	<b>15.3</b>	<b>93.2</b>	<b>2.5</b>	<b>22.0</b>	<b>15.7</b>	<b>12.6</b>
GWY	1999	41	53.1	4.93	29.4	17.1	19.1	79.2	34.0	21.7	88.0	2.5	22.6	11.6	20.2
GWY	2000	37	60.9	4.83	25.7	11.4	11.2	85.3	19.1	7.2	103.7	2.2	23.5	14.7	15.4
<b>GWY</b>	<b>Overall</b>	<b>78</b>	<b>56.8</b>	<b>4.88</b>	<b>27.7</b>	<b>14.4</b>	<b>15.4</b>	<b>82.1</b>	<b>26.9</b>	<b>14.8</b>	<b>95.5</b>	<b>2.3</b>	<b>23.0</b>	<b>13.1</b>	<b>17.9</b>
SCOAT	1999	23	91.7	4.80	37.6	22.5	28.1	77.7	30.0	18.3	86.2	2.6	26.8	15.8	28.2
SCOAT	2000	20	115.4	4.78	31.4	18.6	21.9	68.9	15.9	7.9	80.8	1.9	23.5	16.6	23.1
<b>SCOAT</b>	<b>Overall</b>	<b>43</b>	<b>102.7</b>	<b>4.79</b>	<b>34.7</b>	<b>20.7</b>	<b>25.2</b>	<b>73.6</b>	<b>23.4</b>	<b>13.5</b>	<b>83.7</b>	<b>2.3</b>	<b>25.2</b>	<b>16.2</b>	<b>25.8</b>
ETHR	1999	22	38.7	4.57	53.2	39.1	41.7	65.0	21.8	26.3	73.3	2.5	31.7	26.9	45.3
ETHR	2000	20	49.1	4.48	46.3	31.1	34.7	50.3	12.1	12.8	62.4	1.7	28.4	33.4	40.2
<b>ETHR</b>	<b>Overall</b>	<b>42</b>	<b>43.6</b>	<b>4.52</b>	<b>49.9</b>	<b>35.3</b>	<b>38.4</b>	<b>58.0</b>	<b>17.1</b>	<b>19.9</b>	<b>68.1</b>	<b>2.1</b>	<b>30.1</b>	<b>30.0</b>	<b>42.9</b>

Table 1.3.6b: Annual mean bulk deposition chemistry(volume weighted)

SITE	Period	n	Rain		SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	K <sup>+</sup>	Cond.	H <sup>+</sup>	NMS
			mm	pH	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µScm <sup>-1</sup>	µeqL <sup>-1</sup>
MHAR	1999	39	20.5	4.99	19.2	8.0	6.5	82.5	35.6	16.5	92.9	2.4	19.9	10.2	9.2
MHAR	2000	34	19.8	4.74	18.1	8.8	4.3	71.3	20.9	7.7	82.3	1.9	20.3	18.3	9.4
<b>MHAR</b>	<b>Overall</b>	<b>73</b>	<b>20.2</b>	<b>4.86</b>	<b>18.7</b>	<b>8.3</b>	<b>5.5</b>	<b>77.4</b>	<b>28.9</b>	<b>12.5</b>	<b>88.1</b>	<b>2.1</b>	<b>20.1</b>	<b>13.9</b>	<b>9.3</b>
GWY	1999	41	53.1	5.01	23.2	9.8	11.8	84.7	36.9	16.8	96.6	2.2	21.3	9.7	13.4
GWY	2000	37	60.9	4.91	22.8	7.6	7.5	92.5	20.7	7.0	112.5	2.3	22.9	12.4	11.6
<b>GWY</b>	<b>Overall</b>	<b>78</b>	<b>56.8</b>	<b>4.96</b>	<b>23.0</b>	<b>8.7</b>	<b>9.6</b>	<b>88.6</b>	<b>28.6</b>	<b>11.8</b>	<b>104.7</b>	<b>2.2</b>	<b>22.1</b>	<b>11.1</b>	<b>12.5</b>
SCOAT	1999	23	91.7	4.86	32.9	16.0	20.8	85.0	31.7	16.2	95.1	2.4	25.2	13.9	22.6
SCOAT	2000	20	115.4	4.83	25.8	11.9	13.7	73.4	16.8	6.8	86.8	1.9	21.5	14.7	16.9
<b>SCOAT</b>	<b>Overall</b>	<b>43</b>	<b>102.7</b>	<b>4.84</b>	<b>29.2</b>	<b>13.9</b>	<b>17.1</b>	<b>78.9</b>	<b>24.0</b>	<b>11.3</b>	<b>90.7</b>	<b>2.1</b>	<b>23.2</b>	<b>14.3</b>	<b>19.6</b>
ETHR	1999	22	38.7	4.61	45.9	30.6	34.1	60.3	20.9	22.4	69.0	2.3	28.4	24.6	38.6
ETHR	2000	20	49.1	4.49	39.9	24.2	26.3	52.1	12.4	10.7	64.1	1.6	26.2	32.6	33.5
<b>ETHR</b>	<b>Overall</b>	<b>42</b>	<b>43.6</b>	<b>4.54</b>	<b>42.7</b>	<b>27.2</b>	<b>29.9</b>	<b>55.9</b>	<b>16.3</b>	<b>16.1</b>	<b>66.4</b>	<b>1.9</b>	<b>27.2</b>	<b>28.9</b>	<b>35.9</b>

Tables 1.3.6a and b show that 2000 was a wetter year than 1999 for all sites except the Allt a'Mharcaidh, and acidity deposition was also greater in 2000 at all sites. Both acid anion and base cation concentrations were greater in 1999 for all sites.

Mean data for the CLAM budget year (19th October 1999 to 4th October 2000) show a significant difference in the loading of acid anions at each site, with lowest concentrations of non-marine SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> at the Allt a'Mharcaidh, followed by the Afon Gwy, Scoat Tarn and then largest for all acid anions at the River Etherow. The pH of bulk deposition is, however, surprisingly constant at all sites (c. 4.9) except the Etherow, where bulk deposition is much more acid (pH = 4.5).

Table 1.3.7a: Budget year bulk deposition mean chemistry (raw data)

SITE	Rain		SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	K <sup>+</sup>	Cond.	H <sup>+</sup>	NMS	
	n	mm	pH	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µScm <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	
MHAR	36	868	4.85	19.4	9.4	5.1	76.1	26.9	11.6	87.0	2.4	20.4	14.1	10.2
GWY	37	1983	4.82	25.9	13.3	12.6	76.8	21.7	9.1	92.5	1.9	22.6	15.3	17.0
SCOAT	20	2202	4.81	34.3	18.3	21.2	88.6	24.7	10.3	100.8	2.2	26.7	15.4	23.5
ETHR	23	984	4.50	49.5	32.1	35.8	62.0	16.9	15.2	74.5	1.9	30.3	31.3	42.0

Table 1.3.7b: Budget year bulk deposition mean chemistry (volume weighted)

SITE	Rain		SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	K <sup>+</sup>	Cond.	H <sup>+</sup>	NMS	
	n	mm	pH	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	µScm <sup>-1</sup>	µeqL <sup>-1</sup>	µeqL <sup>-1</sup>	
MHAR	36	868	4.88	16.5	6.5	3.9	74.5	25.8	9.7	85.0	2.0	19.0	13.3	7.4
GWY	37	1983	4.90	21.1	8.9	8.0	74.5	22.4	9.1	90.5	1.8	20.3	12.5	12.6
SCOAT	20	2202	4.87	28.6	11.9	13.2	89.6	24.7	9.1	103.1	2.1	24.3	13.5	17.7
ETHR	23	984	4.48	45.6	27.3	28.7	62.2	17.4	13.9	74.8	1.8	29.2	33.4	38.1

Note that while acid anion concentrations at Scoat Tarn are around half those at the Etherow, rainfall at Scoat Tarn is more than double, indicating that for bulk deposition inputs, acid anion fluxes are of similar magnitude at both sites. At the Allt a'Mharcaidh, the lowest concentrations of acid anions coincide with the lowest rainfall, leading to fluxes in bulk deposition which are much lower than at the other three sites (Table 1.3.8).

Table 1.3.8 Bulk deposition input fluxes(kg ha<sup>-1</sup> yr<sup>-1</sup>)

Site	NM SO <sub>4</sub> <sup>2-</sup> -S	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	TIN
MHAR	1.5	1.1	0.7	1.8
GWY	5.6	3.5	3.1	6.6
SCOAT	8.1	4.8	5.3	10.1
ETHR	6.8	4.2	4.5	8.7

Note that the figures in Table 1.3.8 assume that volume weighted concentrations of bulk deposition samples (weekly at Mharcaidh and Gwy, 2-weekly at Scoat and Etherow) can be extrapolated for missing samples to give an annual value, i.e. mean weekly/2-weekly rainfall and concentrations are representative for the whole year. These figures show that bulk deposition inputs of acidity to Scoat Tarn are greater than for the Etherow, for both non-marine sulphate and total inorganic nitrogen.

It is known that bulk deposition collectors provide only approximate data for wet deposition inputs (and rainfall) and completely neglect dry deposition inputs. For comparison with the bulk deposition fluxes, total deposition figures (wet+dry) from the CEH national database for the most recent available period (1995-97) are provided in Table 1.3.9. While emissions of both S and N may have decreased since 1995-97, the very large difference in fluxes between these data and those for bulk deposition in 1999-2000 will be due largely to the omission of dry deposition from the latter.

Table 1.3.9 Total deposition input fluxes from CEH national data (kg ha<sup>-1</sup> yr<sup>-1</sup>) – mean values for 1995-97

Site	NM SO <sub>4</sub> <sup>2-</sup> -S	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	TIN
MHAR	6.7	3.1	4.2	7.3
GWY	18.7	9.2	17.8	27.0
SCOAT	24.0	11.2	22.4	33.6
ETHR	34.1	12.2	21.6	33.7

These figures are very similar to those for 1996 reported in the AWMN 10 Year Report (Monteith & Evans, 2000), and were derived in the same way.

Compared with the data for 1992-94 used in site selection to ensure that a gradient of N deposition was covered (Table 1.3.1), the 1995-97 data show an increase in TIN deposition at all sites. While the four sites are still ranked in the same order of increasing N deposition, estimated deposition at Scoat Tarn has increased by a much greater proportion, so that while it was deemed to experience a similar level of N deposition to the Afon Gwy during site selection (see Table 1.3.1), more recent data indicate that it seems to experience a higher deposition load than the Gwy, and is much more similar to that found at the highest deposition site, the River Etherow (Table 1.3.9).

Acid anion deposition fluxes are shown in Figure 1.3.5. It can be seen that deposition input fluxes occur in a pattern of pulsed events, which is particularly evident at the Etherow. These large flux events do not coincide with concentration peaks in bulk deposition (Figure 1.3.4) and therefore it is rainfall which drives these large fluxes.



Figure 1.3.4a: Bulk deposition chemistry and rainfall at the Allt a' Mharcaidh

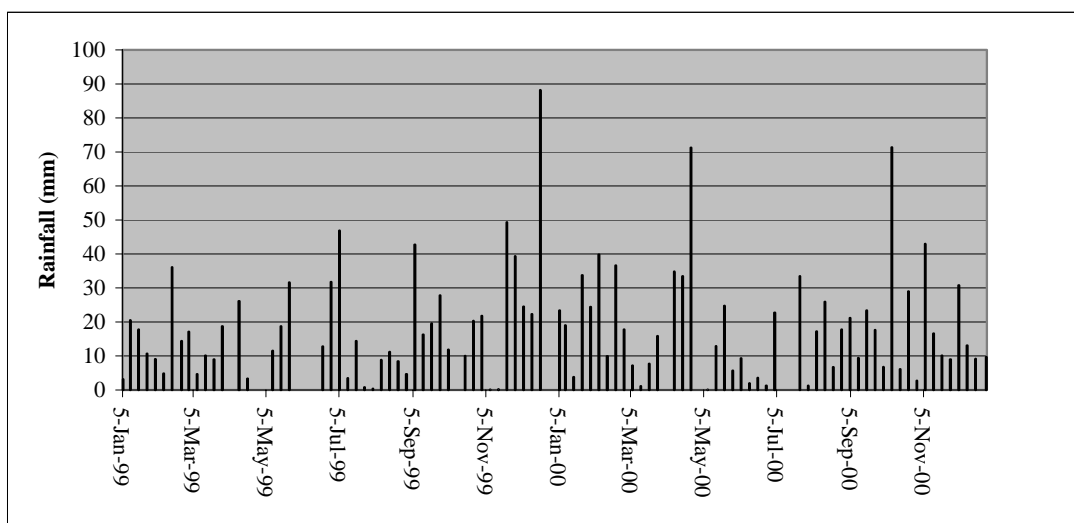
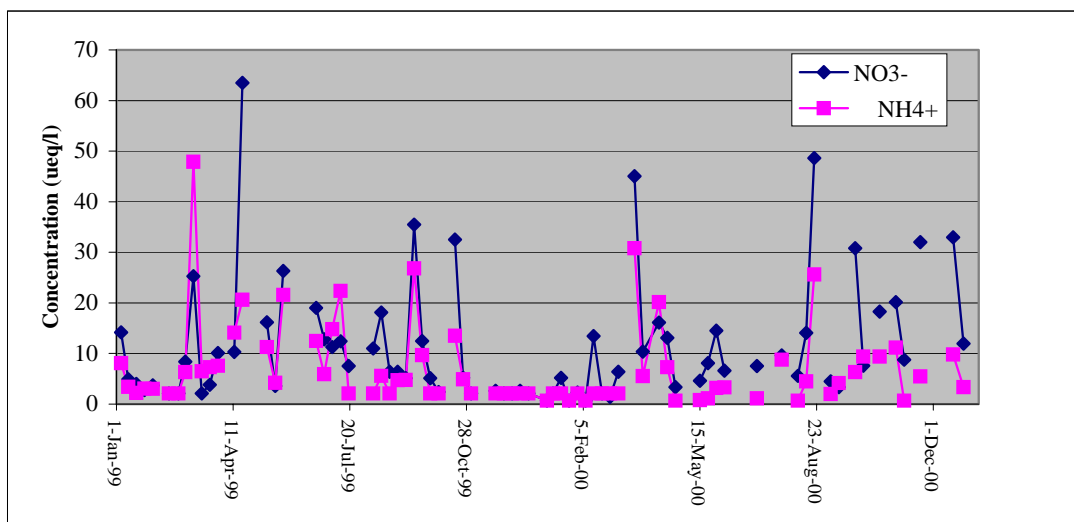
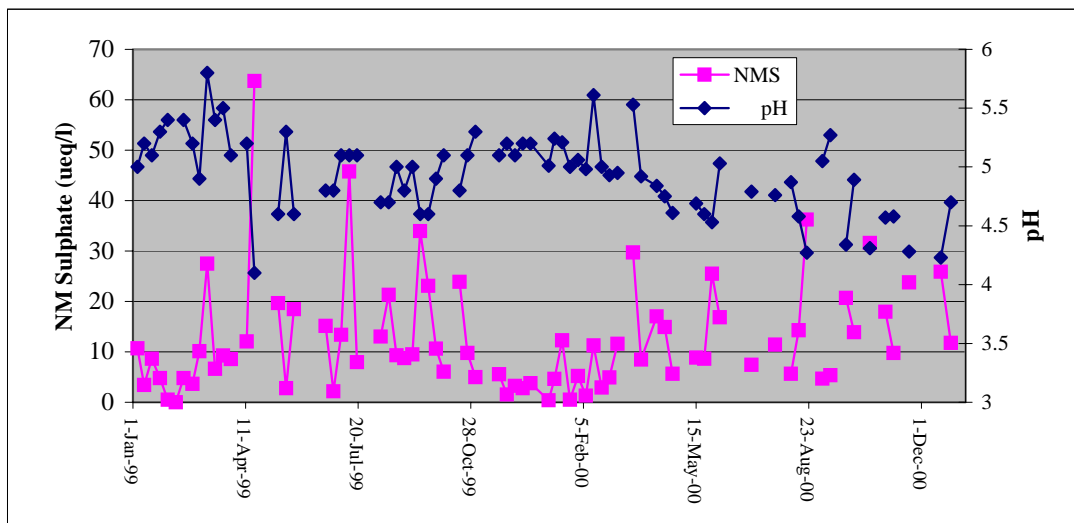


Figure 1.3.4b: Bulk deposition chemistry and rainfall at the Afon Gwy

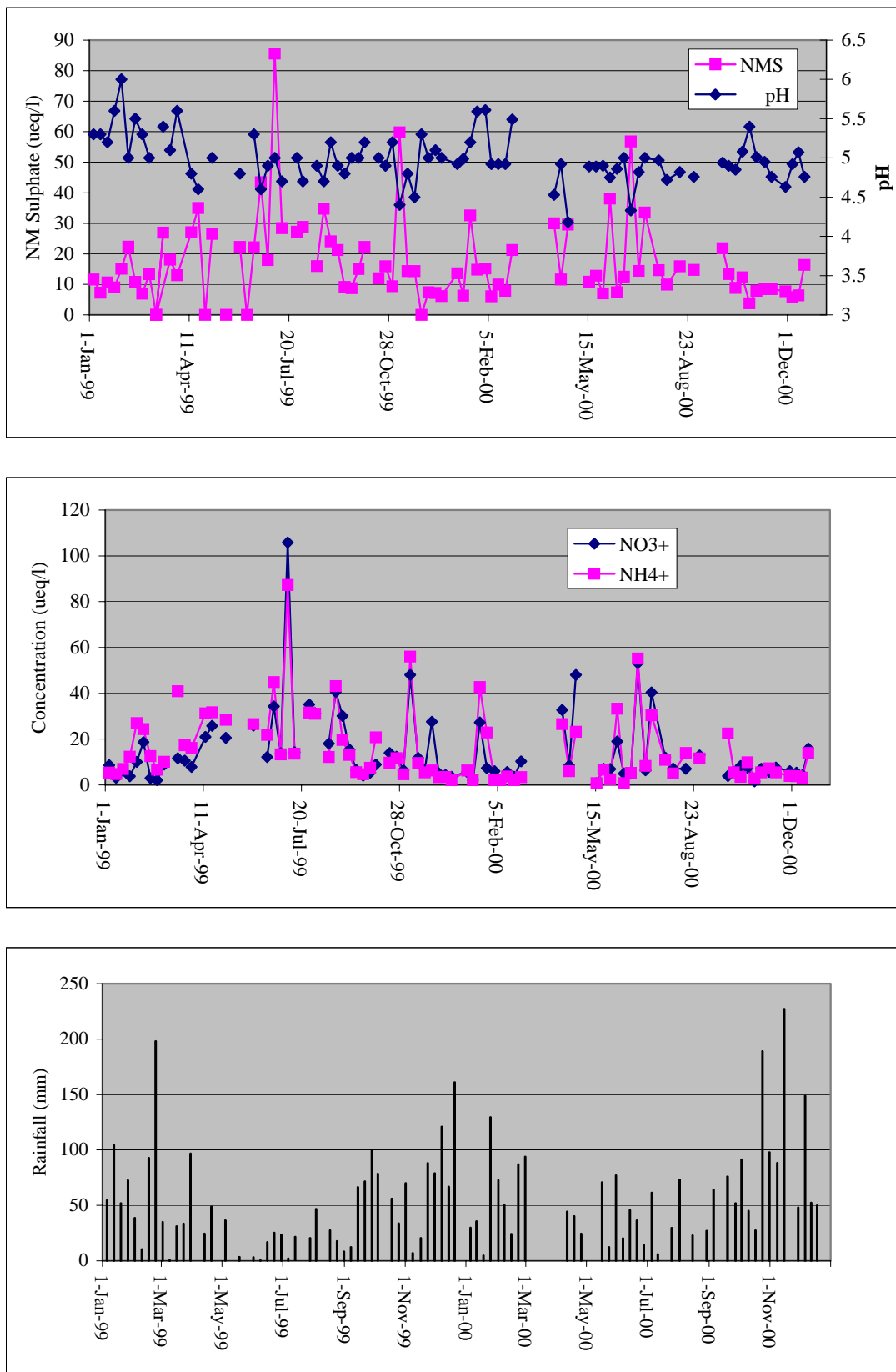


Figure 1.3.4c: Bulk deposition chemistry and rainfall at Scoat Tarn

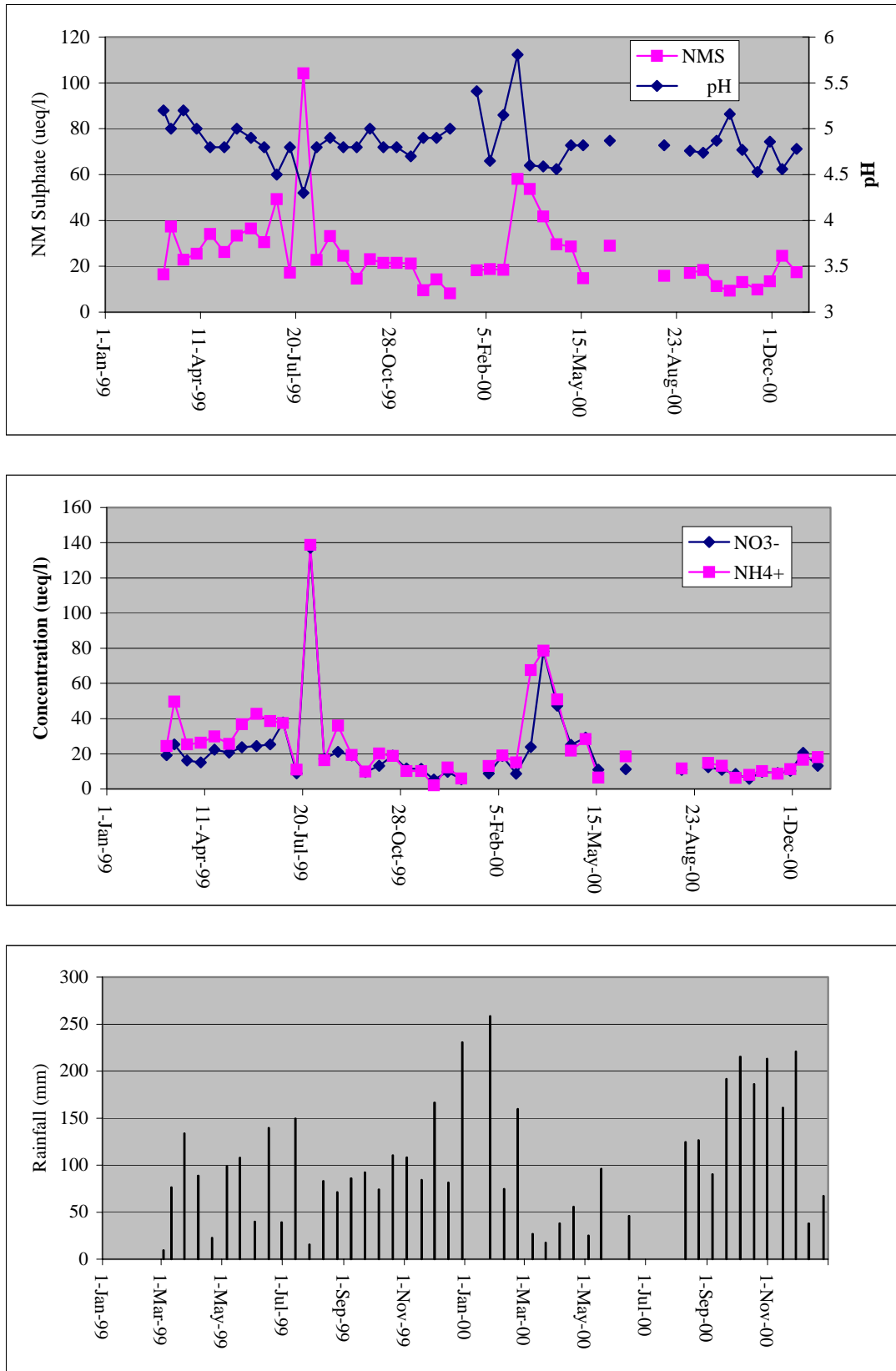


Figure 1.3.4d: Bulk deposition chemistry and rainfall at the River Etherow

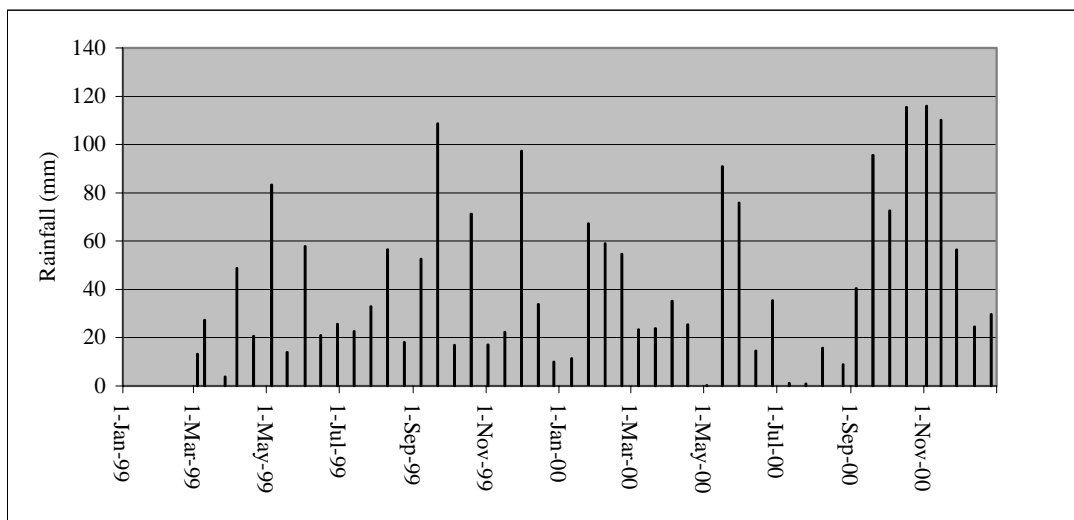
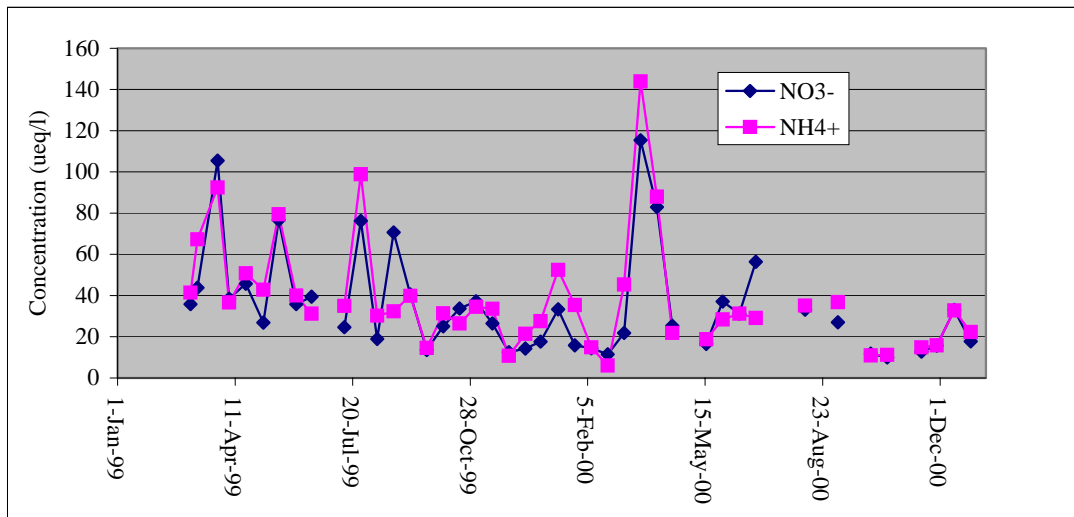
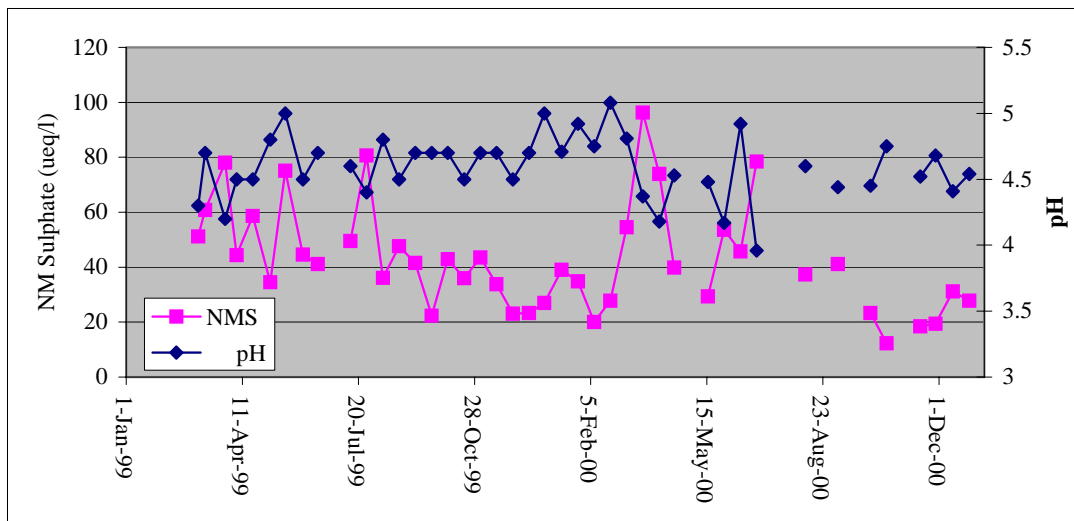
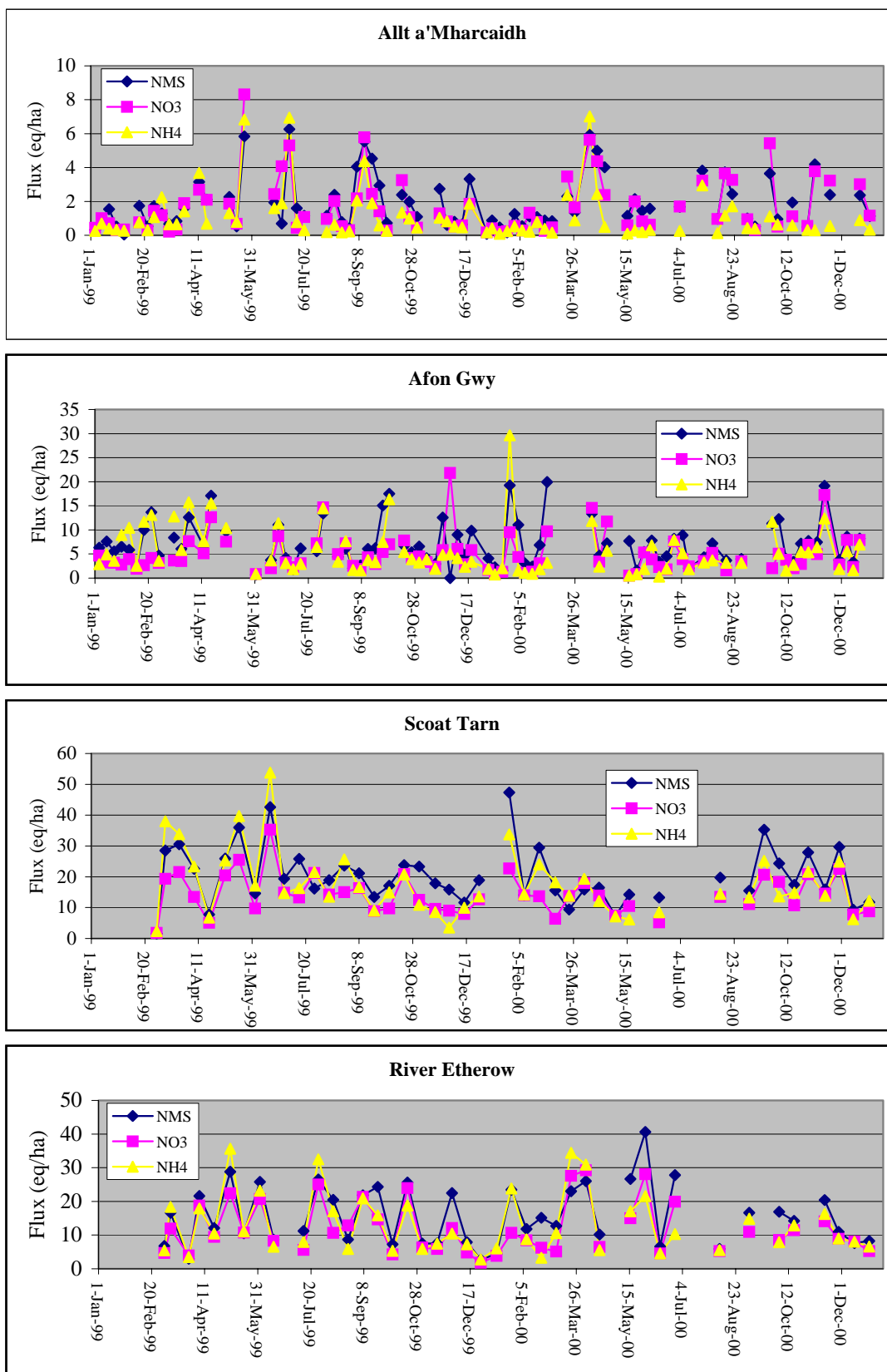


Figure 1.3.5 Acid anion deposition fluxes



### 1.3.3 Water chemistry (leaching outputs)

Mean water chemistry data for the CLAM budget year (19th Oct. 1999 – 18th Oct. 2000) were calculated for all four CLAM sites (not flow weighted) and associated streams (Table 1.3.10). The data show a gradient of acidity, from the highest pH (geometric mean) at the Allt a'Mharcaidh, decreasing through the Afon Gwy and Scoat Tarn to a minimum at the River Etherow.

The acidity gradient across the four primary sites follows the gradient in acid anion concentrations and sea-salt inputs (as chloride), with lowest values of non-marine  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  at the Allt a'Mharcaidh and the highest values in the River Etherow and its tributaries. Similarly, alkalinity and TOC decline with increasing acidity, except at the Etherow which has by far the most coloured of the waters sampled (much greater TOC and organic N).

The mean chemistry data for the Afon Gwy and Scoat Tarn are very similar for all common determinands, the major difference being the higher TOC value in the Gwy, a reflection of the very high clarity (low colour and organic content) of the water at Scoat Tarn.

Table 1.3.10: Budget year mean water chemistry

Site	Alk. $\mu\text{eq l}^{-1}$	pH	$\text{SO}_4^{2-}$ $\mu\text{eq l}^{-1}$	NM $\text{SO}_4^{2-}$ $\mu\text{eq l}^{-1}$	$\text{NH}_4$ $\mu\text{eq l}^{-1}$	$\text{NO}_3$ $\mu\text{eq l}^{-1}$	Org N $\mu\text{g l}^{-1}$	Total N $\mu\text{g l}^{-1}$	TOC $\text{mg l}^{-1}$	Cl $\mu\text{eq l}^{-1}$
<b>Allt a'Mharcaidh</b>	41	6.25	38	28	<b>0.1</b>	<b>1</b>	115	126	3.0	103
<b>Mhar2</b>	33	5.89	36	27	<b>0.0</b>	<b>1</b>	127	138	3.2	91
<b>Mhar3</b>	23	6.08	38	28	<b>0.1</b>	<b>1</b>	105	118	2.7	89
<b>Afon Gwy</b>	5	5.47	52	38	<b>0.0</b>	<b>6</b>	-	-	2.9	132
<b>Scoat Fell stream</b>	0	5.39	57	41	<b>0.6</b>	<b>11</b>	113	258	1.3	158
<b>Red Pike stream</b>	-5	5.10	57	40	<b>0.4</b>	<b>17</b>	98	318	1.0	163
<b>Scoat Tarn</b>	-6	5.10	53	36	<b>0.5</b>	<b>15</b>	125	329	1.5	162
<b>River Etherow</b>	22	4.72	191	152	<b>0.5</b>	<b>42</b>	317	860	8.0	373
<b>Swan Clough</b>	74	4.72	225	207	<b>0.5</b>	<b>58</b>	437	1174	9.1	169
<b>Rose Clough</b>	-83	4.11	191	176	<b>2.0</b>	<b>43</b>	639	1160	17.7	153

The two sampled tributaries of the Allt a'Mharcaidh have, as expected, very similar, dilute chemistry to the main river, the main difference being their slightly lower pH and alkalinity concentrations.

Of the two sampled inflow streams to Scoat Tarn, Red Pike stream has almost identical chemistry except for lower organic content (organic N and TOC), while Scoat Fell stream is slightly less acid and has a lower nitrate concentration and slightly higher alkalinity than the lake itself. The difference in chemistry between the two streams, while not great, probably reflects the difference in catchment characteristics and soil types of their subcatchments.

Even more marked is the difference between the chemistry of the two tributaries to the Etherow, Swan Clough and Rose Clough, which drain the CLAM experimental

area. The two tributaries have very different chemistries from the main body of the Etherow, which is perhaps to be expected given that the catchment of the Etherow is very large and includes much improved pasture and a major road, while the two streams drain a relatively undisturbed area of deep peat.

Of greater interest is the major difference between the chemistry of the two tributaries, which are separated by only a few hundred metres and drain similar terrain either side of the small interfluvium on which the terrestrial experimental plots are located. The difference in alkalinity between the streams is more than 150  $\mu\text{eq l}^{-1}$  and more than half a pH unit (a big difference in  $\text{H}^+$  at such low pH values). The more acid stream, Rose Clough, has a very high organic content, in particular TOC which is almost double the level found in Swan Clough (which does itself have a high TOC content). Rose Clough is also the only water body studied within this part of the work programme which regularly has measurable concentrations of ammonium, while its nitrate concentration, though high, is less than that in Swan Clough. These major differences are presumably due to hydrological factors which could account for dramatic changes in water chemistry, depending on flow routing through the very acid deep peats.

The chemical time series data are shown in Figures 1.3.6 – 1.3.9 and discussed for each catchment below.

#### Allt a'Mharcaidh

The pH of the Mharcaidh and its tributaries is relatively constant at around pH 6.5 but is subject to periodic depressions down to pH 5.0-5.5, associated with high flow events. These acid episodes are sufficient to depress alkalinity to near zero from a mean value of 41  $\mu\text{eq l}^{-1}$  in the main river, and small, negative alkalinity values are occasionally observed in Site 2 (Fig. 1.3.6a). Chloride concentrations are relatively stable at all sample points, with some flow-associated depressions observed.

While mean  $\text{NO}_3^-$  levels are very low in the Mharcaidh system (c. 1  $\mu\text{eq l}^{-1}$ ) a seasonal pattern in leaching can be observed, even at these low levels (Fig. 1.3.6b). Zero values throughout the summer (though less so in 2000 than 1999) are followed by persistent levels up to 3-4  $\mu\text{eq l}^{-1}$  during the winter months. Concentrations of  $\text{NH}_4^+$  are almost all zero, with just a few very low values observed during the two years of monitoring. Concentrations of organic N followed a cyclical (but not obviously seasonal) pattern in 1999 which seemed to overlay an increasing trend throughout the year, but in 2000 this pattern seems to have broken down (Fig. 1.3.6b). At the Mharcaidh, the very low levels of inorganic N mean that the pattern in total N is driven almost entirely by organic N (Fig. 1.3.6c).

Total  $\text{SO}_4^{2-}$  concentrations are low (mean 38  $\mu\text{eq l}^{-1}$ ) and are depressed in high flow events (Fig. 1.3.6c). Non-marine  $\text{SO}_4^{2-}$  is probably quite close to background levels (mean 28  $\mu\text{eq l}^{-1}$ ). TOC values are generally low (c. 2  $\text{mg l}^{-1}$ ) but the mean is increased to 3  $\text{mg l}^{-1}$  by high values due to flushing at high flow events.

Figure 1.3.6a: Allt a'Mharcaidh streams water chemistry (pH, alkalinity and chloride)

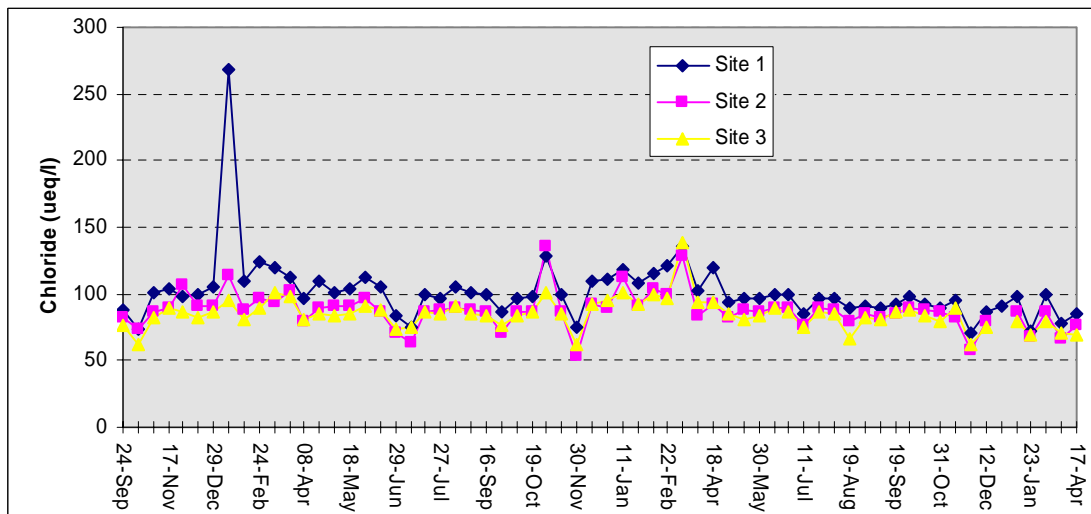
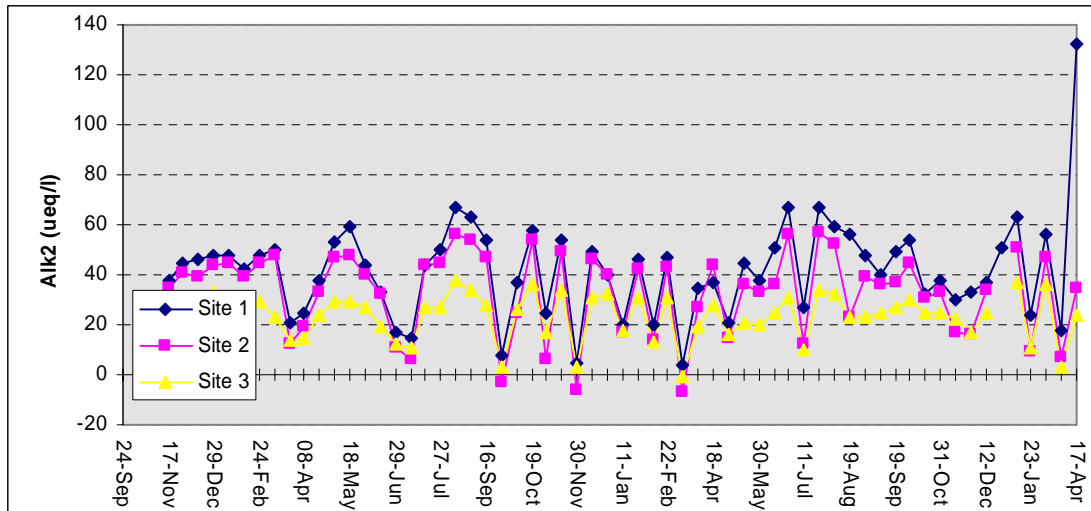
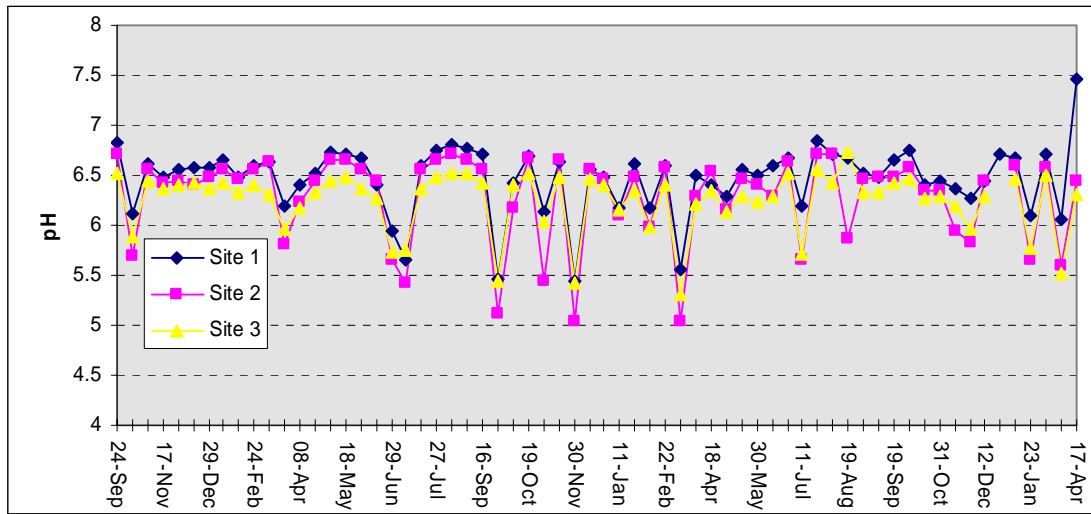




Figure 1.3.6b: Allt a'Mharcaidh streams water chemistry (inorganic N species)

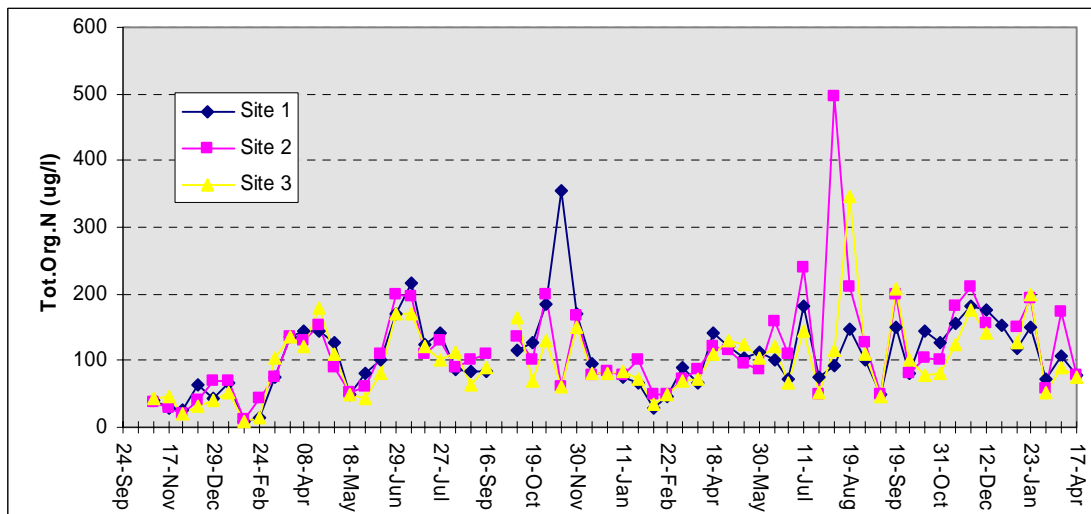
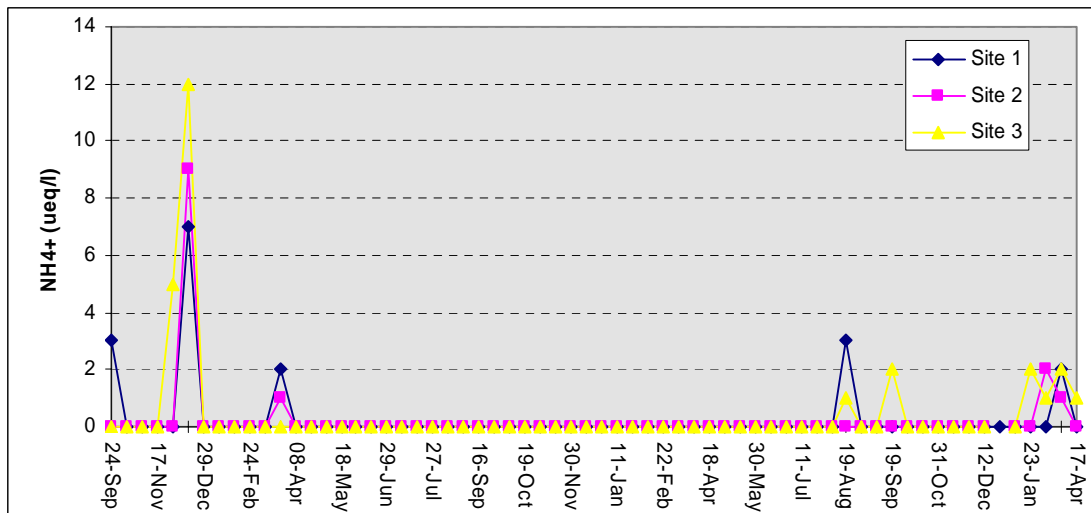
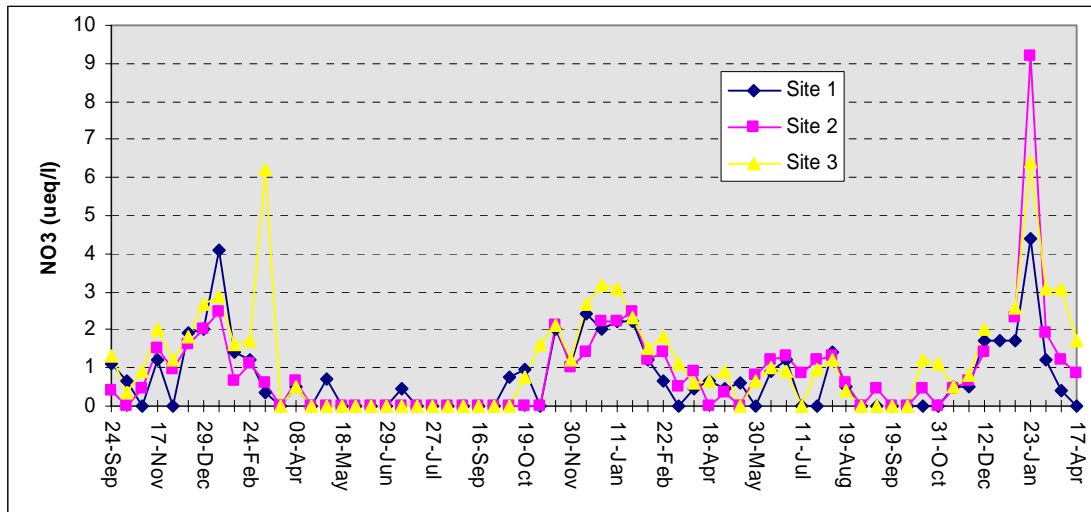


Figure 1.3.6c: Allt a'Mharcaidh streams water chemistry (sulphate and organics)

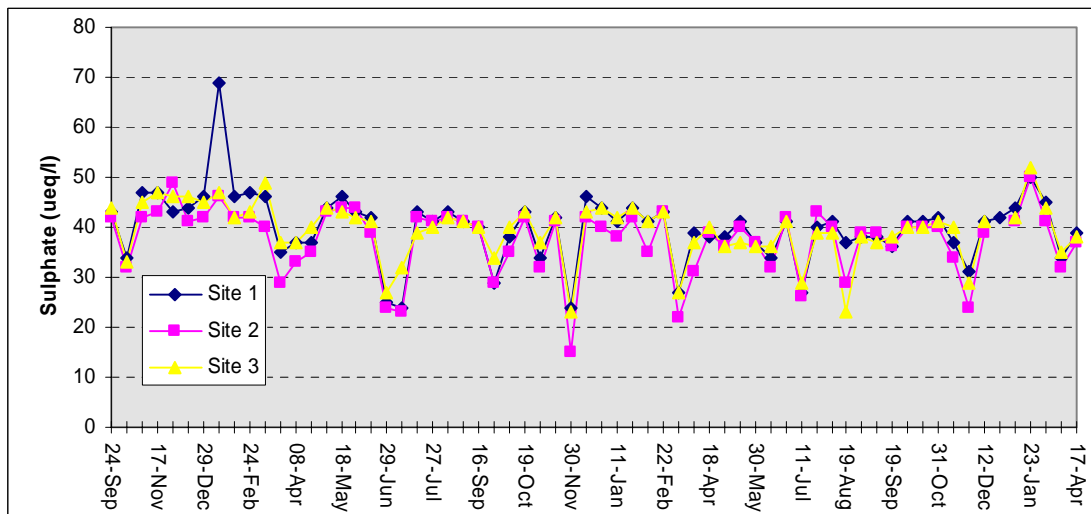
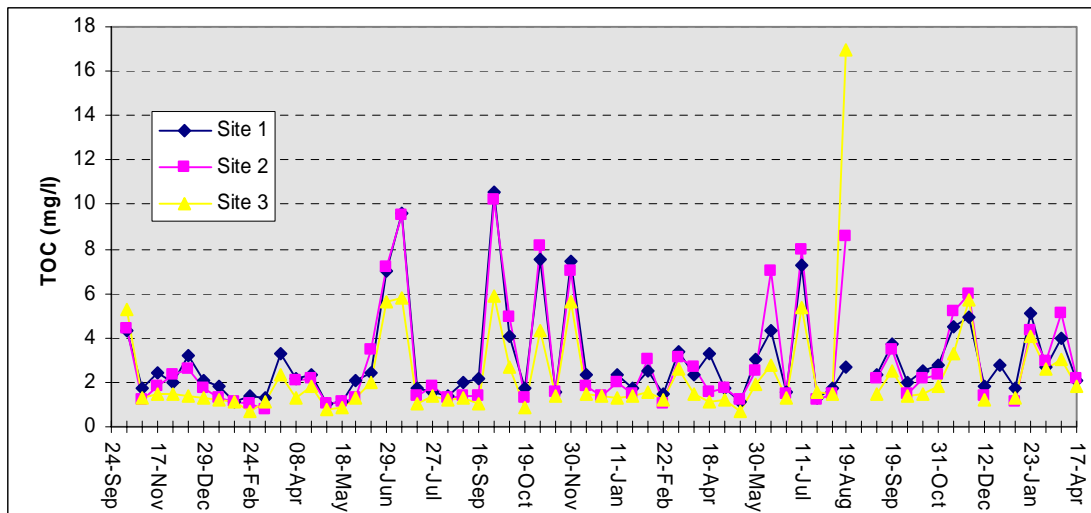
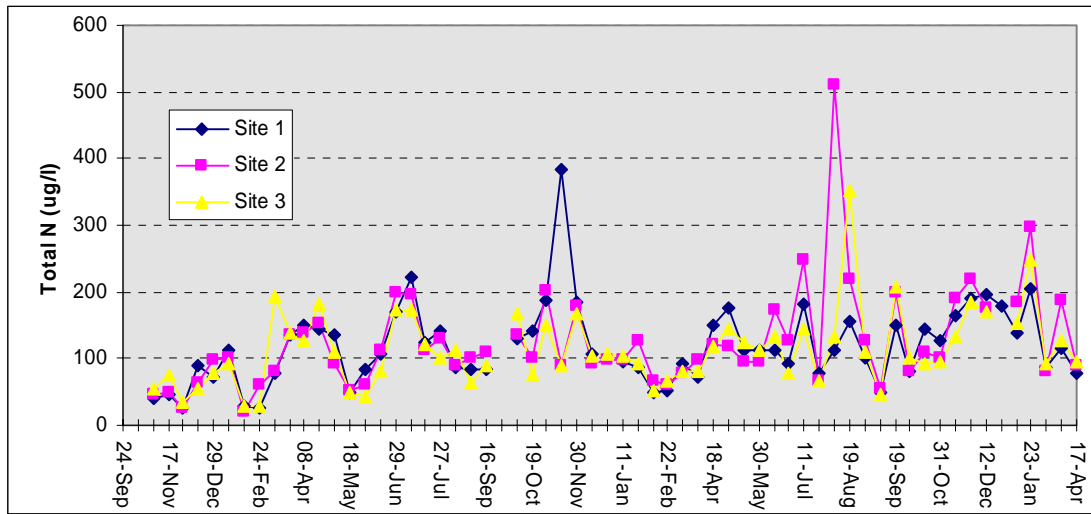


Figure 1.3.7a: Afon Gwy water chemistry (pH, alkalinity and chloride)

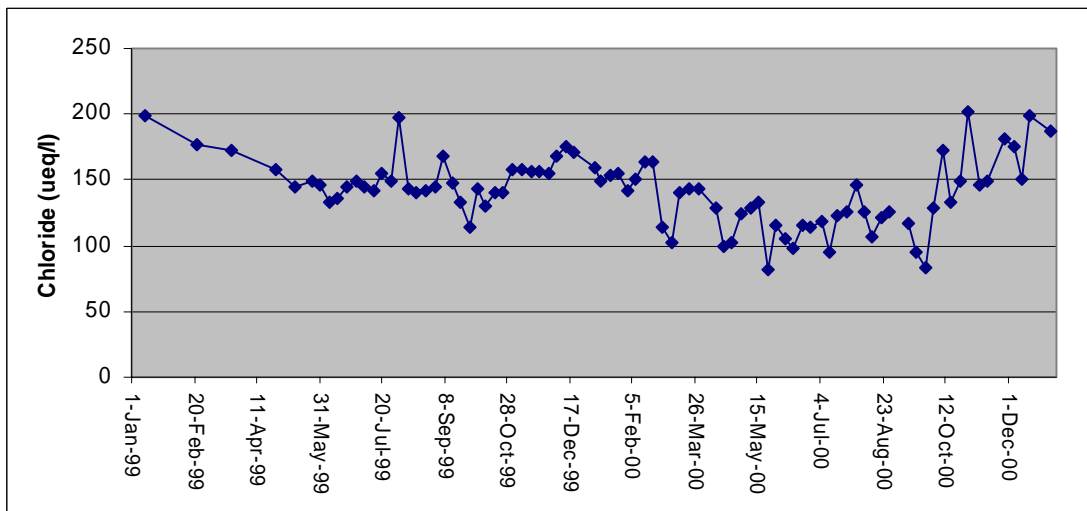
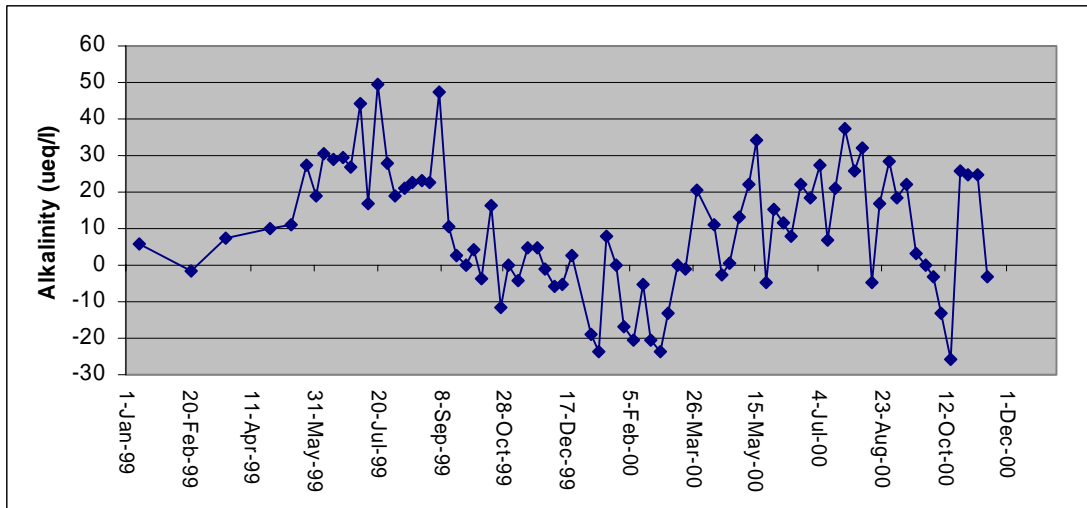
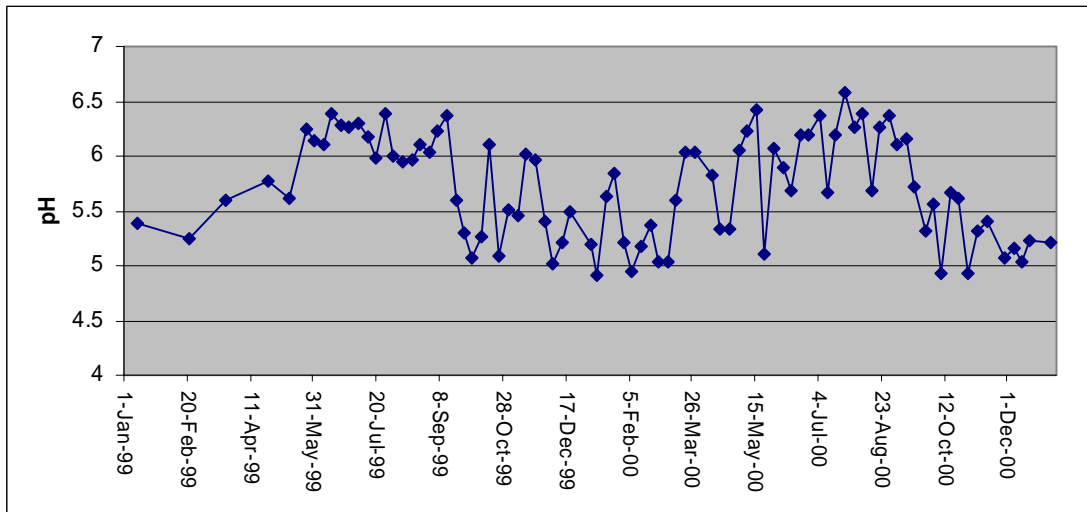


Figure 1.3.7b: Afon Gwy water chemistry (acid anions and DOC)

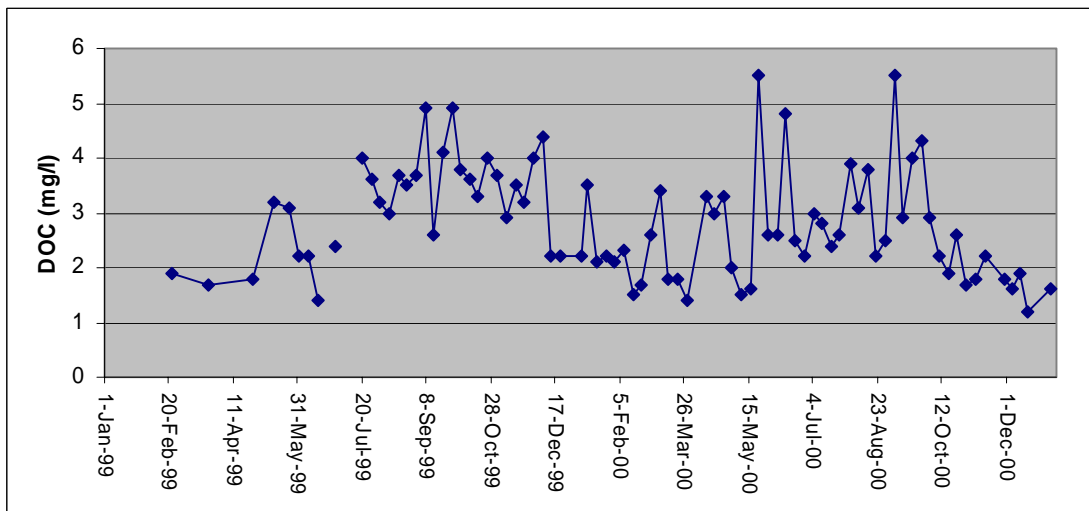
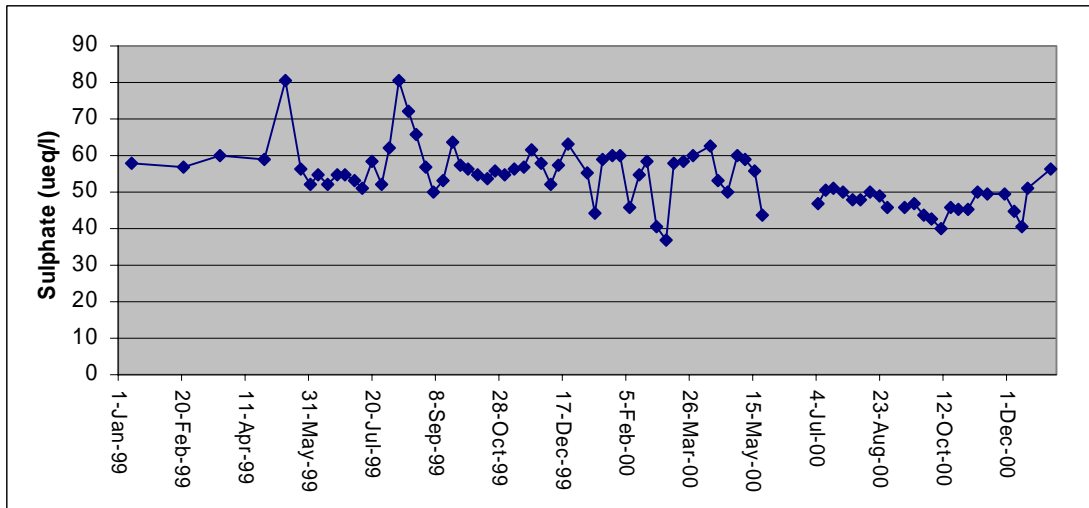
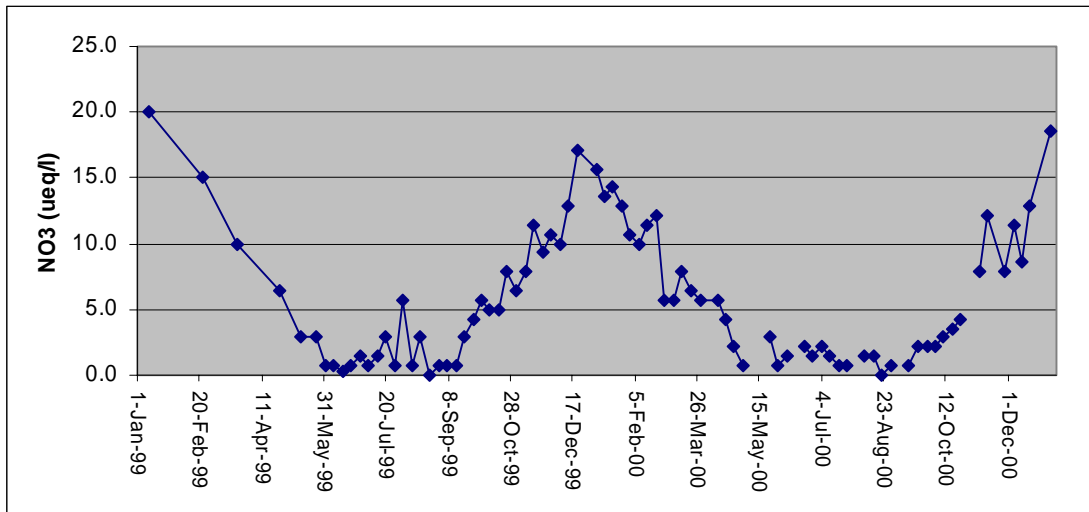


Figure 1.3.8a: Scoat Tarn and inflow streams water chemistry (pH, alkalinity and chloride)

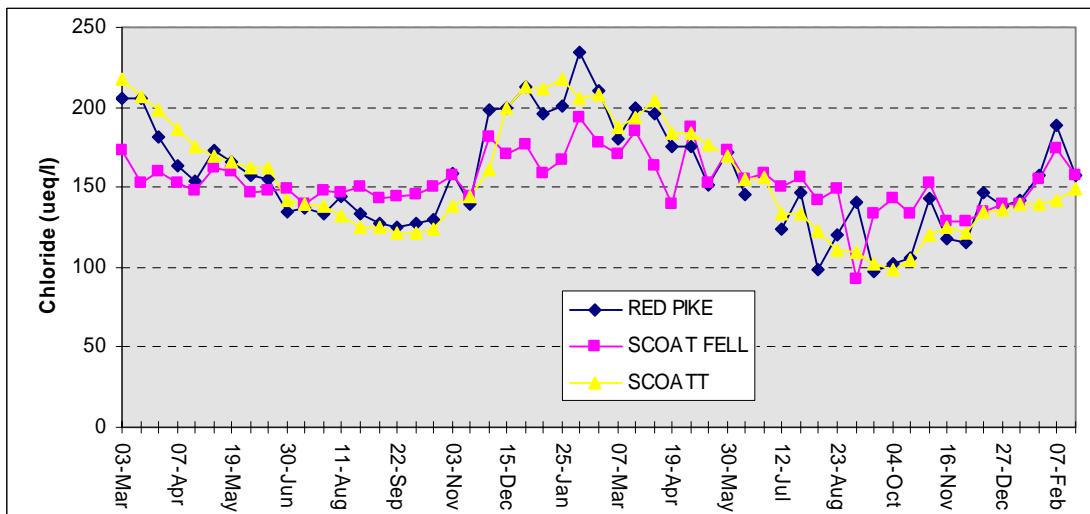
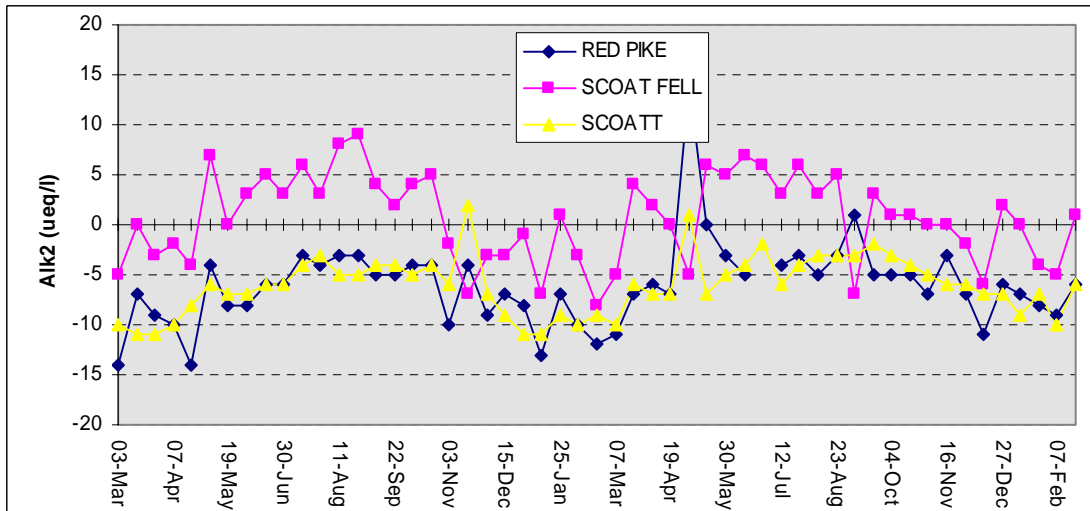
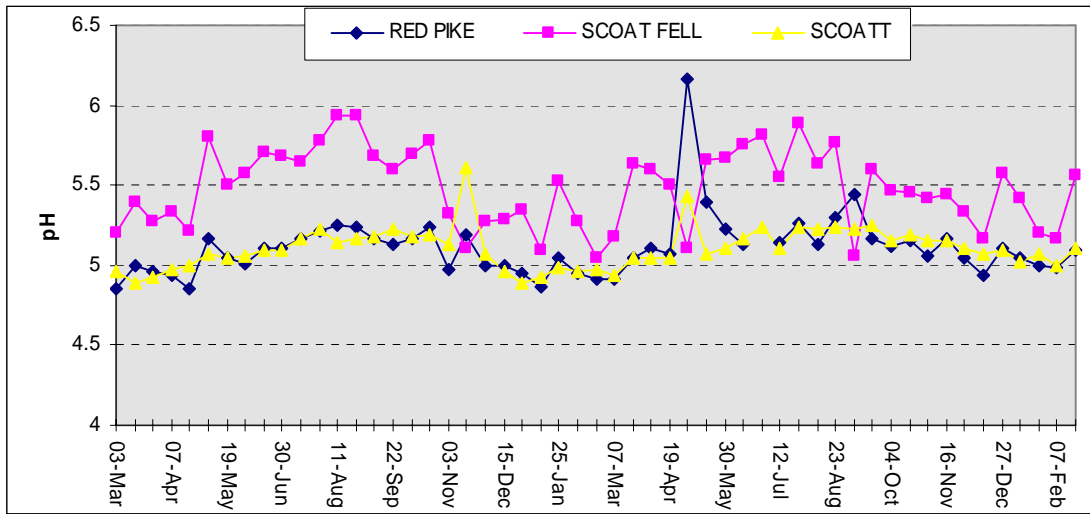


Figure 1.3.8b: Scoat Tarn and inflow streams water chemistry (inorganic N species)

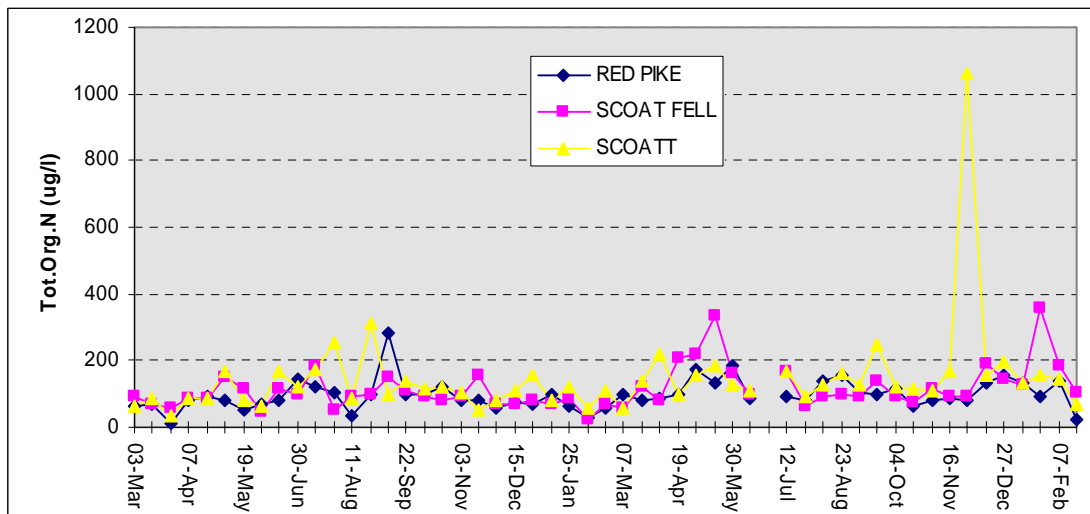
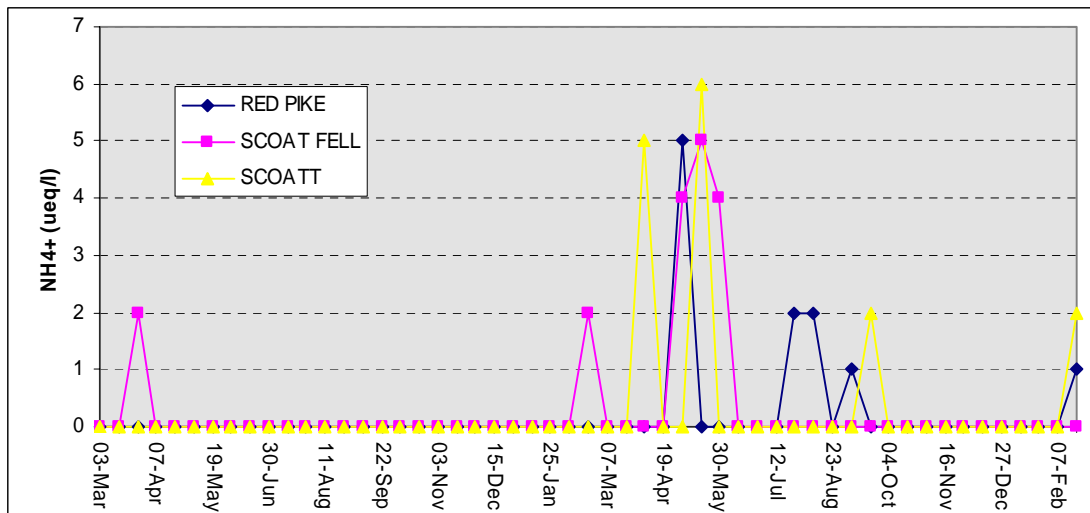
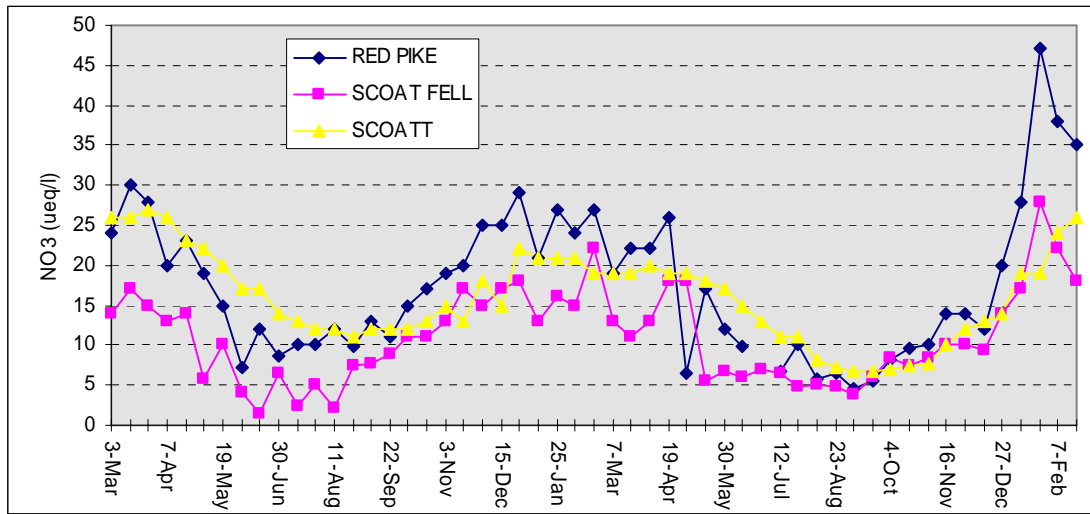


Figure 1.3.8c: Scoat Tarn and inflow streams water chemistry (sulphate and organics)

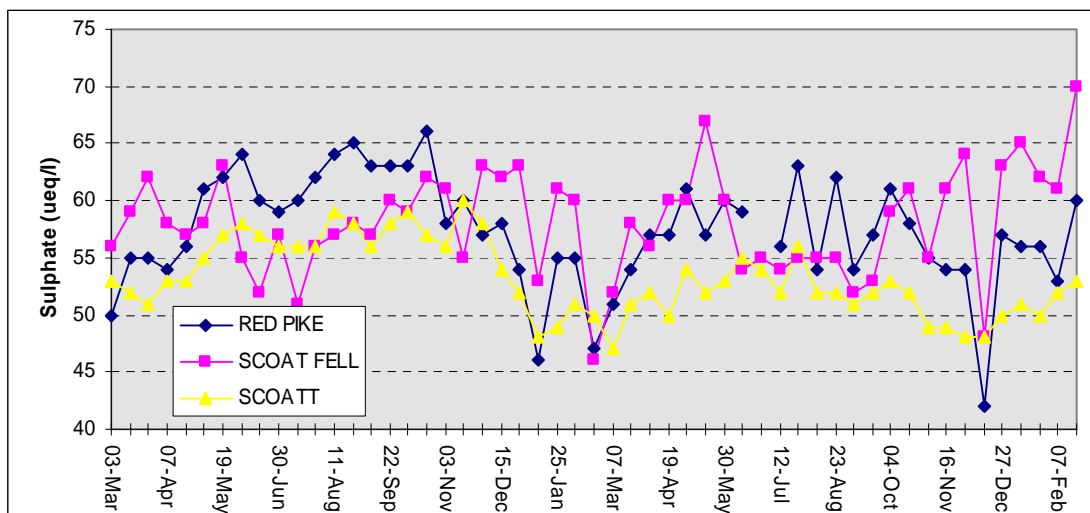
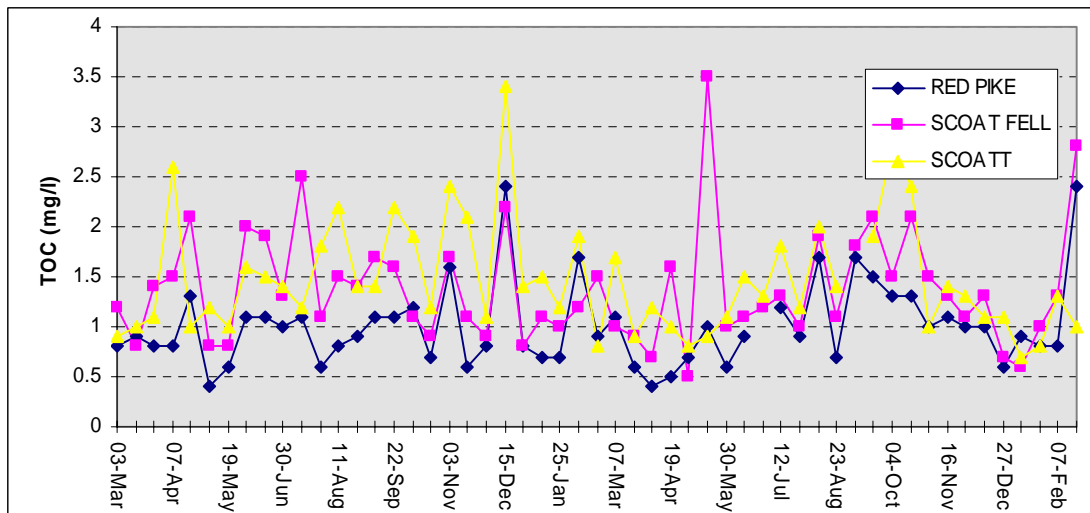
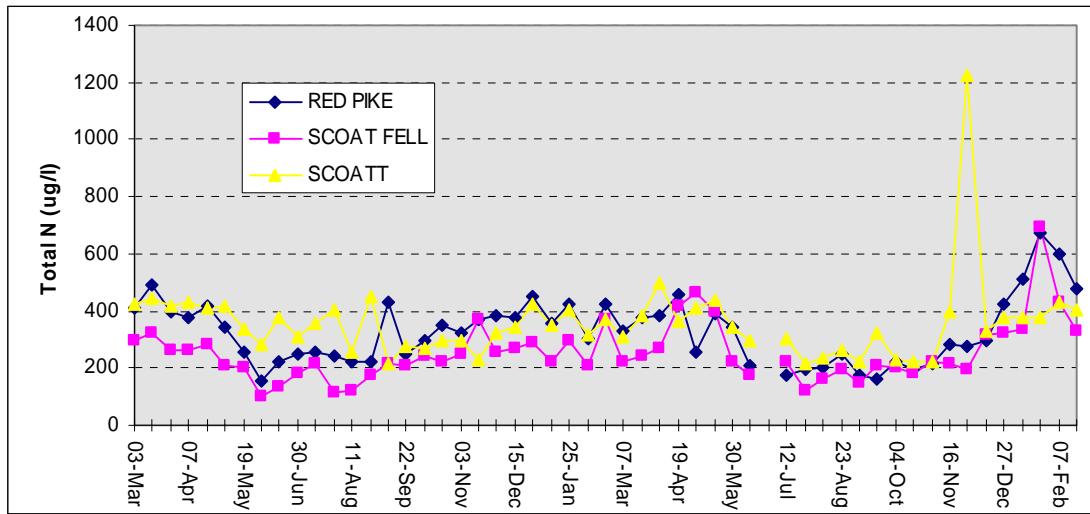


Figure 1.3.8d: Scoat Tarn and inflow streams: comparison of seasonal variations in  $\text{NO}_3^-$ , non-marine  $\text{SO}_4^{2-}$  and chloride

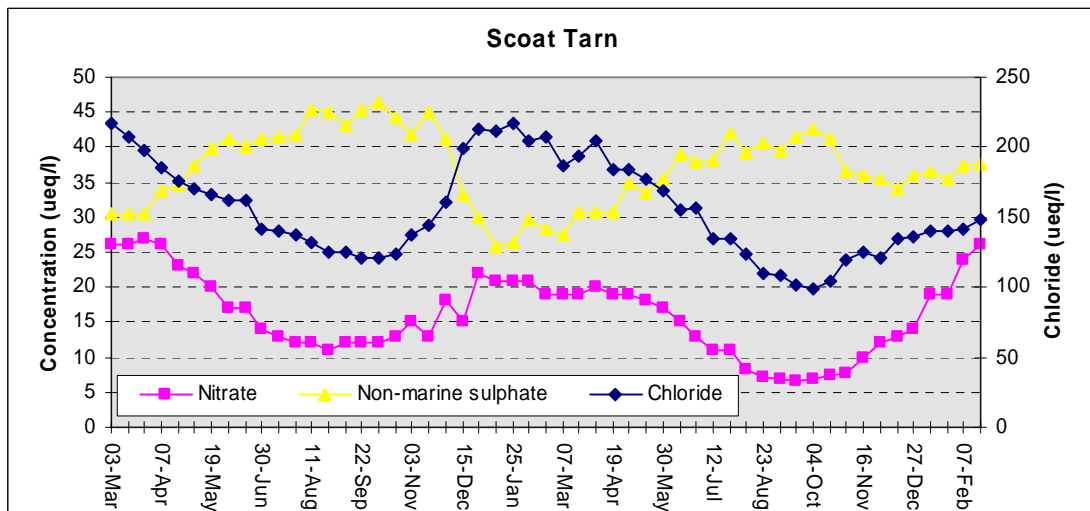
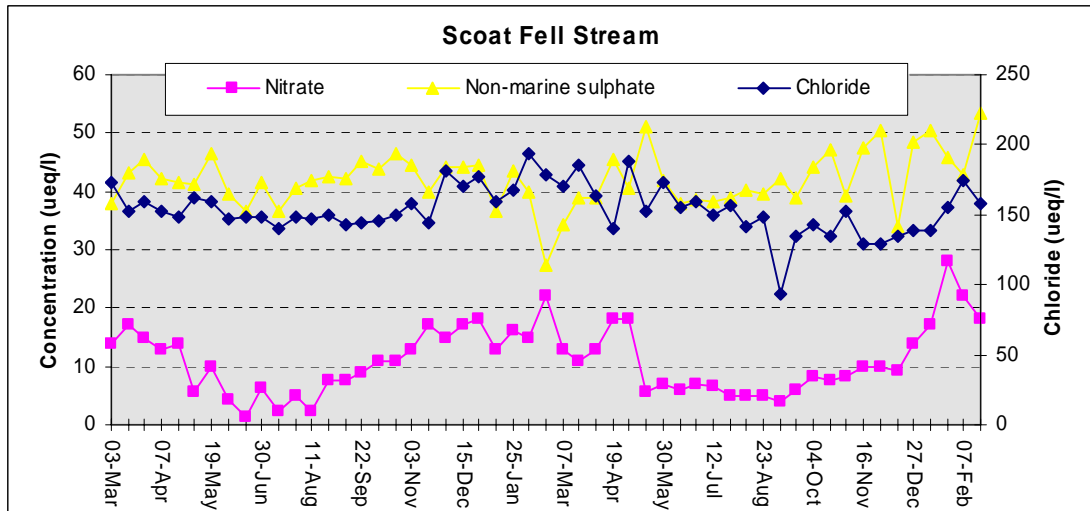
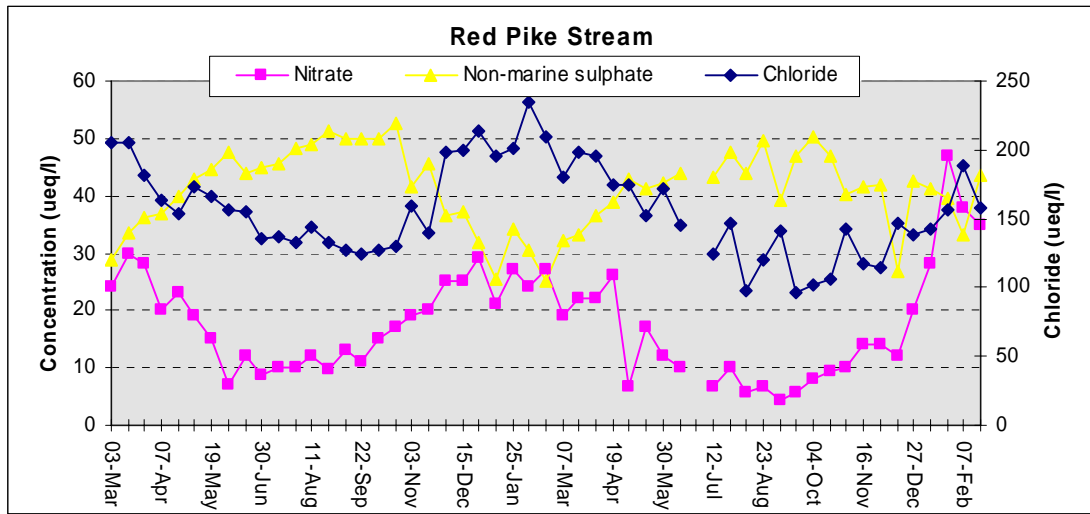




Figure 1.3.9a: Etherow streams water chemistry (pH, alkalinity and chloride)

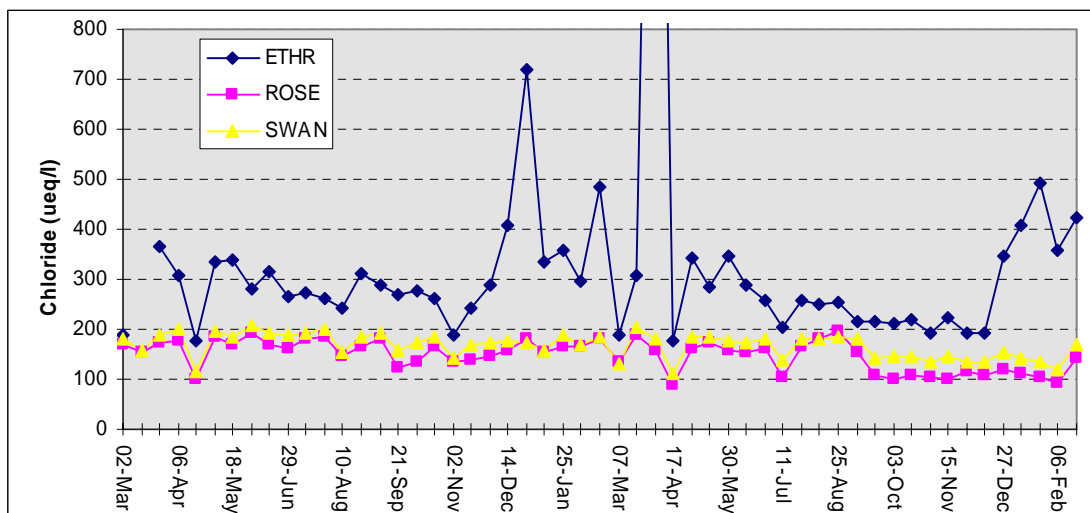
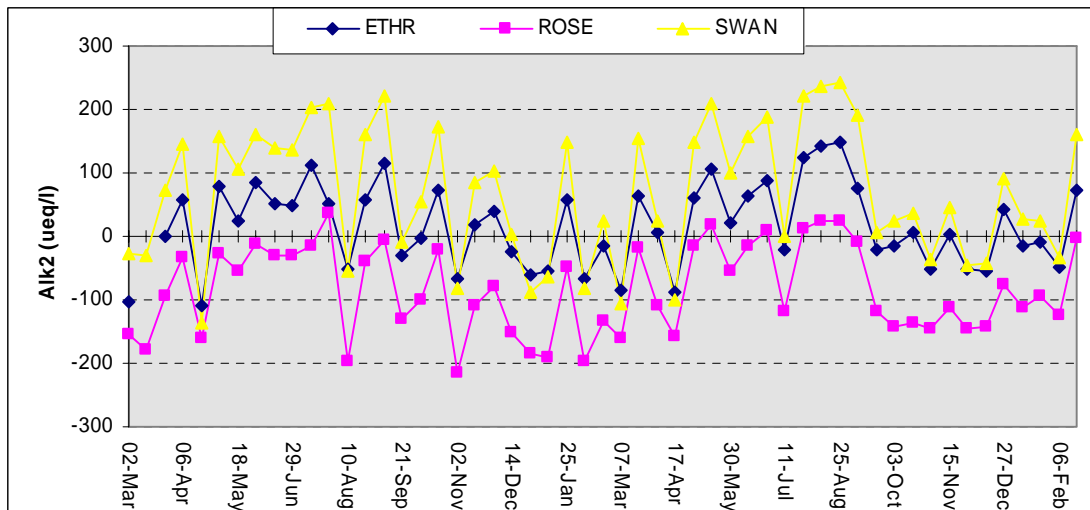
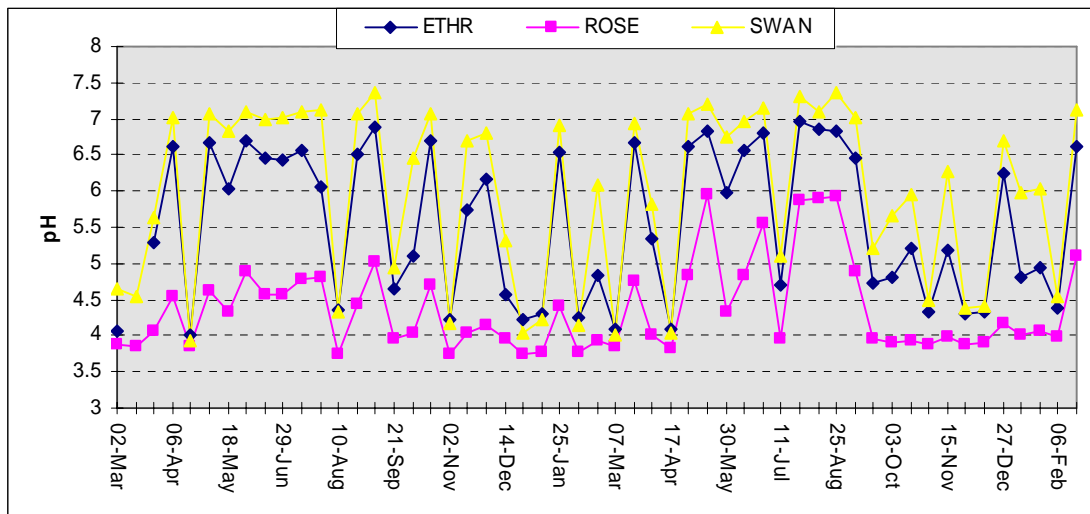


Figure 1.3.9b: Etherow streams water chemistry (inorganic N species)

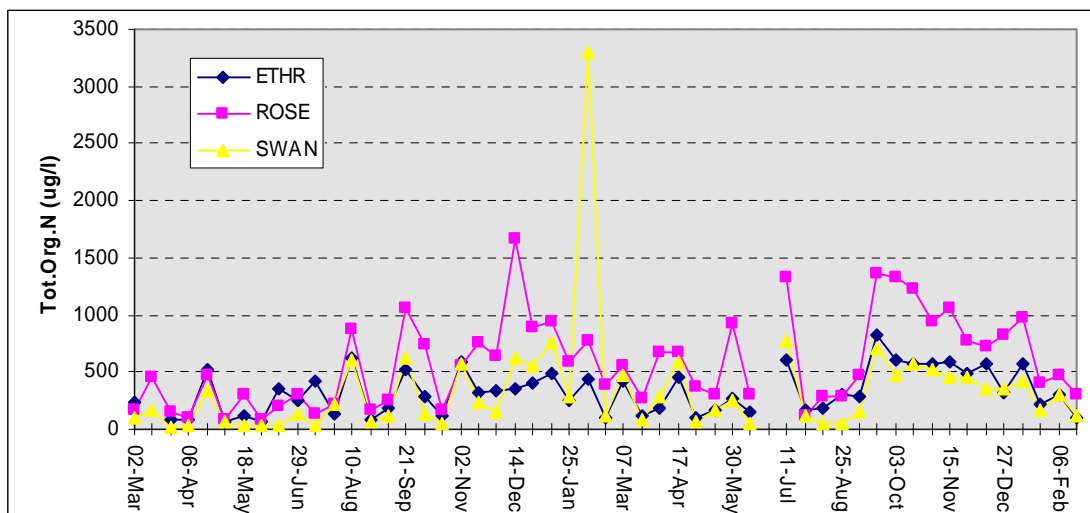
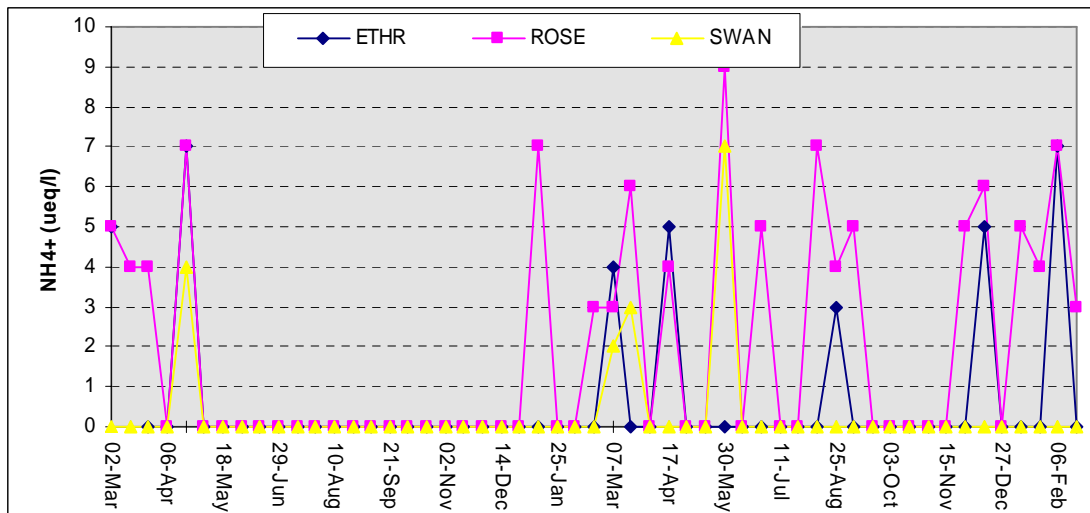
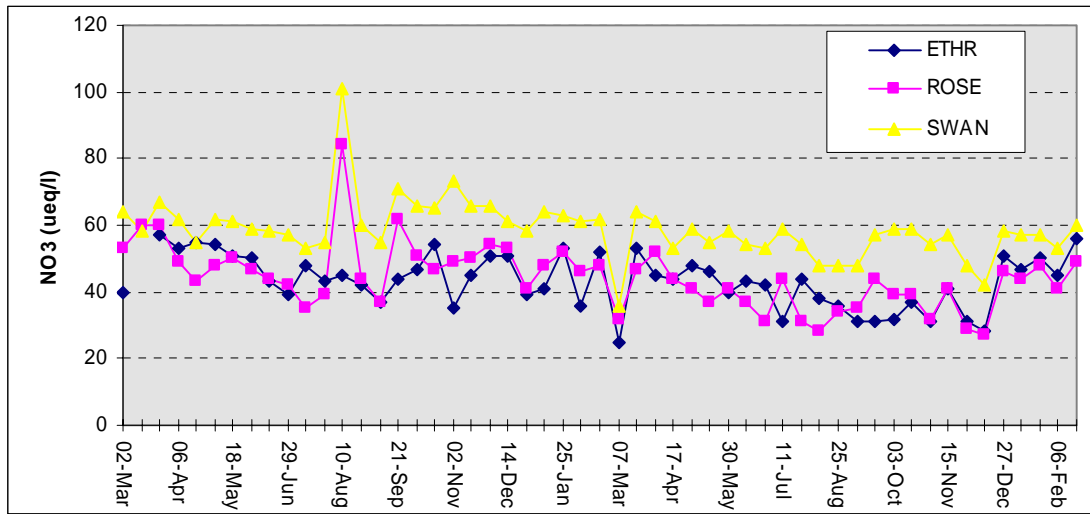
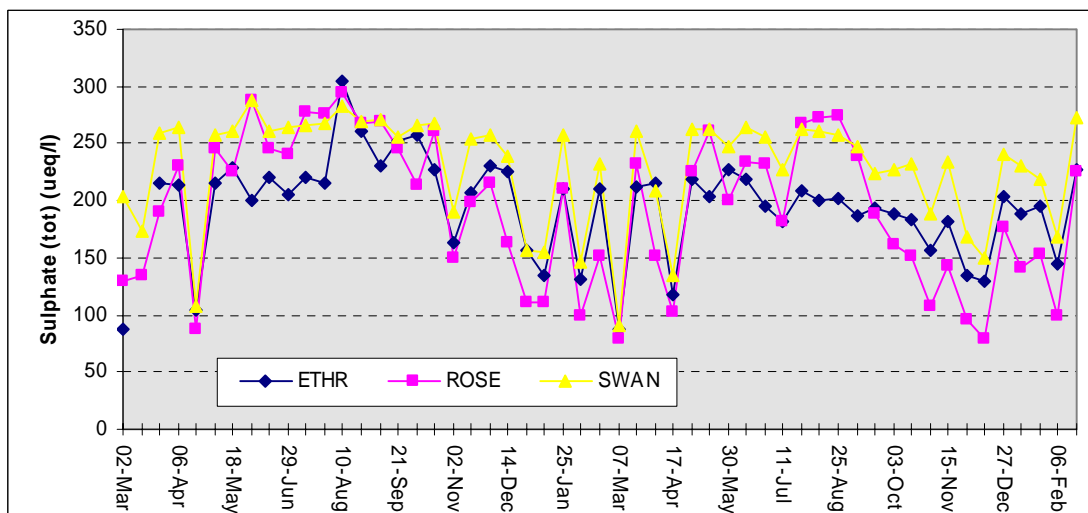
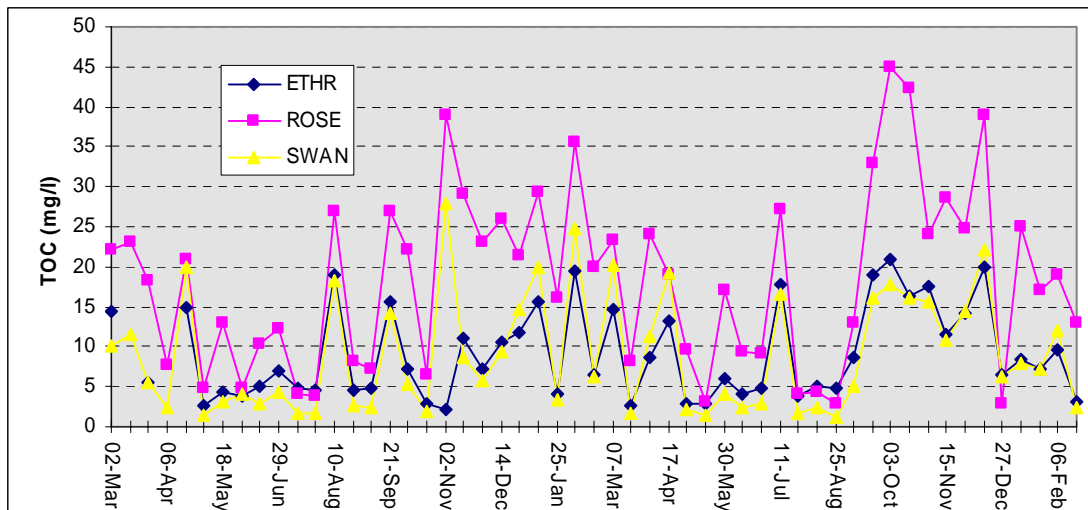
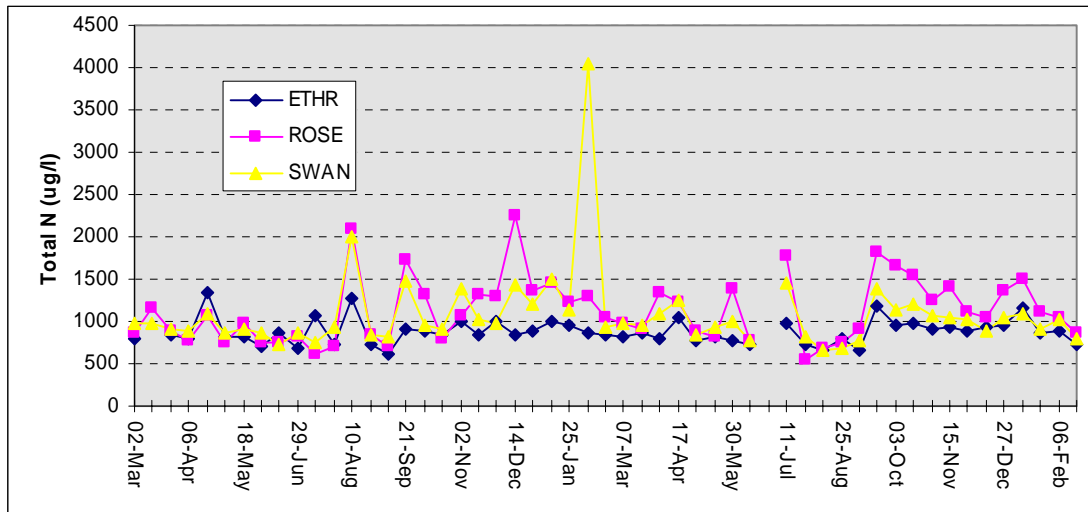


Figure 1.3.9c: Etherow streams water chemistry (sulphate and organics)



### Afon Gwy

While the mean pH of the Gwy (mean 5.47) is lower than that of the Mharcaidh, it varies over a similar range from pH 6.5 down to pH 5.0. Mean alkalinity is only 5  $\mu\text{eq l}^{-1}$  and can be negative for periods of several weeks (Fig. 1.3.7a). Chloride looked like it was following a declining trend through 1999 and most of 2000, but increased again in the last few months of 2000.

A seasonal trend in  $\text{NO}_3^-$  is clearly seen at the Gwy, with concentrations of up to 15-20  $\mu\text{eq l}^{-1}$  in winter declining to near zero through the summer (Fig. 1.3.7b). Total  $\text{SO}_4^{2-}$  values have been relatively constant, but appear to be slightly lower in the later months of 2000. DOC at the Gwy is variable but generally quite low and similar to the Mharcaidh, with a mean of c. 3  $\text{mg l}^{-1}$ . While there is no strong seasonal pattern, DOC does seem to follow the opposite cycle to  $\text{NO}_3^-$ , being lowest in winter.  $\text{NH}_4^+$  was below detection limits whilst organic N was not analysed at the Gwy.

### Scoat Tarn

The pH of Scoat Tarn was quite constant at around pH 5.0, and is closely mirrored in Red Pike stream, but not in Scoat Fell stream (Fig. 1.3.8a). Alkalinity at Scoat Tarn was negative throughout almost all of the monitoring period and reached a maximum of only 2  $\mu\text{eq l}^{-1}$ . Chloride, which reflects sea-salt inputs and presumably storminess and/or prevailing wind direction, follows a distinct seasonal pattern, with highest values in mid-winter declining to a minimum in late summer.

The pronounced seasonal pattern in  $\text{NO}_3^-$  at Scoat Tarn is very highly correlated with chloride (Fig. 1.3.8b, see also Fig. 1.3.8d). The mean value of 15  $\mu\text{eq l}^{-1}$  is high for an acid-sensitive, upland site in the UK, and lake-water  $\text{NO}_3^-$  does not decline to zero even during the summer, indicating a degree of N saturation. The seasonal pattern in the inflow streams is slightly larger, but very similar. Very low levels of  $\text{NH}_4^+$  were recorded on several occasions in 2000, but concentrations were mostly near zero throughout the sampling period. No real seasonal pattern is apparent in organic N, which is relatively constant, although the few higher values seem to occur in the summer. A seasonal pattern is more obvious in total N, which is driven largely by  $\text{NO}_3^-$  (Fig. 1.3.8c). As mentioned above, Scoat Tarn has very low levels of both organic N and TOC, with concentrations of the latter rarely exceeding 1.5  $\text{mg l}^{-1}$ .

Sulphate concentrations in Scoat Tarn and Red Pike stream follow a seasonal pattern, only partly driven by sea-salt inputs (Figs. 1.3.8c-d). When non-marine  $\text{SO}_4^{2-}$  is plotted alongside  $\text{NO}_3^-$  and chloride, it becomes obvious that  $\text{SO}_4^{2-}$  follows the opposite seasonal pattern to the other anions (Fig. 1.3.8d). This is not, however, true for Scoat Fell stream, where non-marine  $\text{SO}_4^{2-}$  concentrations are remarkably constant compared with Red Pike stream and the lake.

### River Etherow

The most striking feature of the River Etherow and at least one of its tributaries, Swan Clough, is that it is subject to very severe episodic acidification, with pH falling from almost circumneutral levels by up to 3 pH units to around pH 4.0 on regular occasions

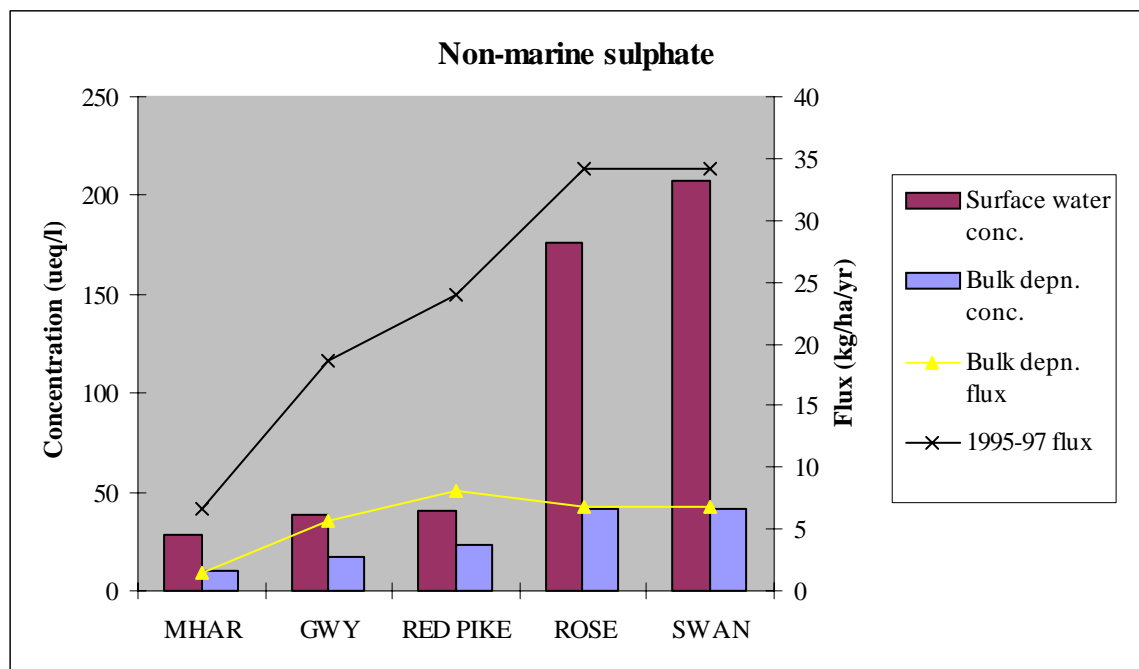
(Fig. 1.3.9a). These acid episodes are also reflected in very large variations in alkalinity, ranging from  $150 \mu\text{eq l}^{-1}$  down to less than  $-100 \mu\text{eq l}^{-1}$ . Chloride in the Etherow itself is much higher and more variable than the monitored tributaries to the south, but this may be attributed at least partly to road salt inputs into the main Etherow channel, which follows a major road. In Rose and Swan Clough which should not be affected by road salt, chloride is tightly correlated and varies in the range  $100\text{-}200 \mu\text{eq l}^{-1}$ .

Concentrations of  $\text{NO}_3^-$  in the Etherow streams are the highest of all sites in this study and the wider AWMN, with levels in Swan Clough being higher than the Etherow and Rose Clough (Fig. 1.3.9b). However, Rose Clough stands out as one of the few upland, acid-sensitive sites in the UK where significant  $\text{NH}_4^+$  concentrations are regularly found, up to  $9 \mu\text{eq l}^{-1}$ . These streams are also distinctive in having much higher levels of organic N and TOC than the other CLAM sites (Figs. 1.3.9b-c). In particular, mean TOC levels in Rose Clough are very high (c.  $18 \text{ mg l}^{-1}$ ) but can rise much higher to almost  $40 \text{ mg l}^{-1}$ . A seasonal pattern of  $\text{NO}_3^-$  leaching is notably absent in the Etherow streams, with very high concentrations year round indicating severe N saturation. Conversely, there does appear to be a seasonal pattern in  $\text{SO}_4^{2-}$  concentrations, as observed also at Scoat Tarn.

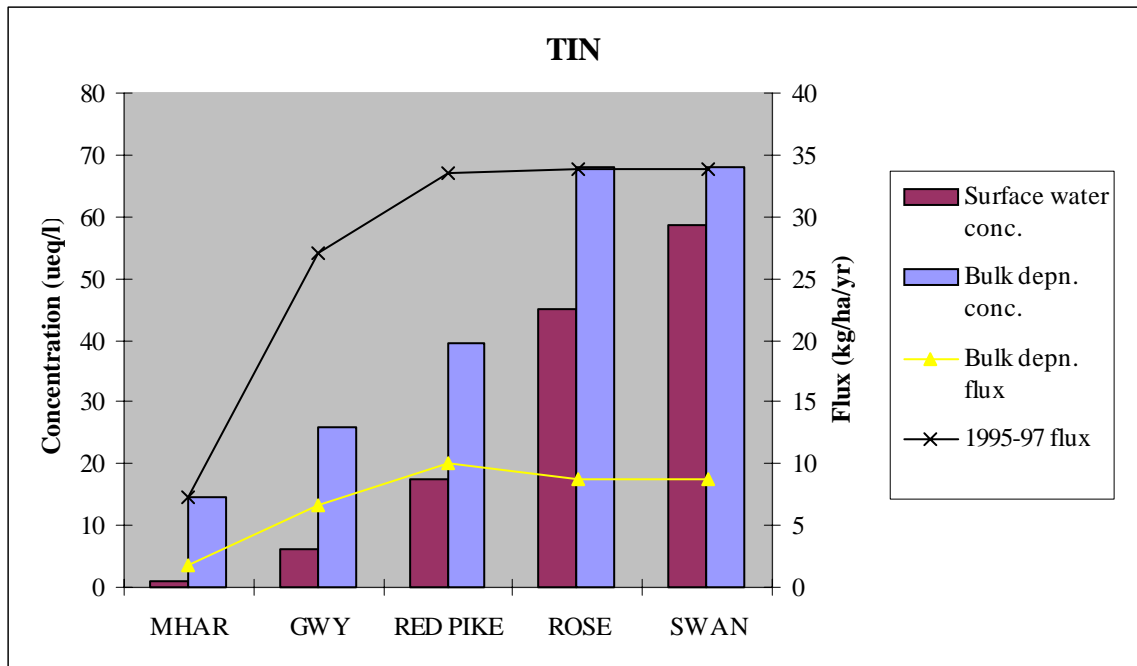
Comparisons with deposition data

The mean chemistry of surface waters and bulk deposition is compared below for the Mharcaidh, Gwy, Red Pike stream (closest to lake chemistry for Scoat Tarn but without problem of in-lake processes) and the two Etherow tributaries (Rose Clough and Swan Clough) in Figures 1.3.10a-d.

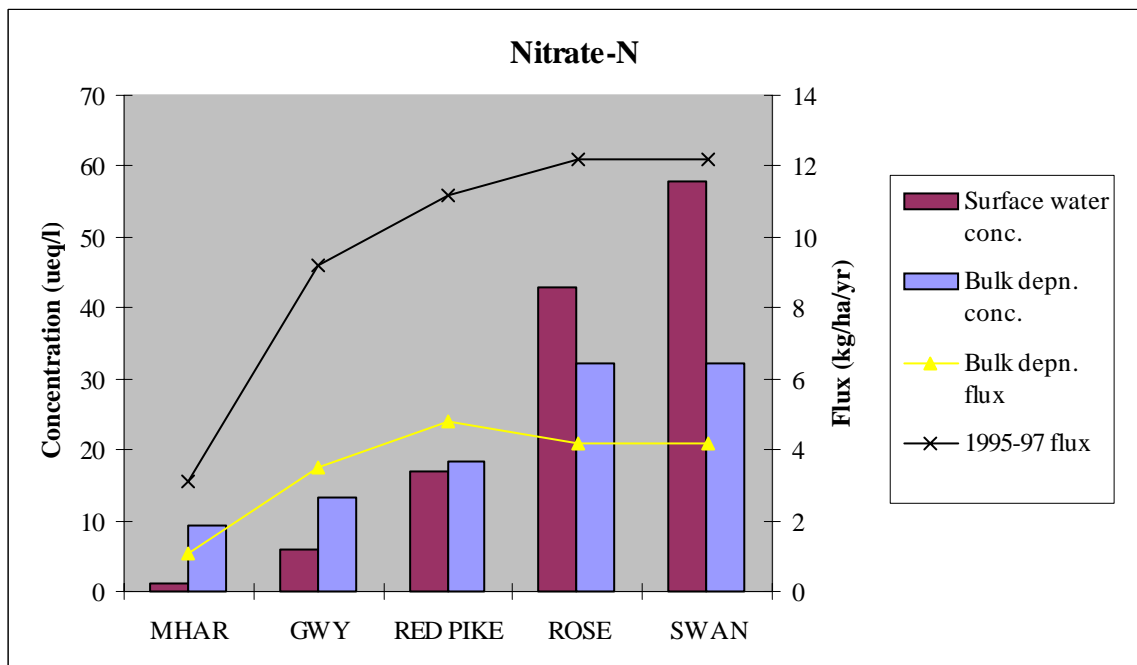
Figure 1.3.10a: Non-marine sulphate concentrations and fluxes



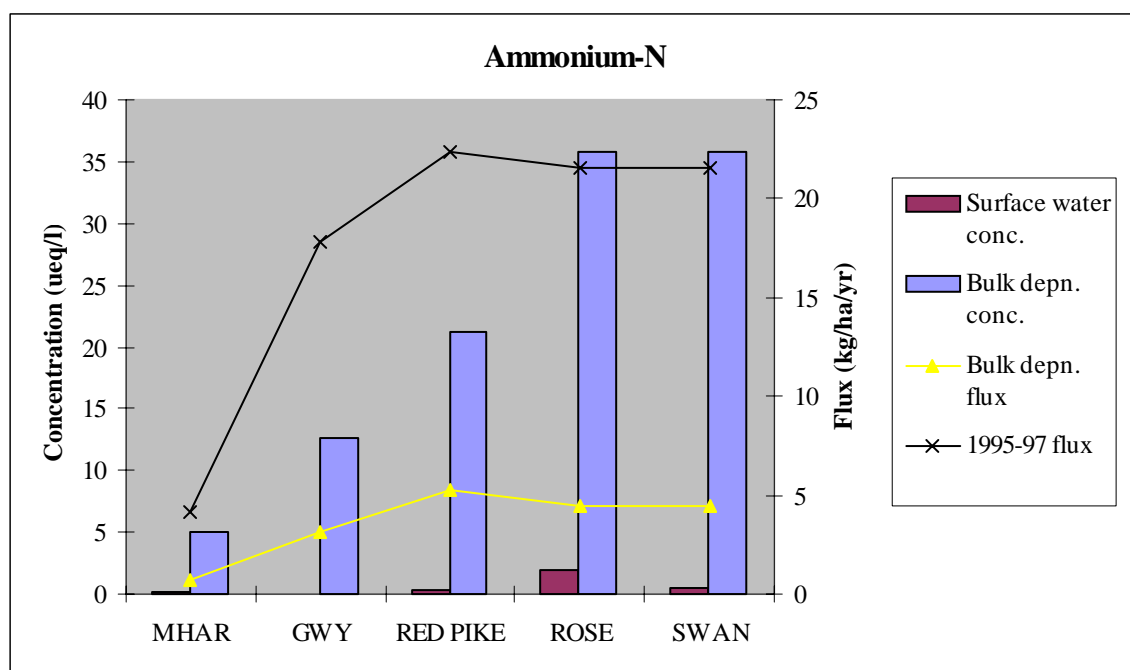
**Figure 1.3.10b: Total inorganic N (TIN) concentrations and fluxes**



**Figure 1.3.10c: Nitrate concentrations and fluxes**



**Figure 1.3.10d: Ammonium concentrations and fluxes**



Deposition input fluxes are also plotted for comparison, and are discussed further below. Bulk deposition mean concentration and (wet) flux was calculated as described in Section 1.3.2 above (Tables 1.3.7 - 1.3.8).

It is apparent in Figure 1.3.10a that non-marine sulphate concentrations are higher in surface waters than in bulk deposition for all sites. This will be partly due to concentration by evaporation/transpiration in surface waters, but is also likely to be due to unquantified dry deposition inputs and possibly to inputs from weathering or mineralisation sources. The same pattern is present in both surface water and bulk deposition, increasing from very low levels at the Mharcaidh, through intermediate levels at Gwy and Red Pike stream (Scot Tarn) to much higher values in the Etherow streams.

The same pattern is followed by total inorganic N concentrations, except that surface water concentrations are less than those in bulk deposition. At the Mharcaidh and Gwy there is a large difference between the two, while at Red Pike and particularly the Etherow streams, surface water concentrations of TIN are much larger as a proportion of bulk deposition (Figure 1.3.10b).

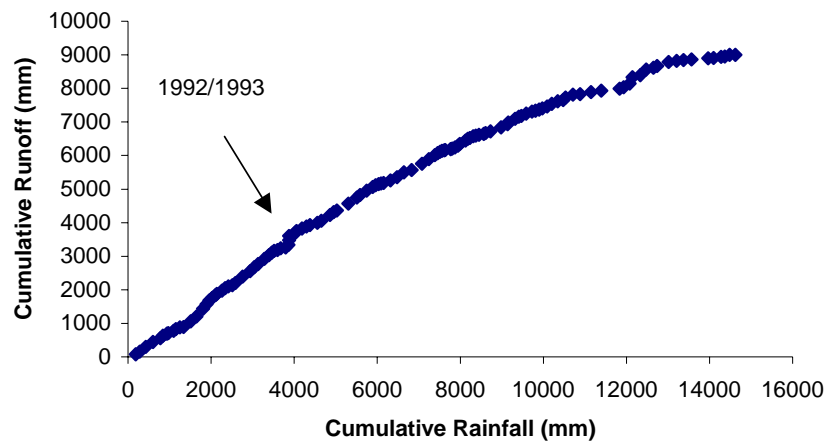
If  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are considered separately it can be seen that  $\text{NH}_4^+$  levels are so low in surface waters that it is almost entirely  $\text{NO}_3^-$  that determines the link in TIN with bulk deposition (Figs. 1.3.10c-d). While  $\text{NH}_4^+$  concentrations in bulk deposition increase across the four catchments, it is barely detected in surface waters even at high (wet) deposition inputs. The pattern is very different for  $\text{NO}_3^-$ ; as bulk deposition concentration increases, the surface water concentration increases disproportionately. In the Mharcaidh,  $\text{NO}_3^-$  concentration is much lower in the stream than in bulk deposition, while in the Gwy  $\text{NO}_3^-$  reaches almost half the level in bulk deposition.

The two values are very close for Red Pike stream, but in the Etherow streams,  $\text{NO}_3^-$  is much greater than in bulk deposition. This could indicate significant dry deposition at the Etherow or nitrification of wet deposited ammonium.

### Comparison of fluxes

Flow was measured at all locations, using existing gauges at the Allt a'Mharcaidh, Etherow and Gwy, and a newly installed pressure transducer gauge at the outflow of Scoat Tarn. However, problems were encountered during the study at three of the sites. At the Allt a'Mharcaidh, the data logger was not operational for part of this sampling period, and a backup pen-trace record of stage was therefore used to determine discharge at times of sampling. At Scoat Tarn, vandalism of the pressure transducer resulted in a two-week period without data, and a potential error in relating stage before and after this incident. In addition, the limited number of dilution gaugings undertaken at this site mean that the stage-discharge relationship is relatively uncertain.

Figure 1.3.11: Deviation in cumulative runoff relative to cumulative rainfall, River Etherow, due to sediment accretion at the weir.

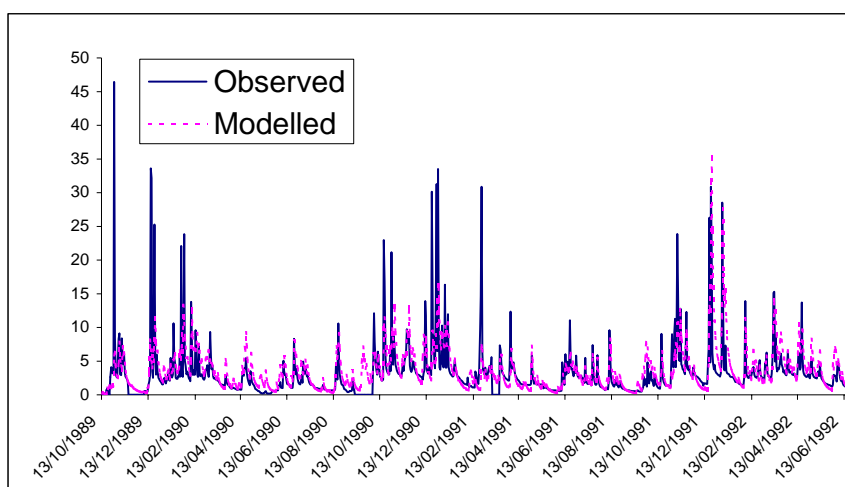


At the River Etherow, an established Northwest Water weir was used for stage measurement. However, severe sediment accretion was found to have occurred at the weir, affecting hydraulic performance and therefore the quality of the flow record. This led to increasing underestimation of runoff from 1993 onwards (Figure 1.3.11). To overcome this problem, the flow estimation model IHACRES, run using daily rainfall data, was calibrated to a reliable flow record for the nearby River Derwent at Slippery Stones. The calibrated model was then transferred to the Etherow, and found to give an acceptable fit to observed flows for 1989-1992 (Figure 1.3.12). Daily simulated flows were used as the basis for output flux calculations at this site.



Output fluxes are based on the regular water chemistry sampling throughout the budget year (see above). For the three sites with continuous flow records, volume weighted mean concentrations were calculated using instantaneous flows at times of sampling. At the Etherow, estimates were based on modelled daily flows for days when samples were collected. Given the considerable uncertainties in discharge estimates at most of the sites, these flux estimates must be considered approximate, and interpreted with caution.

Figure 1.3.12: IHACRES modelled and observed flows at the River Etherow between 1989 and 1992.



Estimated sulphur fluxes (Table 1.3.11) vary as a function of deposition, from 5 kg S/ha/yr at the Allt a’Mharcaidh to 52 kgS ha<sup>-1</sup> yr<sup>-1</sup> at the Etherow. At all four sites, S output fluxes exceed wet deposition inputs, confirming the importance of dry deposition. However there are marked discrepancies between 1995-97 estimated total inputs and estimated outputs. At the Etherow, export is greater than input, consistent with a weathering or mineralisation source of S, which is believed to be present in this catchment. However at the other sites only around a half of inputs are exported in runoff, and since the decline in S deposition between 1995-97 and 1999/2000 is unlikely to be sufficient to explain this imbalance, the implication of these observations is either that (i) output fluxes are under-estimated; (ii) 1995-97 input fluxes are over-estimated; or (iii) these catchments are retaining some S input.

Table 1.3.11: Total S fluxes in deposition and runoff (kgS ha<sup>-1</sup> yr<sup>-1</sup>)

Site	Runoff	Bulk (wet)	Total 1995-97	% leached
MHAR	4.7	3.31	10.4	45.2
GWY	14.7	9.41	28.8	51.0
SCOAT	17.8	13.1	31.52	56.5
ETHR	51.7	8.11	35.68	144.9

Estimates of nitrogen output fluxes vary considerably between sites, as a function primarily of variations in concentration (Tables 1.3.12 – 1.3.13). The smallest inorganic N output flux, 0.08 kgN ha<sup>-1</sup> yr<sup>-1</sup>, was observed at the Allt a’Mharcaidh, where virtually all deposited N is retained. Intermediate levels of leaching were observed at the Afon Gwy (1.8 kgN ha<sup>-1</sup> yr<sup>-1</sup>) and Scoat Tarn (4.9 kgN ha<sup>-1</sup> yr<sup>-1</sup>), and a maximum level of 11.0 kgN ha<sup>-1</sup> yr<sup>-1</sup> at the River Etherow. The Etherow is the only site at which NH<sub>4</sub><sup>+</sup> contributes measurably to outputs, but even here it represents only around 3% of the inorganic N total.

Table 1.3.12: Fluxes of NO<sub>3</sub>-N and NH<sub>4</sub>-N

Site	NO <sub>3</sub> -N				NH <sub>4</sub> -N			
	Runoff	Bulk	Tot.1995-97	% out	Runoff	Bulk	Tot.1995-97	% out
MHAR	0.08	1.1	3.1	2.6	0	0.7	4.2	0.0
GWY	1.8	3.5	9.2	19.6	0	3.1	17.8	0
SCOAT	4.86	4.8	11.2	43.4	0	5.3	22.4	0.0
ETHR	10.63	4.2	12.2	87.1	0.36	4.5	21.6	1.7

**Table 1.3.13: Fluxes of Total Inorganic N**

Site	Total Inorganic N			
	Runoff	Bulk	Tot.1995-97	% out
MHAR	0.08	1.8	7.3	1.1
GWY	1.8	6.6	27	6.7
SCOAT	4.86	10.1	33.6	14.5
ETHR	10.99	8.7	33.8	32.5

There is clearly a correlation between inorganic N leaching and deposition, but the relationship appears non-linear, with the *proportion* of N leached increasing with deposition. This pattern is more obvious for NO<sub>3</sub><sup>-</sup> than for TIN because of the retention of almost all the NH<sub>4</sub><sup>+</sup> at all sites. The percentage of N leached (based on 1995-97 total deposition) rises from 1% at the Allt a’Mharcaidh to 33% at the River Etherow. At the Etherow, it is notable that of an estimated 34 kgN ha<sup>-1</sup> yr<sup>-1</sup> total deposition, only 11 kgN ha<sup>-1</sup> yr<sup>-1</sup> occurred as NO<sub>x</sub>. Since the NO<sub>x</sub> deposition figure from 1995-97 could be an overestimate for the sampling period, the figure of 87% export may be an underestimate for NO<sub>3</sub><sup>-</sup>, indicating a near-zero net retention of deposited NO<sub>x</sub> at this site.

### 1.3.4 Soil water chemistry

Mean soilwater N species data for 2-weekly samples throughout the budget year are presented in Tables 1.3.14a-d. While these tables indicate the spatial variability of soilwater chemistry within each soil type, the major differences occur between soil types and between sites. An inter-site comparison is provided in Table 1.3.15.

Table 1.3.14a: Nitrogen species in soilwaters at the Allt a'Mharcaidh (mg l<sup>-1</sup>)

Soil	Plot	Total N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	Org.N
M1	M1D1	0.43	0.03	0.00	0.40
M1	M1D2	0.32	0.02	0.00	0.30
M1	M1D3	0.39	0.02	0.00	0.37
<b><u>M1 average</u></b>		<b>0.38</b>	<b>0.02</b>	<b>0.00</b>	<b>0.36</b>
M2	M2D1	0.65	0.03	0.00	0.63
M2	M2D2	0.65	0.03	0.00	0.62
M2	M2D3	0.51	0.01	0.00	0.47
<b><u>M2 average</u></b>		<b>0.60</b>	<b>0.02</b>	<b>0.00</b>	<b>0.57</b>
M3	M3D1	0.31	0.02	0.00	0.28
M3	M3D2	0.57	0.03	0.00	0.53
M3	M3D3	0.40	0.02	0.00	0.36
<b><u>M3 average</u></b>		<b>0.43</b>	<b>0.02</b>	<b>0.00</b>	<b>0.39</b>
M4	M4D1	0.27	0.03	0.00	0.23
M4	M4D2	0.79	0.09	0.00	0.67
M4	M4D3	0.46	0.01	0.00	0.43
<b><u>M4 average</u></b>		<b>0.51</b>	<b>0.04</b>	<b>0.00</b>	<b>0.45</b>

Table 1.3.14b: Nitrogen species in soilwaters at the Afon Gwy (mg l<sup>-1</sup>)

Soil	Plot	Total N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	Org.N
G1	G1D1	1.77	0.10	0.00	1.67
G1	G1D2	0.88	0.07	0.00	0.80
G1	G1D3	0.73	0.04	0.00	0.69
<b><u>G1 average</u></b>		<b>1.13</b>	<b>0.07</b>	<b>0.00</b>	<b>1.05</b>
G2	G2D1	0.61	0.04	0.00	0.57
G2	G2D2	0.58	0.03	0.00	0.55
G2	G2D3	0.66	0.04	0.01	0.61
<b><u>G2 average</u></b>		<b>0.62</b>	<b>0.04</b>	<b>0.00</b>	<b>0.58</b>
G3	G3D1	0.38	0.05	0.01	0.32
G3	G3D2	0.42	0.02	0.00	0.40
G3	G3D3	0.25	0.03	0.00	0.22
<b><u>G3 average</u></b>		<b>0.35</b>	<b>0.03</b>	<b>0.00</b>	<b>0.32</b>
G4	G4D1	2.10	0.05	0.00	2.05
G4	G4D2	2.07	0.05	0.00	2.02
G4	G4D3	0.81	0.05	0.00	0.76
<b><u>G4 average</u></b>		<b>1.66</b>	<b>0.05</b>	<b>0.00</b>	<b>1.61</b>

Table 1.3.14c: Nitrogen species in soilwaters at Scoat Tarn ( $\text{mg l}^{-1}$ )

Soil	Plot	Total N	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Org.N
S1	S1D1	0.61	0.04	0.15	0.42
S1	S1D2	0.44	0.03	0.13	0.28
S1	S1D3	0.41	0.03	0.07	0.30
<b>S1 average</b>		<b>0.49</b>	<b>0.03</b>	<b>0.12</b>	<b>0.34</b>
S2	S2D1	0.74	0.04	0.17	0.53
S2	S2D2	0.50	0.03	0.19	0.28
S2	S2D3	0.46	0.02	0.09	0.35
<b>S2 average</b>		<b>0.56</b>	<b>0.03</b>	<b>0.15</b>	<b>0.39</b>
S3	S3D1	0.53	0.03	0.12	0.37
S3	S3D2	0.44	0.02	0.01	0.41
S3	S3D3	0.38	0.04	0.00	0.35
<b>S3 average</b>		<b>0.45</b>	<b>0.03</b>	<b>0.04</b>	<b>0.38</b>

Table 1.3.14d: Nitrogen species in soilwaters at the River Etherow ( $\text{mg l}^{-1}$ )

Soil	Plot	Total N	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Org.N
E1	E1D1	1.16	0.09	0.28	0.79
E1	E1D2	3.90	0.48	0.01	3.41
E1	E1D3	8.29	0.28	3.59	4.41
<b>E1 average</b>		<b>4.45</b>	<b>0.28</b>	<b>1.29</b>	<b>2.87</b>
E2	E2D1	6.96	2.32	0.02	4.62
E2	E2D2	8.49	2.83	0.04	5.61
E2	E2D3	9.59	2.81	0.07	6.71
<b>E2 average</b>		<b>8.35</b>	<b>2.66</b>	<b>0.04</b>	<b>5.65</b>

The most striking feature of the data in Table 1.3.15 is the complete absence of  $\text{NO}_3^-$  in the soilwaters of the Mharcaidh and Gwy, over a range of soil types. At Scoat Tarn, however,  $\text{NO}_3^-$  is present in all soil types, but particularly the podsol and peaty gley soils. Table 1.3.14c shows that high levels of  $\text{NO}_3^-$  were measured in all three replicate plots on these soils. At the Etherow sites, the highest  $\text{NO}_3^-$  values found within the whole study occur in the deep peats under burnt *Calluna* (Soil E1), but the very large mean value is driven by inexplicably high measurements at one particular plot (E1D3 – see Table 1.3.14d). This is an order of magnitude greater than the mean value for the nearby plot E1D1, which otherwise has the highest  $\text{NO}_3^-$  concentrations of all the remaining study plots.

Unlike  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  was found in all 39 plots, especially in peats. At the Allt a'Mharcaidh, mean  $\text{NH}_4^+$  concentrations are very similar for all soils and plots (mean  $0.02 \text{ mg l}^{-1}$ ), with just one plot in the shallow peat (M4D2) having a higher value and leading to a higher mean for the shallow peat soil there (M4). In the Gwy soils, soilwaters have higher  $\text{NH}_4^+$  concentrations than at the Mharcaidh, but values are still low. Plots on the hilltop (M1) and valley (M4) peats consistently show the highest

NH<sub>4</sub><sup>+</sup> concentrations at the Gwy (Table 1.3.14b). At Scoat Tarn very similar NH<sub>4</sub><sup>+</sup> concentrations are observed in all three soil types studied there (Table 1.3.14c), with values similar to the peaty gley and podsol soils (the lowest) at the Gwy (G2 and G3). Again, the extreme values are found at the Etherow, although not in the same study area. The high NO<sub>3</sub><sup>-</sup> concentrations were found in the deep peat under burnt vegetation, and while the NH<sub>4</sub><sup>+</sup> levels there are much higher than at the other three sites, they are an order of magnitude greater still under the mature *Calluna* (E2). These extreme values, observed in all three E2 plots (Table 1.3.14d) are almost two orders of magnitude greater than all soils at other sites (Table 1.3.15).

Table 1.3.15: Nitrogen species in soilwaters (mg l<sup>-1</sup>) - comparison by site

Soil	Type	Total N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	Org.N	pH
M1	Peaty ranker	0.38	0.02	0.00	0.36	3.4
M2	Valley peat	0.60	0.02	0.00	0.57	3.7
M3	Peaty podsol	0.43	0.02	0.00	0.39	4.0
M4	Shallow peat	0.51	0.04	0.00	0.45	3.9
G1	Hilltop peat	1.13	0.07	0.00	1.05	3.4
G2	Peaty gley	0.62	0.04	0.00	0.58	3.6
G3	podsol	0.35	0.03	0.00	0.32	4.1
G4	Valley peat	1.66	0.05	0.00	1.61	3.8
S1	Podsol	0.49	0.03	0.12	0.34	3.9
S2	Peaty gley	0.56	0.03	0.15	0.39	3.8
S3	Deep peat	0.45	0.03	0.04	0.38	3.9
E1	Deep peat (burnt <i>Calluna</i> )	4.45	0.28	1.29	2.87	3.0
E2	Deep peat ( <i>Calluna</i> )	8.35	2.66	0.04	5.65	3.3

Organic N concentrations follow the same pattern as NH<sub>4</sub><sup>+</sup>, being low at the Mharcaidh and Scoat Tarn, higher at the Gwy, especially the peats at G1 and G4, and highest by a large margin at the Etherow. The pattern in organic N is linked to peat soils more closely than for NH<sub>4</sub><sup>+</sup>, the only exception being the deep peat at Scoat Tarn (S3).

Soilwater pH is comparable at the Mharcaidh, Gwy and Scoat Tarn sites, with values generally close to pH 4.0. The more acid soils at the Mharcaidh and Gwy are also the highest altitude soils (M1, G1), with average pH values around pH 3.5. The Etherow is again the odd site with much more acid soilwaters, especially under burnt vegetation where the mean value is pH 3.0.

#### Surface lysimeters

During a preliminary assessment of the existing data in March 2000 it had been noted that despite the presence of appreciable NO<sub>3</sub><sup>-</sup> concentrations in streamwaters at the Afon Gwy, 2-weekly soilwater samples almost all showed zero NO<sub>3</sub><sup>-</sup>. It was initially feared that the suction samplers could have been installed too deep (generally at 20-30 cm) to detect NO<sub>3</sub><sup>-</sup>, and that it was perhaps being denitrified or taken up microbially within the surface organic horizons.

It was therefore decided to install surface zero-tension lysimeters at selected plots in all study catchments to investigate whether this indeed was the case, and whether significant NO<sub>3</sub><sup>-</sup> concentrations occurred in near-surface soilwaters. These lysimeters were installed in April 2000 and after a short settling-in period, sampling commenced in May, continuing throughout the summer period until the end of the budget year in October. The results of the sampling are shown in Table 1.3.16.

Table 1.3.16: Deep and surface lysimeter (SL) chemistry

<b>Shallow vs. Deep lysimeters (May-Oct.2000)</b>							
ID	NO3-N	NH4-N	Org.N	Tot.N	NH4-N	NO3-N	pH
	mg/l	mg/l	mg/l	mg/l	ueq/l	ueq/l	
M4D1	0.0	0.1	0.2	0.3	5.0	0.0	5.0
M4D2	0.0	0.2	0.8	0.9	11.3	0.0	4.0
M4D3	0.0	0.0	0.5	0.5	0.4	0.0	4.0
M4SL1	0.0	0.0	0.5	0.6	1.9	0.0	4.2
M4SL2	0.0	0.0	0.5	0.5	1.7	0.0	4.2
M4SL3	0.0	0.1	0.6	0.7	4.2	0.0	4.0
G1D1	0.0	0.1	1.3	1.4	8.8	0.0	3.8
G1D2	0.0	0.1	1.0	1.1	6.3	0.0	3.7
G1D3	0.0	0.0	0.8	0.8	3.4	0.0	3.9
G1SL1	0.0	0.1	1.1	1.3	9.0	0.0	3.7
G1SL2	0.0	0.1	0.9	1.0	5.7	0.0	3.9
G1SL3	0.0	0.1	1.0	1.0	5.2	0.0	3.9
G4D1	0.0	0.1	1.6	1.7	4.2	0.0	3.8
G4D2	0.0	0.1	2.0	2.0	4.0	0.0	3.9
G4D3	0.0	0.1	0.8	0.8	4.8	0.0	4.4
G4SL1	0.0	0.1	1.1	1.2	7.5	0.0	4.0
G4SL2	0.0	0.1	1.5	1.5	5.8	0.0	4.4
G4SL3	0.0	0.1	1.7	1.8	5.9	0.0	4.6
S3D1	0.0	0.0	0.5	0.5	2.1	0.0	4.3
S3D2	0.0	0.0	0.6	0.6	1.7	1.9	4.7
S3D3	0.0	0.1	0.5	0.5	4.3	0.0	4.7
S3SL1	0.0	0.1	0.7	1.0	4.7	1.3	4.8
S3SL2	0.0	0.0	0.6	0.6	0.6	0.0	4.6
S3SL3	0.0	0.0	0.5	0.5	2.7	0.1	5.0
E1D1	0.6	0.1	0.9	1.6	4.5	44.8	3.2
E1D2	0.0	0.3	2.1	2.5	22.1	1.7	3.2
E1D3	3.5	0.3	0.8	4.6	22.3	246.6	3.3
E1SL1	0.6	1.1	1.4	3.0	76.1	41.8	4.1
E1SL2	0.3	0.3	1.5	2.2	20.5	23.9	3.6
E1SL3	0.0	0.4	0.8	1.2	29.4	2.2	3.7
E2D1	0.0	2.2	2.4	4.7	160.4	0.8	3.6
E2D2	0.0	2.7	2.9	5.6	194.3	3.1	3.4
E2D3	0.0	2.5	3.5	6.0	180.3	3.0	3.5
E2SL1	0.1	1.6	1.8	3.5	116.9	5.9	3.8
E2SL2	0.0	2.0	2.5	4.6	143.5	1.8	3.4
E2SL3	0.1	1.3	2.5	3.9	89.8	4.0	3.7

Inspection of the data in Table 1.3.16 shows that there is no evident difference in soilwater chemistry between surface and deep soilwater samplers. For the deeper suction samplers used throughout the budget year, sampler depth does not therefore appear to be responsible for the lack of  $\text{NO}_3^-$  in sampled soilwaters.

### 1.3.5 Denitrification measurements

There were two complementary aspects to the denitrification work at the CLAM N budget sites; field measurements throughout the budget year and laboratory assessment of potential denitrification rates.

Analysis of “baseline” samples for ambient levels of N<sub>2</sub>O shows that random variations between two ambient samples can result in calculated denitrification fluxes of  $\pm 0.3 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ . In other words, the sensitivity of the method only provides a detection limit of  $0.3 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ . In the analyses below, individual values below this detection limit have therefore been assumed to be zero in the calculation of mean values through time or by soil type.

#### Field measurement of denitrification

Actual denitrification rates were measured in the field on a 4-weekly basis in each of the 39 primary study plots. Additional measurements were made at a subset of secondary plots where NH<sub>4</sub>NO<sub>3</sub> additions were made to determine whether denitrification was limited by N supply in these areas.

Mean denitrification rates for the budget year are provided in Tables 1.3.17a-d.

*Table 1.3.17a: Denitrification fluxes at the Allt a’Mharcaidh ( $\text{kgN ha}^{-1} \text{ yr}^{-1}$ )*

<b>M1: PEATY RANKER</b>		<b>M2: VALLEY PEAT</b>		<b>M3: PEATY PODSOL</b>		<b>M4: SHALLOW PEAT</b>	
Plot	Field rate	Plot	Field rate	Plot	Field rate	Plot	Field rate
M1D1	0.00	M2D1	0.00	M3D1	0.00	M4D1	0.05
M1D2	0.00	M2D2	0.00	M3D2	0.08	M4D2	0.00
M1D3	0.00	M2D3	0.00	M3D3	0.00	M4D3	0.00
<b>Mean</b>	<b>0.00</b>	<b>Mean</b>	<b>0.00</b>	<b>Mean</b>	<b>0.03</b>	<b>Mean</b>	<b>0.02</b>
Plot	+NH <sub>4</sub> NO <sub>3</sub>	Plot	+NH <sub>4</sub> NO <sub>3</sub>	Plot	+NH <sub>4</sub> NO <sub>3</sub>	Plot	+NH <sub>4</sub> NO <sub>3</sub>
-	-	-	-	M3A1	0	M4A1	0.75
-	-	-	-	M3A2	0	M4A2	0.27
-	-	-	-	M3A3	1.46	M4A3	0.00
-	-	-	-	<b>Mean</b>	<b>0.49</b>	<b>Mean</b>	<b>0.34</b>

*Table 1.3.17b: Denitrification fluxes at the Afon Gwy ( $\text{kgN ha}^{-1} \text{ yr}^{-1}$ )*

<b>G1: HILLTOP PEAT</b>		<b>G2: PEATY GLEY</b>		<b>G3: PODSOL</b>		<b>G4: VALLEY PEAT</b>	
Plot	Field rate	Plot	Field rate	Plot	Field rate	Plot	Field rate
G1D1	0.00	G2D1	0.10	G3D1	0.00	G4D1	0.36
G1D2	0.06	G2D2	0.06	G3D2	0.00	G4D2	0.00
G1D3	0.00	G2D3	0.00	G3D3	0.04	G4D3	0.00
<b>Mean</b>	<b>0.02</b>	<b>Mean</b>	<b>0.05</b>	<b>Mean</b>	<b>0.01</b>	<b>Mean</b>	<b>0.12</b>
Plot	+NH <sub>4</sub> NO <sub>3</sub>	Plot	+NH <sub>4</sub> NO <sub>3</sub>	Plot	+NH <sub>4</sub> NO <sub>3</sub>	Plot	+NH <sub>4</sub> NO <sub>3</sub>
G1A1	0.00	G2A1	0.08	G3A1	0.00	-	-
G1A2	0.07	G2A2	0.00	G3A2	0.04	-	-
G1A3	0.07	G2A3	0.08	G3A3	0.00	-	-
<b>Mean</b>	<b>0.05</b>	<b>Mean</b>	<b>0.05</b>	<b>Mean</b>	<b>0.01</b>	-	-



Table 1.3.17c: Denitrification fluxes at Scoat Tarn ( $\text{kgN ha}^{-1} \text{ yr}^{-1}$ )

<b>S1: HILLTOP PEAT</b>		<b>S2: PEATY GLEY</b>		<b>S3: PODSOL</b>	
Plot	Field rate	Plot	Field rate	Plot	Field rate
S1D1	0.00	S2D1	0.00	S3D1	0.00
S1D2	0.00	S2D2	0.00	S3D2	0.09
S1D3	0.00	S2D3	0.03	S3D3	0.05
<b>Mean</b>	<b>0.00</b>	<b>Mean</b>	<b>0.01</b>	<b>Mean</b>	<b>0.05</b>

Table 1.3.17d: Denitrification fluxes at the River Etherow ( $\text{kgN ha}^{-1} \text{ yr}^{-1}$ )

<b>E1: Burnt Calluna</b>		<b>E2: Calluna</b>	
Plot	Field rate	Plot	Field rate
E1D1	0.68	E2D1	0.00
E1D2	0.00	E2D2	0.05
E1D3	0.03	E2D3	0.00
<b>Mean</b>	<b>0.24</b>	<b>Mean</b>	<b>0.02</b>
Plot	+ $\text{NH}_4\text{NO}_3$	Plot	+ $\text{NH}_4\text{NO}_3$
E1A1	0.16	E2A1	0.00
E1A2	0.00	E2A2	0.00
E1A3	0.07	E2A3	0.00
<b>Mean</b>	<b>0.08</b>	<b>Mean</b>	<b>0.00</b>

These results show that significant mean annual denitrification rates were observed in only a small number of plots, even at the high deposition sites, indicating large spatial variability in denitrification. While some plots were denitrifying, replicate plots on the same soils often were not, hence mean rates for each soil type without N additions are low, typically  $<0.5 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  for any given plot and a maximum for a soil type of  $0.24 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  (burnt *Calluna* at the Etherow; Table 1.3.17d).

Addition of  $\text{NH}_4\text{NO}_3$  had little effect on mean denitrification rates at most secondary plots, with only 3 plots at the Mharcaidh showing increased values (Table 1.3.17a).

Inspection of the raw data shows that in addition to the great spatial variability in denitrification, there is also significant temporal variation on a seasonal basis. For example, the plot showing the highest mean rate without N additions at the Etherow (E1D1) only denitrifies from late spring to early autumn (Figure 1.3.13), while the other two plots on the burnt *Calluna* (area E1) show very low values all year round.

In the secondary plots with N additions this temporal variation is even more pronounced, with large denitrification “events” driving the higher figures at the Allt a’Mharcaidh (Figure 1.3.14). However, inspection of the field records for these plots reveals that these events were associated with waterlogging of the static chambers, leading to elevated denitrification. Hence at the denitrifying Mharcaidh plots it is only the combination of elevated N inputs from  $\text{NH}_4\text{NO}_3$  additions with waterlogging of the chambers which produces the  $\text{NO}_3^-$  rich, anaerobic conditions necessary for denitrification.

Figure 1.3.13: Temporal variation in denitrification flux at the River Etherow (burnt Calluna) site ( $\text{kgN ha}^{-1} \text{yr}^{-1}$ )

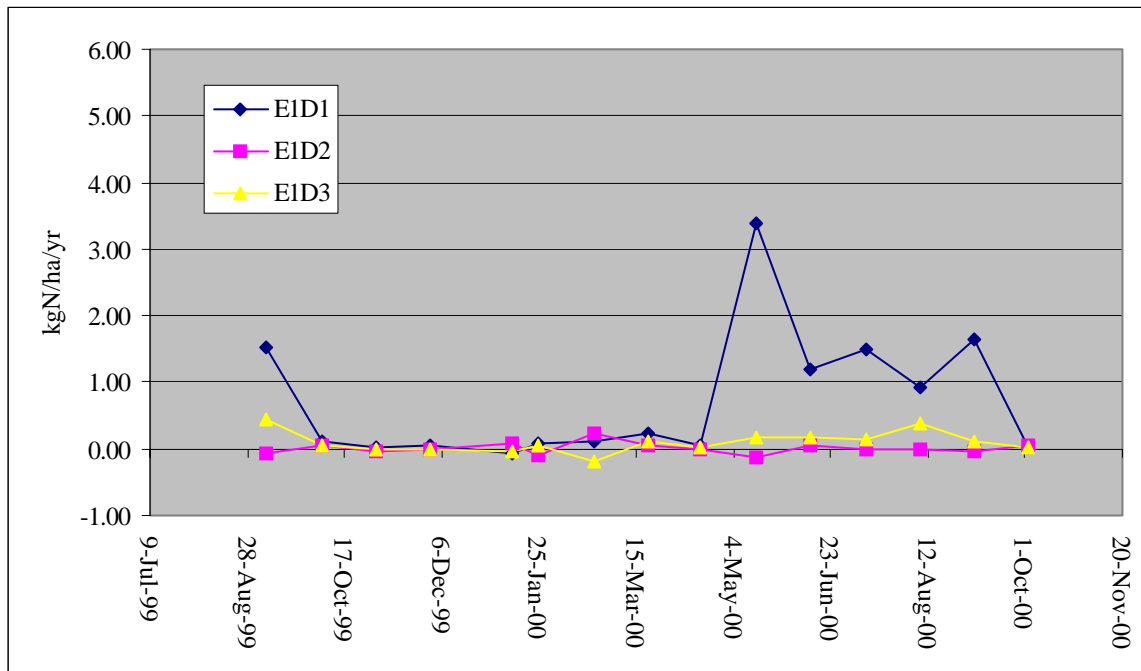
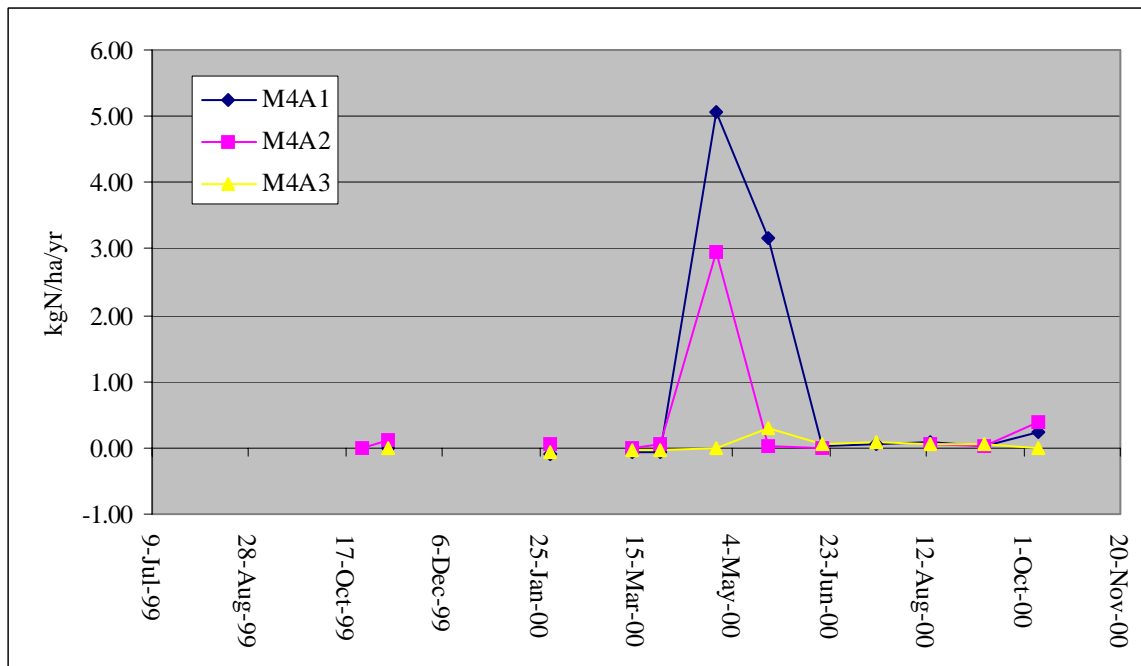
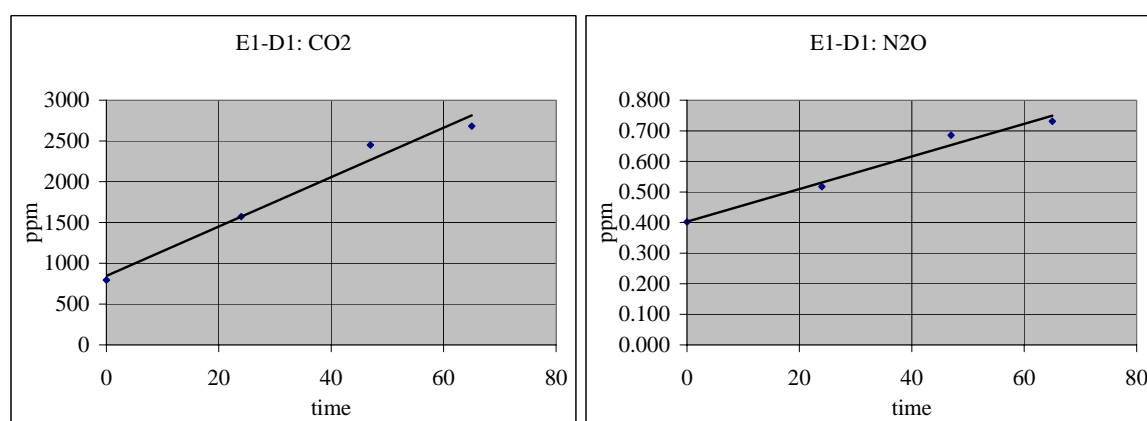


Figure 1.3.14: Denitrification “event” at the Allt a’Mharcaidh (shallow peat) site due to waterlogging ( $\text{kgN ha}^{-1} \text{yr}^{-1}$ )



The very low denitrification rates presented in the above Tables are lower than values published previously for acid upland soils in the UK. To ensure that the field method was robust, periodic testing of the static chambers was carried out. Gas samples were removed from the chamber headspace (with the lid fitted) at several intervals over a 1-2 hour period, to check that N<sub>2</sub>O was accumulating in a linear fashion, thereby ruling out significant leakage of the chambers or feedback which could suppress denitrification as other gases (CO<sub>2</sub>, CH<sub>4</sub>) accumulated. The results of one such test at the River Etherow are shown in Figure 1.3.15. In the majority of checks carried out, linear increases in CO<sub>2</sub> and N<sub>2</sub>O (where found above background concentrations) were observed, providing confidence in the static chamber method in the field.

Figure 1.3.15: Linearity of gas accumulation in static chamber at plot E1D1, Etherow.



#### Laboratory assessment of potential denitrification

In order to maximise the comparability of results from field and laboratory experiments, soil samples for the laboratory studies were taken from the primary field plots. Since the great spatial variability of soil processes is well known (see field measurement results above), soil cores were taken from five locations (A-E) within each plot to increase spatial representativeness. Sample locations were chosen to minimise the likelihood of disturbance from (and to) field installations.

Sampling was carried out over the period 20-26<sup>th</sup> July 2000. With three replicated plots per soil type on 13 soil types over 4 catchments, the total number of complete soil cores was 195. Soil cores were split horizontally into the uppermost, biologically active organic horizons (top 5cm) and the deeper organic and mineral soils (5 to c.20 cm), so that the most important depths for denitrification could be assessed. Extra splits were made for the two soil types in the Afon Gwy catchment containing well defined mineral horizons (G2 – peaty gley and G3 – podsol).

Logistical constraints on the number of incubations for denitrification meant that some soil samples had to be bulked together. In addition, it was necessary to split

samples for the separate denitrification and mineralisation experiments (see next section). The following strategy was therefore adopted to maximise spatial representativeness of samples while minimising the number of bulked samples for incubation :

1. All A-D samples (tops, bottoms and mineral) were split vertically into two halves. For each sample pair, one half was used in denitrification experiments while the other corresponding half was used in the N mineralisation incubations.
2. For the denitrification samples, tops and bottoms were treated differently. For core top experiments, four half cores from locations A-D were bulked into one sample (e.g. G11 Top). With the longer core bottoms it was not possible to fit four half cores into a Mason jar, so instead diagonally opposite half cores were paired, A with C and B with D (e.g. G11 AC and G11 BD Bottoms). Each plot therefore generated one top ( $n_{\text{tot}} = 39$ ) and two bottom ( $n_{\text{tot}} = 78$ ) samples, plus the extra mineral samples at G2 and G3 ( $n_{\text{tot}}=12$ ).

Denitrification from soil cores was measured in sealed Mason jars with butyl rubber septa. Soil samples were generally wetted up with de-ionised water and placed in a Mason jar with an air-tight lid. Teflon tape around the thread was used to ensure a good seal. Gas samples were removed from the jar via a septum through which a hypodermic needle on a 20ml gas syringe was inserted. The syringe was pumped three times to mix the gases inside the jar, then a needle without an attached syringe was inserted through a second septum while the actual sample was taken, to allow equilibration of air pressure. Both needles were then removed to leave the jar sealed again.

The rate of production of gases was measured simply as the difference in concentrations (ppm) over a known period of time, i.e. a baseline sample was taken at  $t=0$  and a second sample was taken after a fixed period. Samples were analysed for  $\text{N}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  by gas chromatograph using identical methods to those for field samples (see above).

Since the volume of the soil sample was known, the total production of  $\text{N}_2\text{O}$  could be calculated. The rate of denitrification could then be expressed in terms of production per unit surface area of soil (cores had a 5cm surface diameter) or per gram dry weight of soil.

The laboratory denitrification experiments were split into two phases. The first phase was designed to test and validate the methods employed through a series of experiments on a small number of extra test samples. The first phase experiments included checks on the linearity of gas production, effects of wetting, and the acetylene test to inhibit gaseous  $\text{N}_2$  production. The second phase comprised a full analysis of actual and potential denitrification rates on the bulked soil samples from all experimental plots.

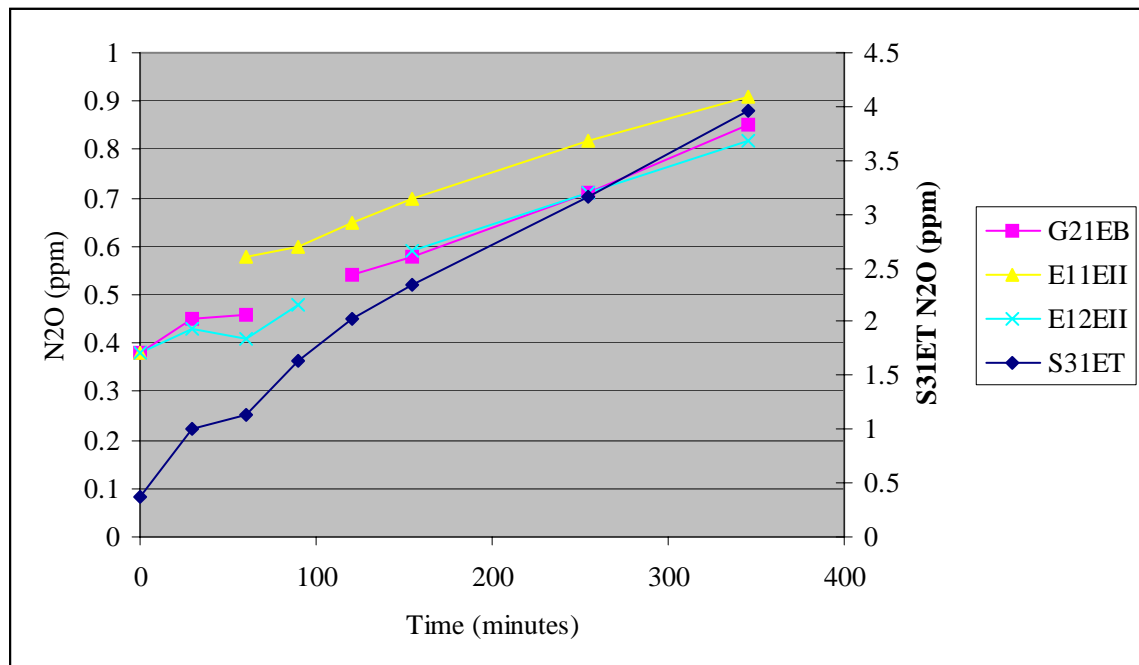
#### *Linearity checks*

To assess the appropriate time period over which gas production should be measured and to ensure that denitrification was linear over this period, it was necessary to check the method through a series of linearity checks.

10 samples from “spare” soil cores (selected from the “E” samples remaining after the sample bulking procedures above) were placed in Mason jars and gas samples taken at intervals over a period of several hours (after 30, 60, 90, 120, 155, 255 and 345 minutes) without removing the lids from the jars. In this way the build-up of gases over a prolonged period could be measured, and an appropriate sample period determined. A graphical plot of the increase in gas concentrations through time would then reveal whether the rate of production was linear and for how long, as concentrations increased within the jar.

Figure 1.3.16 shows that in 4 cores which were denitrifying, accumulation of N<sub>2</sub>O was reasonably linear over several hours. Hence the Mason jar technique was appropriate for studying denitrification over these short timescales.

Figure 1.3.16: Linearity of N<sub>2</sub>O accumulation in 4 soil cores



### Wetting effects

Previous work on denitrification has demonstrated that there may be a pulse of N<sub>2</sub>O production within a very short time after wetting of soils. Since the soil samples were to be wetted up in the laboratory to prevent a moisture limitation of denitrification, it was necessary to test the effect of sample wetting prior to incubation. This would prevent the measurement of production rates too soon after wetting.

Gas production rates were measured for a small number of samples (10 – selected across all soil types and depths) at different times after wetting (30, 60, 90, 120 and 150 minutes). No pulse of denitrification was observed, and linear accumulation of N<sub>2</sub>O commenced immediately after wetting. Wetting up of soil samples prior to

measuring denitrification was therefore deemed acceptable for ensuring that moisture limitation was minimised.

#### Acetylene test

A major assumption of the above technique is that the major denitrification product is  $N_2O$ . However, it is known that under certain conditions denitrification processes can liberate free nitrogen ( $N_2$ ), the proportion of which is notoriously difficult to measure directly, due to its great abundance in the atmosphere. To circumvent this problem and check whether  $N_2$  is a significant denitrification product from a sample, the acetylene block technique was used. Acetylene inhibits the step in the denitrification process by which  $N_2O$  is reduced to  $N_2$ . Comparison of  $N_2O$  production rates from a sample with and without acetylene would indicate whether  $N_2$  production is important.

The  $N_2O$  production rate for a sample was first measured in the standard way (see above). Acetylene gas, produced by adding water to calcium carbide, was then injected into the sealed sample jar and the procedure was repeated. An increase in  $N_2O$  production rate after the introduction of acetylene would indicate the proportion of the denitrification product which was in the form of  $N_2$  and which was therefore not detected in the GC analysis.

16 samples selected from all soil types and depths were used in the acetylene tests. A wide range of denitrification rates spanning three orders of magnitude were measured. No systematic increase in denitrification rate was observed after addition of acetylene (Table 1.3.18). More samples experienced a decrease in  $N_2O$  production than an increase. The only two samples showing a large increase in measured  $N_2O$  production (c. 50%) are also among the slowest denitrifiers. While these results are difficult to interpret, there is no evidence that reduction of  $N_2O$  to  $N_2$  is leading to a significant underestimate of denitrification in these sites.

#### Actual and potential denitrification rates from spatial samples

Having tested the methods in the experiments described above, the full analysis of the pre-prepared spatial survey samples was carried out next. Samples were analysed in three batches. For each batch, four consecutive experiments were carried out before moving onto the next batch:

- 1) Denitrification at 5°C
- 2) Denitrification at 15°C
- 3) Denitrification at 5°C with added N
- 4) Denitrification at 15°C with added N

Each batch was first wetted up with de-ionised water prior to the series of four experiments (i.e. samples were only wetted up once). Gas production was measured after an incubation period of 90-120 minutes. For the two N addition experiments N was added just once, as  $NH_4NO_3$  solution. The solution was made up to a concentration of  $200\text{ mg l}^{-1}$   $NH_4NO_3$  (equivalent to  $35\text{ mg l}^{-1}$  of both  $NH_4\text{-N}$  and  $NO_3\text{-N}$ ) and 20ml were added to each soil sample by dripping from a syringe, to maximise the dispersion of the solution through the sample.

Table 1.3.18: Rate of increase of N<sub>2</sub>O concentration before and after addition of acetylene

Sample	Baseline ppb/min	Plus C <sub>2</sub> H <sub>2</sub> ppb/min	% change
S2 Bottom	94.1	22.9	-76
S3 Top	144.1	40.4	-72
M1 Top	1.3	0.4	-71
G3 Top	2.0	0.6	-67
E1 Bottom	0.3	0.1	-61
M2 Bottom	304.3	197.5	-35
S1 Top	528.0	376.1	-29
G4 Bottom	99.6	74.9	-25
G1 Top	9.0	7.8	-14
S1 Top	220.3	226.6	3
S2 Bottom	14.3	14.8	3
S3 Top	97.8	107.0	9
M3 Top	7.5	8.4	13
E2 Top	98.7	112.6	14
M1 Top	4.0	5.9	48
G2 Bottom	1.8	2.8	55

Summary results averaged by soil type are shown in Table 1.3.19. The laboratory experiments confirmed that no measurable denitrification occurs in the soils at the Mharcaidh unless N is added. Addition of N to core tops (active organic horizon in top 5cm of profile) can result in high rates of up to 6 kgN ha<sup>-1</sup> yr<sup>-1</sup>, but in the deeper organic soil only very low rates occur, even when the cores are warmed to 15°C with N additions.

Denitrification is found to occur in some of the Gwy soils even without N additions, with the highest rates occurring in the mineral horizons of the peaty gley (G2) and podsol (G3) soils. Very low rates of denitrification also occur without added N in the hilltop peat soil but not in the valley peat. Note that incubation at 15°C results in very small increases in the hilltop peat and lower organic horizons in the peaty gley, but the high rates in the mineral horizons have ceased. This is presumably due to exhaustion of the available substrate, whether NO<sub>3</sub><sup>-</sup> or carbon.

Addition of N to the Gwy soils at 5°C results in increased denitrification in all soils except the mineral horizons (perhaps indicating a lack of available carbon) and the lower organic horizon of the podsol. Most notable is the increase in the surface organic horizons of all the soils, with the smallest increase in the hilltop peat and the largest in the valley peat (top and bottom) where no denitrification was recorded without N additions. These levels are increased further still at 15°C, particularly in the hilltop peat and peaty gley.

Denitrification was measured in all soils at Scoat Tarn at 5°C except the surface organic horizon of the peaty gley (S2). Increasing the soil temperature to 15°C increased rates in the core tops of the podsol and peaty gley but not the deep peat (S3), while rates in all the lower horizons decreased, again perhaps due to exhaustion of substrate. Additions of N had the most dramatic effect in the Scoat Tarn soils, even at 5°C, especially in the surface horizons of the peaty gley and deep peat, with a maximum rate of almost 8 kgN ha<sup>-1</sup> yr<sup>-1</sup> for the peaty gley. Upon warming to 15°C an even greater rate of denitrification was observed, this time in the surface horizon of the podsol, at almost 12 kgN ha<sup>-1</sup> yr<sup>-1</sup>. Rates were also increased in most other samples.

*Table 1.3.19: Laboratory denitrification rates averaged by soil type for 3 replicate soil core tops and bottoms (kgN ha<sup>-1</sup> yr<sup>-1</sup>). Blanks indicate zero values.*

AREA	SECTION	5C	15C	5C +N	15C +N
M1	TOP			6.0	
M1	BOTTOM			0.3	1.5
M2	TOP			4.7	0.6
M2	BOTTOM				0.2
M3	TOP			3.7	
M3	BOTTOM				0.4
M4	TOP			1.5	
M4	BOTTOM		0.1		
G1	TOP	0.2	0.3	0.5	1.0
G1	BOTTOM	0.1	0.4	0.4	2.2
G2	TOP	0.6	1.3	2.4	3.4
G2	MINERAL	2.4		0.3	0.6
G2	BOTTOM		0.3	0.6	1.5
G3	TOP			1.6	1.0
G3	MINERAL	2.3			
G3	BOTTOM				0.4
G4	TOP			4.4	4.4
G4	BOTTOM			1.5	1.8
S1	TOP	0.2	2.0	2.2	11.8
S1	BOTTOM	1.5	0.5	0.5	0.9
S2	TOP		0.5	7.9	4.8
S2	BOTTOM	1.2	0.3	2.6	4.2
S3	TOP	0.3	0.2	6.1	6.3
S3	BOTTOM	2.2	0.2	0.7	0.9
E1	TOP		0.1	0.2	0.9
E1	BOTTOM	1.1	2.3	0.4	0.9
E2	TOP			1.8	0.7
E2	BOTTOM	2.1	0.1		

Prior to N additions very little denitrification was found in the surface horizons of the Etherow soils at 5°C, but appreciable rates occurred in the deeper soils. Warming to 15°C increased the rate markedly only for the deeper soil under burnt *Calluna* (E1); the comparable soil at E2 showed a near cessation of denitrification, presumably through running out of substrate. Addition of N resulted in the onset of denitrification in the surface horizons of both soils, but at low rates compared with soils from the



other 3 sites. Denitrification did not recommence in the deeper E2 soil and failed to reach its original, pre-addition levels in the deeper E1 soil. Since N had been added, this must have been due to lack of available carbon.

To determine representative denitrification rates for the whole soil profiles (to the sampled depth of c. 20cm), rates from the different horizons were simply summed (Table 1.3.20).

Without N additions at 5°C the highest rates were found in the peaty gley (G1) and podsol (G2) at the Gwy, the deep peat (S3) and the podsol (S1) at Scoat Tarn, and under mature *Calluna* (E2) in the deep peat at the Etherow. No denitrification was measured at the Mharcaidh or in the valley peat (G4) at the Gwy. The anticipated increase in rates upon warming to 15°C occurred only in the podsol at Scoat Tarn and the deep peat under burnt *Calluna* (E1) at the Etherow. This general lack of an increase in denitrification rate with temperature was presumably due to the exhaustion of substrate within the soil cores after incubation at 5°C, which was carried out prior to incubation at 15°C.

*Table 1.3.20: Total denitrification rates for whole soil cores (kgN ha<sup>-1</sup> yr<sup>-1</sup>). Blanks indicate zero values.*

AREA	5C	15C	5C +N	15C +N
M1			6.3	1.5
M2			4.7	0.9
M3			3.7	0.4
M4		0.1	1.5	
G1	0.3	0.7	1.0	3.2
G2	3.0	1.5	3.3	5.4
G3	2.3		1.6	1.3
G4			6.0	6.2
S1	1.8	2.5	2.7	12.7
S2	1.2	0.8	10.5	9.1
S3	2.5	0.5	6.9	7.2
E1	1.1	2.4	0.6	1.8
E2	2.1	0.1	1.8	0.7

Addition of N to the soil cores at 5°C resulted in dramatic increases in denitrification in all the Mharcaidh soils (previously at or near zero), in the valley peat at the Gwy, and in all the Scoat Tarn soils. N additions did not increase denitrification overall in the Etherow soils. The maximum rate with N additions at 5°C was observed in the peaty gley (S2) from Scoat Tarn, at 10.5 kgN ha<sup>-1</sup> yr<sup>-1</sup>, while an even greater rate was measured in the podsol from the same site (S1) at 15°C, rising to 12.7 kgN ha<sup>-1</sup> yr<sup>-1</sup>. In the Mharcaidh soils, the large increase in denitrification induced by N additions was short lived; the subsequent incubation at 15°C resulted in significant reductions in N<sub>2</sub>O production in all soils there.

Overall the laboratory incubation experiments revealed that potential denitrification rates from a variety of soils at all four sites were much greater than those observed in the

field. Addition of N as  $\text{NH}_4\text{NO}_3$  solution had a much greater effect than warming from 5C to 15C. The highest rates were not found in the same soil types within each of the four catchments. For example, at 5C without added N the highest rates occurred in the peaty gley at the Gwy and the deep peat at Scoat Tarn, but the lowest values at the Gwy were found in the deep valley peats.

#### Comparison of field and laboratory data

Addition of N induced denitrification in soils where none was previously measured, for example the Mharcaidh soils and the valley peat at the Gwy. The implication is that denitrifying bacteria are ubiquitous and can respond rapidly to available  $\text{NO}_3^-$  under appropriate anaerobic conditions. However, warming of soils in the laboratory and addition of N did not always result in increased denitrification; in some cases rates decreased, indicating that some other factor had become limiting. Presumably, the available carbon was exhausted.

This rapid response to N additions in the laboratory may explain why no increase in denitrification was observed from the secondary plots in the field. Since N additions were carried out *after* measurement of denitrification fluxes, there was a 2-week interval between the most recent addition and gas sampling. This could allow ample time for the exhaustion or removal of the introduced  $\text{NH}_4\text{NO}_3$ .

The regular field samples demonstrated the great temporal variability in denitrification, and these data, when compared with the laboratory data, imply that the measurement of low or zero denitrification rates in the field does not mean that significant denitrification cannot occur there. While field measurements were very low compared with published rates from the British uplands, laboratory incubation measurements with N additions showed rates up to two orders of magnitude greater than field measurements, and the same order of magnitude as published rates. These results seem to indicate that denitrification is likely to be episodic, so that while the high rates found in the laboratory may occur in the field soon after N deposition events, the field sampling frequency was too low to pick up many of these events.

The actual field rate of denitrification must therefore lie somewhere between the measured field rates ( $0\text{-}0.5 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ ) and the maximum potential rates in the laboratory incubation studies ( $0.1 - 3.0 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  without added N, rising to  $0.4 - 12.7 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  with added N). The literature-based range of values used in Britain (1, 2 or  $4 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ , representing low, medium and high rates of denitrification), based largely on soil drainage characteristics (Hall *et al.*, 1997), closely matches the rates observed in laboratory incubations without added N. Since the default values also lie between the minimum field and maximum laboratory values, they therefore seem to provide a reasonable range for British soils.

The decision to use the default values in UK FAB modelling applications, rather than the 10-80% range recommended by the UNECE Mapping Manual, would appear to be vindicated by these studies.

#### **1.3.6 Available N, potential mineralisation and nitrification**

Mineralisation and nitrification potentials were assessed by the aerobic incubation method. Baseline and post-incubation samples from the soil cores described above

(Section 1.3.5) were stored together prior to the initial baseline analysis in the cold room at 3-4°C for 4 weeks while preliminary sample preparation (core splitting and weighing) was completed. The sample for baseline analysis should therefore have had sufficient time to overcome any initial changes in chemistry induced by the sampling process.

#### Sample preparation

Each sample comprised a pair of quartered cores from diagonally opposite locations within a study plot. Samples were also split into top and bottom levels. As close as possible to the start of the incubation period the minimally disturbed baseline samples were prepared for analysis. Roots and stones (>c.2mm) were removed from the soil as far as possible by hand and the soil broken up and homogenised. Corresponding samples for incubation were placed intact into sealed, gas-permeable polythene bags and incubated at 15°C for one month. The bags prevented moisture loss from the samples while permitting gaseous exchange, to minimise the build-up of CO<sub>2</sub> and other gases which might affect the analysis. After the incubation period the samples were prepared for analysis in the same way as the baseline samples.

Available NH<sub>4</sub>-N and NO<sub>3</sub>-N were measured by KCl extraction (Page *et al.*, 1982) from a 10g subsample of well mixed soil. A further subsample taken at the same time was used for analysis of dry-weight and loss on ignition (LOI). Ammonium-N and nitrate-N were analysed by Skalar SA-40 autoanalyser using the indol-phenol blue and sulphanilamide/NEDA/Cd/Cu reduction methods respectively.

#### Available nitrogen by potassium chloride extraction

Results of the KCl extractions on the baseline (pre-incubation) soil samples are shown in Figure 1.3.17. Extractable NH<sub>4</sub><sup>+</sup> is generally much higher in core tops (top 5cm active organic horizon) than deeper soils, and is highest in Scoat Tarn and Etherow soils. Very high values occur in the surface of the peaty gley (S2) at Scoat and the deep peat under Calluna (E2) at the Etherow. Elsewhere very low values are found in deeper soils, but reasonably high levels occur in the valley peat (M2) at the Mharcaidh and the surface soils of the Gwy.

Fewer soils show high levels of extractable NO<sub>3</sub><sup>-</sup> when plotted on the same scale (Fig. 3.1.17). While Scoat Tarn soils again show high values in the core tops, albeit highest in the podsol rather than peaty gley for NO<sub>3</sub><sup>-</sup>, low levels are found at the Etherow. Very little NO<sub>3</sub><sup>-</sup> was measured in the Mharcaidh soils, and at the Gwy only the peaty gley (G2) showed a high value.

Actual values for extractable NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> are provided in Table 1.3.21, and show that even for soils with very low values, extractable NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> are higher in the surface soil sample in every case, the only exception being the higher NH<sub>4</sub><sup>+</sup> in deeper soils at the Mharcaidh.

Figure 1.3.17: Available  $\text{NO}_3^-$  and  $\text{NH}_4^+$  by KCl extraction

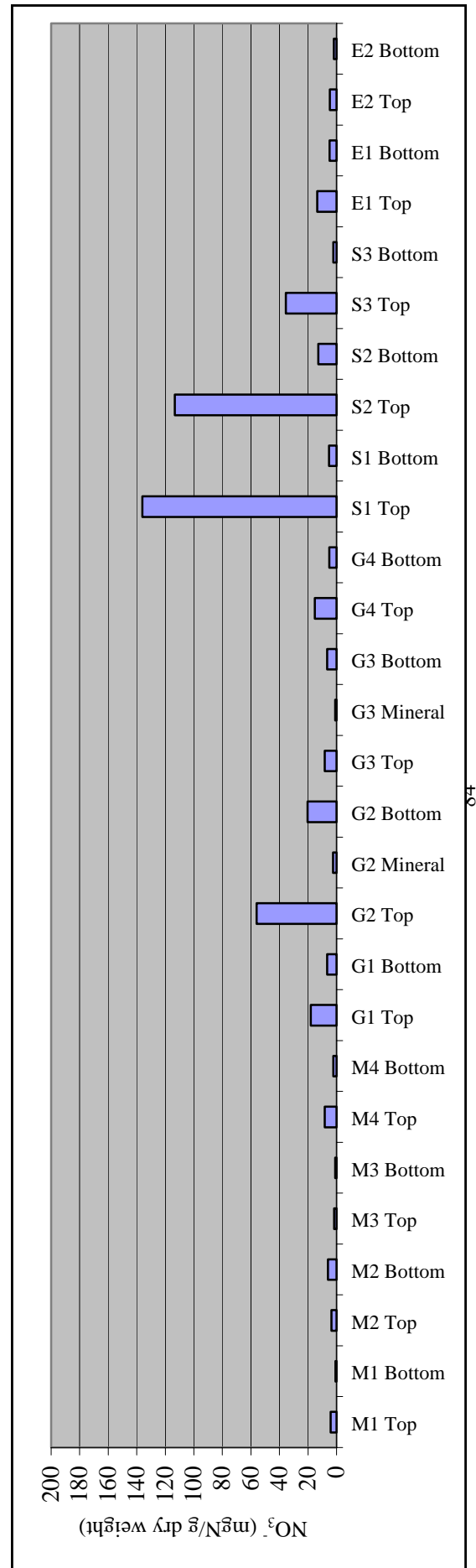
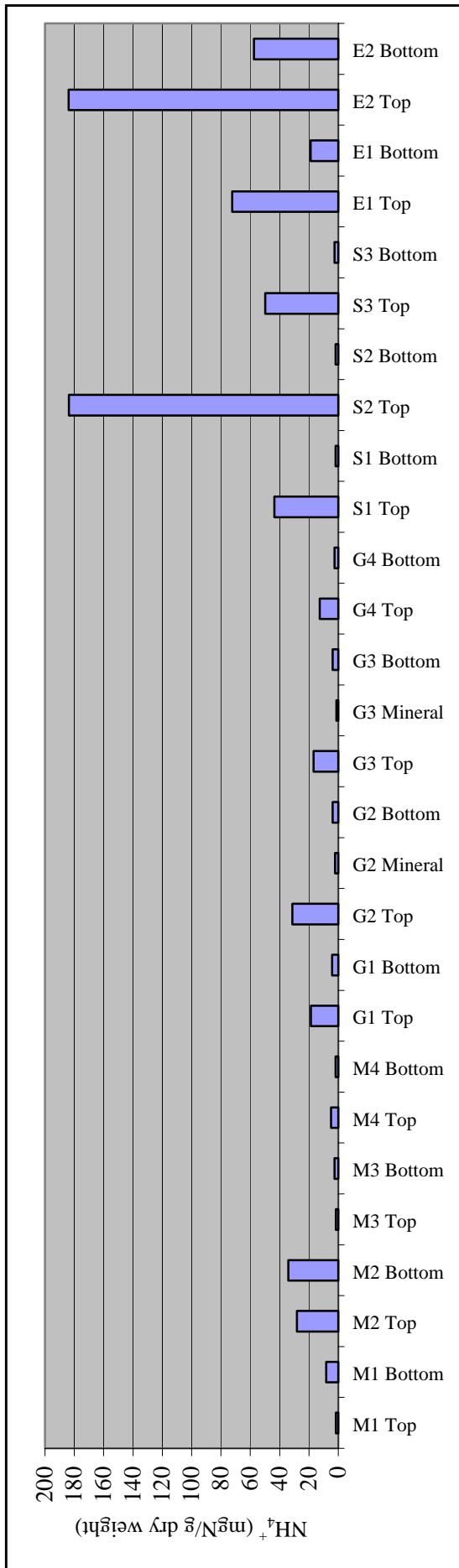


Table 1.3.21: Available  $\text{NO}_3^-$  and  $\text{NH}_4^+$  by KCl extraction

Section	mgN/g dry weight			mgN/g organic		
	$\text{NH}_4^+$	$\text{NO}_3^-$	TIN	$\text{NH}_4^+$	$\text{NO}_3^-$	TIN
M1 Top	2	4	6	2	4	6
M1 Bottom	8	1	9	9	1	10
M2 Top	28	4	32	29	4	33
M2 Bottom	34	6	40	37	7	44
M3 Top	2	2	3	3	2	5
M3 Bottom	3	1	3	8	3	11
M4 Top	5	8	13	5	9	14
M4 Bottom	2	2	4	3	3	5
G1 Top	19	18	37	20	19	39
G1 Bottom	4	7	11	5	7	11
G2 Top	31	56	87	36	64	99
G2 Mineral	2	2	5	18	21	40
G2 Bottom	4	20	24	6	30	36
G3 Top	17	8	25	29	17	46
G3 Mineral	1	1	2	13	9	22
G3 Bottom	4	7	10	12	21	33
G4 Top	13	15	28	14	17	30
G4 Bottom	2	5	8	3	6	9
S1 Top	44	136	180	60	192	252
S1 Bottom	2	5	7	9	23	31
S2 Top	184	113	297	229	138	368
S2 Bottom	2	13	15	4	25	29
S3 Top	50	35	85	72	54	126
S3 Bottom	3	2	5	4	3	7
E1 Top	72	13	86	86	16	102
E1 Bottom	19	5	24	21	7	27
E2 Top	184	5	189	199	5	205
E2 Bottom	58	2	60	64	2	66

#### Potential mineralisation and nitrification

The rate of net mineralisation is given by the difference in total inorganic N concentrations in baseline and post-incubation samples, divided by the incubation period:

$$\text{Net N mineralisation} = (\text{NH}_4\text{-N} + \text{NO}_3\text{-N})_{\text{post-incubation}} - (\text{NH}_4\text{-N} + \text{NO}_3\text{-N})_{\text{baseline}}$$

$$\text{Net nitrification} = \text{NO}_3\text{-N}_{\text{post-incubation}} - \text{NO}_3\text{-N}_{\text{baseline}}$$

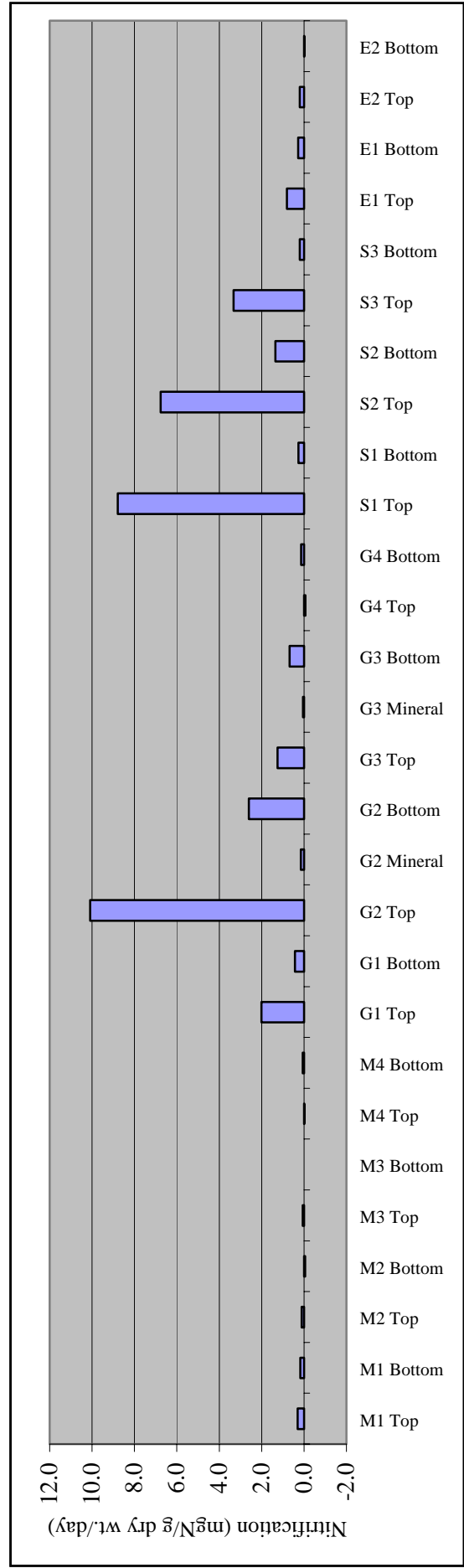
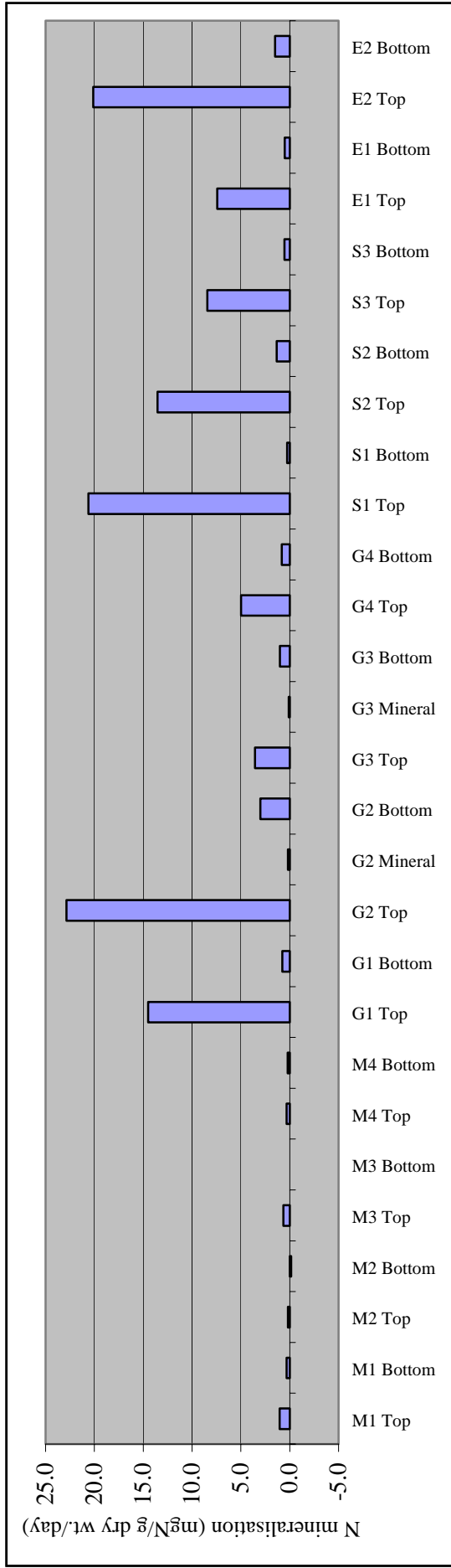
The relatively high incubation temperature of 15°C was selected to ensure that maximum feasible values for potential mineralisation and denitrification would be obtained.

Potential mineralisation and nitrification rates are illustrated in Figure 1.3.18. As anticipated, the highest mineralisation rates occur in the surface organic horizons. Mineralisation rates are high in all soils from the Scoat and Etherow catchments, and in the hilltop peat (G1) and peaty gley (G2) at the Gwy. Lower rates are found in the other Gwy soils and are close to zero at the Mharcaidh.

The highest nitrification rates are found in the same soils with high mineralisation rates, the exceptions being the Etherow soils and the hilltop peat at the Gwy (Fig. 3.1.18).

Table 1.3.22 shows that, as for levels of extractable  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , rates of net N mineralisation and nitrification are greatest in the surface organic horizon (top 5cm) in all cases, even at the very low values found in the Mharcaidh soils.

**Figure 1.3.18: Net N mineralisation and nitrification**



**Table 1.3.22: Net N mineralisation and nitrification rates**

Section	Mineralisation		Nitrification	
	mgN/g dry weight		mgN/g organic	
M1 Top	1.0	0.3	1.1	0.3
M1 Bottom	0.3	0.2	0.4	0.2
M2 Top	0.2	0.1	0.3	0.1
M2 Bottom	-0.1	-0.1	-0.1	-0.1
M3 Top	0.7	0.1	0.9	0.1
M3 Bottom	0.0	0.0	0.3	0.0
M4 Top	0.3	0.0	0.4	0.0
M4 Bottom	0.2	0.1	0.3	0.1
G1 Top	14.5	2.0	15.5	2.2
G1 Bottom	0.7	0.4	0.8	0.5
G2 Top	22.9	10.1	25.2	11.2
G2 Mineral	0.2	0.2	1.0	1.0
G2 Bottom	3.0	2.6	4.2	3.6
G3 Top	3.6	1.3	7.3	2.6
G3 Mineral	0.1	0.0	0.9	0.4
G3 Bottom	1.0	0.7	2.7	1.9
G4 Top	5.0	-0.1	5.6	-0.1
G4 Bottom	0.8	0.1	1.0	0.1
S1 Top	20.6	8.8	26.1	11.0
S1 Bottom	0.3	0.3	1.1	1.1
S2 Top	13.5	6.8	15.4	7.8
S2 Bottom	1.3	1.4	2.5	2.5
S3 Top	8.4	3.3	8.9	3.4
S3 Bottom	0.5	0.2	0.7	0.3
E1 Top	7.4	0.8	8.7	0.9
E1 Bottom	0.5	0.3	0.6	0.3
E2 Top	20.1	0.2	21.8	0.2
E2 Bottom	1.5	0.0	1.7	0.0



### 1.3.7 Discussion of N budget studies

The implications of all the various studies described above for the 4 CLAM N-budget studies are discussed below for each site in order of increasing N deposition & N saturation.

#### Allt a'Mharcaidh

Of the four CLAM N budget sites, the Allt a'Mharcaidh is effectively the “control” site, since it experiences a much lower deposition of N (around 25%) than the others, and the stream itself has near-zero concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Likewise, soilwater concentrations of inorganic N are very low, with a mean value of zero for  $\text{NO}_3^-$ . The general lack of available inorganic N is confirmed by KCl extractions of the soils, with very low values for both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  compared with other sites. Only in the valley peat soils (M2) are appreciable levels of extractable  $\text{NH}_4^+$  found. The potential rates of N mineralisation and nitrification are also very low in the Mharcaidh soils, so internal generation of inorganic N is very slow.

The lack of inorganic N in the soils and soilwaters at the Mharcaidh explains the absence of measurable denitrification there. The potential for denitrification is, however, demonstrated by the laboratory N additions experiment, whereby significant denitrification from surface organic horizons of all soils was induced.

Although the inputs of inorganic N at the Mharcaidh are small, the percentage retained within the catchment is very high, at 99%. Since nitrification and denitrification rates are very low, retention is presumably due to uptake of both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  followed by immobilisation in soil organic matter.

#### Afon Gwy

When the Gwy was selected as a CLAM N budget site, it was thought to experience a fairly high total N deposition load, but a much lower one than the highest value at the Etherow. While this would appear to be true for bulk (wet) deposition measured at the site, according to the most recent modelled data it was subject to a total (wet + dry) N load of  $27 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ , 80% of the load at the Etherow. The catchment leaks  $\text{NO}_3^-$  during the winter but very little during the summer, leading to a mean annual value of only  $6 \mu\text{eq l}^{-1}$ . No data are available for  $\text{NH}_4^+$  but it is assumed to be very low in the stream.

Soils within the Gwy catchment are very variable, with peats on the flat hilltops and in the valley bottoms, and peaty gleys or podsols on the slopes. These soils exhibit different properties with respect to N. Concentrations of  $\text{NO}_3^-$  in all the soilwaters are very low (mean  $< 1 \mu\text{eq l}^{-1}$ ) compared with the streamwater (mean  $6 \mu\text{eq l}^{-1}$ ). Concentrations of  $\text{NH}_4^+$  are also low and comparable to the Mharcaidh, with slightly higher levels in the hilltop peat ( $5 \mu\text{eq l}^{-1}$ ).

Extractable  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are high in the surface organic horizon of the peaty gley (G2), but much lower in the other soils, especially  $\text{NO}_3^-$  in the podsol. The potential mineralisation and nitrification rates in the surface horizon of the peaty gley are the largest of all the soils studied, even though very little  $\text{NH}_4^+$  or  $\text{NO}_3^-$  was found in the soilwaters there. Presumably,

uptake is very rapid in this soil. A high mineralisation rate was also measured in the hilltop peat, and in this case this was reflected in the higher soilwater  $\text{NH}_4^+$  concentration.

The peaty gley at the Gwy was also notable for showing the greatest potential denitrification rate. Removal of inorganic N by nitrification and denitrification may therefore be important in this soil, and this could account at least in part for the low soilwater concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ .

In the podsol (G3) and valley peat (G4) at the Gwy, low extractable  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are accompanied by the lowest N mineralisation and nitrification rates of all soils except those at the Mharcaidh (where very limited N input is the reason). This is reflected in very low soilwater concentrations of inorganic N, leading also to very low denitrification rates (prior to N additions). An unexplained pulse of denitrification was measured from the mineral horizon of the podsol (also the peaty gley) but disappeared even with warming and N additions, presumably due to exhaustion of carbon substrate for the denitrifiers.

Addition of N in the laboratory induced denitrification from all soils, mainly from the surface organic horizons and particularly in the valley peat (G4) and peaty gley (G2). The valley peat also stood out as the soil with the highest annual mean denitrification rate measured in the field outside of the Etherow catchment, albeit from only 1 of the 3 replicate plots. It was further distinguished by having very high organic N in the soilwater, along with the hilltop peat (G1).

### Scoat Tarn

Despite a superficial similarity to the Gwy catchment, in terms of vegetation, soil types and N deposition, the chemistry of the soils and waters from the Scoat catchment was very different.

While total inorganic N deposition at Scoat Tarn was only 25% higher than at the Gwy, the streamwater leaching flux of  $\text{NO}_3^-$  and the percent leached were both more than double the Gwy values. Surface water  $\text{NO}_3^-$  remains above zero all year round, indicating a degree of “N saturation”, with an annual mean concentration of  $15 \mu\text{eq l}^{-1}$  in the lake itself.

The Scoat soil and surface waters are distinctive in having much lower levels of organics (both N and C) than all the other sites including the Mharcaidh. The soilwaters of the Scoat Tarn catchment have  $\text{NO}_3^-$  concentrations an order of magnitude greater than in the Gwy, while  $\text{NH}_4^+$  levels are similar, or even lower than the Gwy peats. These high  $\text{NO}_3^-$  values are matched by the extractable  $\text{NO}_3^-$  values which are far greater than in all other soils except the peaty gley at the Gwy (see above). However, the low soilwater  $\text{NH}_4^+$  concentrations are not matched by low KCl *extractable*  $\text{NH}_4^+$  in the soils; values of the latter are an order of magnitude greater than in the Gwy peats, for example, where soilwater  $\text{NH}_4^+$  concentrations are double those at Scoat Tarn.

The high  $\text{NO}_3^-$  and lack of soilwater  $\text{NH}_4^+$  at Scoat despite its very high extractable  $\text{NH}_4^+$  could be explained by the very high potential nitrification rates. This seems especially likely for the podsol and peaty gley at Scoat, where very high values of extractable  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , potential mineralisation and nitrification, and soilwater  $\text{NO}_3^-$ , all coincide.

All the Scoat soils show significant denitrification in the laboratory (though not in field measurements) even without N additions, which is a result of the availability of soilwater  $\text{NO}_3^-$ . Furthermore, N additions to laboratory soil samples increases denitrification rates by up to an order of magnitude, particularly in the surface organic horizons, indicating that the process is limited primarily only by  $\text{NO}_3^-$  availability and could therefore reach very high rates during N deposition events.

### River Etherow

While the Etherow was selected as the highest N deposition site of the 4 CLAM sites, more recent data show that its N deposition load is in fact very similar to that at Scoat Tarn. However, the leaching flux of  $\text{NO}_3^-$  in the Etherow streams is more than double that of the Scoat catchment, while surface water concentrations are 3-4 times greater, with means of  $43 \mu\text{eq l}^{-1}$  and  $58 \mu\text{eq l}^{-1}$  in Rose Clough and Swan Clough, respectively. The Etherow streams are also unique in having appreciable concentrations of  $\text{NH}_4^+$  which result in a small but measurable leaching flux of around  $0.4 \text{ kg NH}_4\text{-N ha}^{-1} \text{ yr}^{-1}$ . For total inorganic N, retention in the catchment of the Etherow streams is only 67%, while for  $\text{NO}_3^-$ , net retention is less than 15%.

The very high  $\text{NO}_3^-$  and presence of  $\text{NH}_4^+$  in surface waters is matched by very high concentrations in the soilwaters. An extreme value for mean  $\text{NO}_3^-$  under burnt *Calluna* (E1) is driven mainly by concentrations in one plot, but another of the 3 replicates also shows a high value. Levels of  $\text{NH}_4^+$  are even more extreme here; while  $\text{NH}_4^+$  in the soilwaters under burnt *Calluna* is an order of magnitude greater than in most soils at the other sites, it is two orders of magnitude greater under the mature *Calluna*.

The extreme values of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the Etherow soilwaters are not matched by extreme values of extractable N. While extractable  $\text{NH}_4^+$  is very high, particularly under the unburnt, mature *Calluna*, it is very similar to the levels found in Scoat soils. Furthermore, extractable  $\text{NO}_3^-$  is much lower at the Etherow than at Scoat. Similarly, a high potential mineralisation rate was measured under *Calluna*, but was lower under burnt *Calluna*, and potential nitrification rates were very low. Hence, unlike in the Scoat soils, the high soilwater  $\text{NO}_3^-$  at the Etherow cannot be due to high nitrification rates. The lack of nitrification at the Etherow may be due to the very acid soils with a mean pH of 3.0-3.3, compared with pH 3.8-4.0 in most of the other soils studied, since nitrification is known to be inhibited by low pH.

Despite the very low nitrification rates, high soilwater  $\text{NO}_3^-$  concentrations result in significant denitrification from the Etherow soils. Field rates were among the highest measured (although still very low) and rates comparable to the Gwy and Scoat soils (without further N additions) were measured in the laboratory. Unlike the Gwy and Scoat soils, however, those from the Etherow did not show an increase in denitrification with  $\text{NH}_4\text{NO}_3$  additions in the laboratory, presumably because some other factor is limiting. This could explain why rates in the field were not larger than at other sites despite the higher soilwater  $\text{NO}_3^-$ .

The properties of the soil and soilwater in the burnt *Calluna* area are characterised by great spatial variability and extreme values, which is undoubtedly a result of the major biological and chemical disturbance associated with recent burning.

## Conclusions

The CLAM N budget work has revealed some major differences between the 4 studied sites. Although the sites were originally selected using previous data to span fairly evenly a gradient of total N deposition and N saturation status, more recent measured and modelled data have indicated that in fact three of the four sites have rather similar, very high N deposition loads, with only 1 site (Allt a'Mharcaidh) having a very different, low deposition. This potential problem for intercomparisons does not appear to have materialised, though, and the budget studies have shown that each of the 4 sites is different from all the others in terms of the relative importance of N processes and the net results for terrestrial N retention and saturation. These uncertainties in the quantification of N deposition inputs highlight the need for strong links between deposition modelling and catchment specific budget studies.

First, the low N deposition site (Allt a'Mharcaidh) shows all the anticipated characteristics of a nitrogen-poor system, with a strongly N-limited terrestrial ecosystem retaining 99% of inorganic N deposition. There is a general absence of inorganic N in the soils, the soil waters and the streams, and as a result, denitrification rates are very low. Laboratory incubation and field studies showed that denitrification rates could increase dramatically if  $\text{NO}_3^-$  availability increased.

At the other extreme, the River Etherow system is severely acidified from very high deposition inputs of both sulphur and nitrogen based acidity. The terrestrial ecosystem seems to be severely N-saturated, and a manifestation of this is the low retention (13% for  $\text{NO}_3^-$ , 67% for total inorganic N) of atmospheric N inputs, leading to very high  $\text{NO}_3^-$  concentrations and a small leaching flux of  $\text{NH}_4^+$ . The low extractable  $\text{NO}_3^-$  and potential nitrification rates measured in the laboratory suggest that  $\text{NO}_3^-$  is acting as a mobile anion at the Etherow, with little retention in the soil and little produced by nitrification of the abundant  $\text{NH}_4^+$ . The high soilwater and streamwater concentrations support this hypothesis. The lack of nitrification, probably resulting from the very low soilwater pH, would also account for the high levels of extractable and soilwater  $\text{NH}_4^+$ .

Intermediate between these two extremes are the Afon Gwy and Scoat Tarn catchments, which support very different N dynamics despite other superficial similarities. Total N deposition at the Gwy is around 75% of the levels at Scoat Tarn and the River Etherow, which experience almost identical N deposition loads according to modelled data. The Scoat Tarn catchment leaches more than double the flux (and proportion) of N as the Gwy, even though N deposition is only 30% greater.

The  $\text{NO}_3^-$  status of the Gwy soils is quite low, with little extractable  $\text{NO}_3^-$ , and very low potential nitrification rates, in all but the peaty gley soils. Concentrations of  $\text{NO}_3^-$  in all the soilwaters are near zero, despite a mean concentration of  $6 \mu\text{eq l}^{-1}$  in the stream. There is no obvious explanation for the general lack of  $\text{NO}_3^-$  in the soil system, unless rapid uptake or denitrification is occurring. Levels of soilwater  $\text{NH}_4^+$  are more comparable to Scoat (and the Mharcaidh), with slightly higher values only in the peat. Extractable  $\text{NH}_4^+$  was also low in all soils, but highest in the peaty gley. Denitrification was observed in some of the Gwy soils despite the low soilwater  $\text{NO}_3^-$  concentrations, perhaps indicating a  $\text{NO}_3^-$  limitation of the process as speculated above.

Scoat Tarn, on the other hand, seems to be very  $\text{NO}_3^-$  rich, with high soilwater concentrations and very high extractable  $\text{NO}_3^-$ . Furthermore, high values of extractable  $\text{NH}_4^+$  combined with high potential nitrification rates are likely to contribute to the abundance of  $\text{NO}_3^-$ . Rapid nitrification would also account for the lack of  $\text{NH}_4^+$  in soil waters. Denitrification rates from the Scoat soils in the laboratory are similar to those for the Gwy (and Etherow) despite the apparent differences in  $\text{NO}_3^-$  availability.

The reasons for the differences in  $\text{NO}_3^-$ , and to a lesser extent  $\text{NH}_4^+$ , availability, are not obvious, but nitrification would appear to be a key process. Another difference between the two sites is the level of soluble organic compounds, of both carbon and nitrogen. TOC in Gwy streamwater is double that in Scoat Tarn, while organic N in Gwy soilwaters is also much higher. Decomposition processes are therefore exerting a much greater influence on N cycling at the Gwy than at Scoat Tarn. It could also be speculated that the carbon pool is much greater at the Gwy, potentially providing a bigger immobilisation sink. Results from the  $^{15}\text{N}$  additions work should provide useful information in this respect.

A key finding from these plot and catchment studies is the spatial heterogeneity in terms of inorganic N abundance in each compartment and the relative importance of different processes. This heterogeneity crosses several scales and emphasises the need for improved understanding. At the regional scale, three catchments with notionally similar N inputs have very different outputs. Within catchments, soils behave differently and hotspots of activity occur even within the same soil type. While it is assumed that within catchment heterogeneity is due to soil or land-use effects, the fine scale variability in deposition inputs is not known.

# Task 1.3.8: Nitrogen dynamics in forest and moorland catchments: the Loch Grannoch case study, Galloway, south -west Scotland

R. Harriman, R.C. Helliwell, R.C. Ferrier,  
A.W. Watt, A. Mc Cartney

### **1.3.8 Nitrogen dynamics in forest and moorland catchments: the Loch Grannoch case study, Galloway, south -west Scotland.**

R. Harriman, R.C. Helliwell, R.C. Ferrier, A.W. Watt and A.McCartney

#### **Summary**

1. These results highlight the major role of forest age and structure in controlling the rate of nitrate leaching from catchments receiving similar N deposition. In addition, immobilisation of deposited nitrogen appears to be relatively high (15-20 kg/ha/yr), although the sustainability of such a high immobilisation rate is uncertain.
2. There is no positive relationship between forest age and the leaching of organic forms of carbon and nitrogen while organic nitrogen constitutes the largest (and probably non-acidifying) component of the total N output from 4 of the 6 study catchments.
3. There may also be further benefit in evaluating the link between immobilisation rates and the proportion of the NH<sub>4</sub>-N component of deposition as an additional predictor of nitrate leaching.

#### **1. Background**

The Loch Grannoch catchment covers an area of around 1545 ha of which the surface area of Loch Grannoch covers 111 ha at an elevation of 214m. The catchment forms part of the Cairnsmore of Fleet granite pluton which is overlain predominantly by a variety of peaty soils, ranging from organic peats of varying depth, peaty podzols, peaty gleys and rankers at higher elevation on steeper terrain. Mean annual rainfall averages around 2000mm and the 1995-97 Total N deposition was estimated to be 28kg/ha/yr for mature forest catchments and 24kg/ha/yr for moorland and young forest catchments.

Commercial forest planting commenced in 1961-62, mainly with Sitka Spruce and Douglas Fir, on the north and east side of the catchment. Further extensive planting occurred during 1977-78 on the western slopes giving a total forested area of around 908ha (63% of the land area). The remaining vegetation cover is comprised mainly of rough grassland (*Molinia*) and heather.

Six sub-catchments were selected for the nitrogen study (Fig. 1.3.19), three on the east and three on the west side of Loch Grannoch. Catchments 1-3 were covered by 80% mature forest, catchment 4 by 55 % mature and 35 % young forest, catchment 5 with 46% young forest and catchment 6 with 85% rough grassland/heather moorland (Table 1.3.23). These catchments

thus provided an excellent comparison of forest effects on nitrogen runoff in a catchment with simple geology and relatively homogeneous soil characteristics.

**Table 1.3.23: Physical Characteristics of Loch Grannoch Catchments**

Sampling	NGR	Catchment Area (ha)	% Forest Area		Runoff (mm)
			<25 yr	>25 yr	
Site 1	NX 552714	25	-	80	1667
Site 2	NX 552712	66	-	80	1667
Site 3	NX 547698	57	-	80	1667
Site 4	NX 543708	301	35	55	1700
Site 5	NX 537699	586	46	-	1740
Site 6	NX 537686	84	-	8	1740

Between February 1998 and February 2001 twice monthly samples of stream water, bulk deposition and mist were collected. Some earlier data were available based on three monthly samples. In the summer of 1999, thirty soil samples from the top 10cm of the organic horizons were collected from the six catchments, representing the full range of environmental attributes, including land-use, topography and soil types (Fig 1.3.20). These samples were analysed for total carbon and nitrogen using a Carlo Erba NA1500 Elemental Analyser. In addition, nine samplers were installed on each soil type under the forest canopy and in open moorland sites on the eastern slopes to measure denitrification fluxes (although one was abandoned due to continuous waterlogging of the soil)



Table 1.3.24

A summary of chemical variables in the Loch Grannoch catchment (Feb 1995 - Jan 2001)

Site name	pH	Alk ueq-l	Alk2 ueq-l	Cond uS/cm	Na ueq-l	NH4 ueq-l	K ueq-l	Mg ueq-l	Ca ueq-l	Cl ueq-l	NO3 ueq-l	SO4 ueq-l	SiO2 ueq-l	P04-P ueq-l	Total P ueq-l	Total N ueq-l	T ORGN ueq-l	Al-TM ueq-l	Al-NL ueq-l	Al-L ueq-l	Abs-250 mg-l	TOC mg-l	
<b>SITE 1</b>	Max	5.84	27	18	88	372	2	8	108	150	484	82	173	9930	18	1680	862	1112	324	1042	0.332	7.6	
	Min	4.26	-51	-59	44	173	0	2	33	16	125	6	74	2800	0	2.5	203	2	27	21	4	0.042	1.6
	Mean	4.63	-23	-28	62	273	0	4	67	49	307	36	105	5374	1	4.1	663	174	97	97	485	0.128	3.6
<b>SITE 2</b>	Max	5.29	9	0	90	397	4	10	98	133	520	110	183	8440	14	16	1984	1033	1278	201	1211	0.717	15.6
	Min	4.37	-39	-45	39	108	0	2	35	24	116	6	71	1980	0	2.5	244	2	99	20	77	0.036	1.3
	Mean	4.66	-22	-24	63	279	0	4	70	54	313	49	113	4691	0	3.6	813	167	634	81	551	0.101	3
<b>SITE 3</b>	Max	6.39	90	86	98	410	4	17	162	407	522	47	359	7990	8	23	1437	1050	535	288	351	1.171	26
	Min	4.08	-83	-99	42	146	0	2	32	29	113	3	55	1220	0	2.5	200	53	116	64	0	0.114	3.5
	Mean	4.79	-5	-24	62	276	0	5	69	86	306	17	87	3865	1	7.7	530	339	285	177	108	0.505	10.6
<b>SITE 4</b>	Max	6.64	87	81	94	352	0	7	134	193	453	18	196	13180	16	28	796	747	298	204	167	1.543	34
	Min	4	-89	-109	29	141	0	0	27	20	101	0	40	570	0	0.5	183	96	56	53	0	0.288	3
	Mean	4.91	-1	-25	56	250	0	3	68	74	263	6	76	5731	2	7.6	419	349	187	128	56	0.639	12.4
<b>SITE 5</b>	Max	5.98	24	16	75	340	3	7	85	130	443	32	188	12450	4	53	845	733	321	218	207	1.575	36
	Min	4.24	-45	-72	25	108	0	1	24	20	81	0	35	700	0	2.5	113	12	46	30	7	0.098	2.7
	Mean	4.91	-4	-17	41	199	0	4	47	47	207	6	63	2754	0	4.6	301	226	155	86	68	0.266	6.2
<b>SITE 6</b>	Max	6.24	42	34	67	293	3	11	78	154	356	29	188	10770	8	10	791	603	205	173	84	0.652	15
	Min	4.46	-35	-40	25	113	0	1	24	31	90	1	34	380	0	2.5	221	33	42	39	0	0.133	3.4
	Mean	5.04	2	-10	40	198	0	6	44	60	200	10	61	2781	1	3.3	378	253	127	96	31	0.31	7
<b>OUTFLOW</b>	Max	5.04	2	-7	72	327	10	10	74	57	401	57	131	13260	3	15	941	530	556	171	419	0.554	12.8
	Min	4.27	-54	-58	32	143	0	2	32	26	114	6	49	190	0	2.5	267	40	106	22	38	0.089	3
	Mean	4.6	-30	-28	50	225	1	6	54	42	249	18	72	1840	1	4.8	468	245	240	90	146	0.248	5.6
<b>Rain</b>	Max	8.2			84	3969	464	87	939	255	4345	144	524										
	Min	4.48			9	17	0	1	7	7	20	0	16										
	Mean	5.33			29	190	40	8	53	26	210	22	49										
<b>Mist</b>	Max	8.2			3370	24412	1732	477	6574	2577	27877	4573	3368										
	Min	3.78			94	91	0	5	32	19	101	6	19										
	Mean	5.25			747	4553	305	117	1131	465	4956	606	752										

## 2. General chemical comparisons

### Deposition chemistry

A summary of the chemical composition of bulk deposition and mist/cloud deposition is given in Table 1.3.24. The contribution of sea-salts and acidic components varied considerably between samples but average non-marine sulphate concentrations of  $28 \mu\text{eq l}^{-1}$  reflected the general decline in pollutant loadings to Galloway lochs and streams. Deposition of N from the atmosphere is influenced by the type of vegetation cover. Forest vegetation, particularly coniferous species including Sitka Spruce and Douglas Fir, have a greater ability to capture occult and dry deposition than moorland vegetation (Fowler *et al.*, 1989). Thus the sub-catchments that support extensive, mature forest (sites 1-3) receive larger inputs of atmospheric N than those sites with young forest (sites 4-5) and moorland (site 6) (Table 1.3.25). Concentrations of similar pollutants from the mist-only collector were frequently 20-30 fold greater than in bulk deposition and although the volume of mist samples was small compared with those in the bulk collector this form of deposition made a significant contribution to total deposition in the Grannoch catchments.

**Table 1.3.25: Nitrogen budgets for Loch Grannoch Catchments**

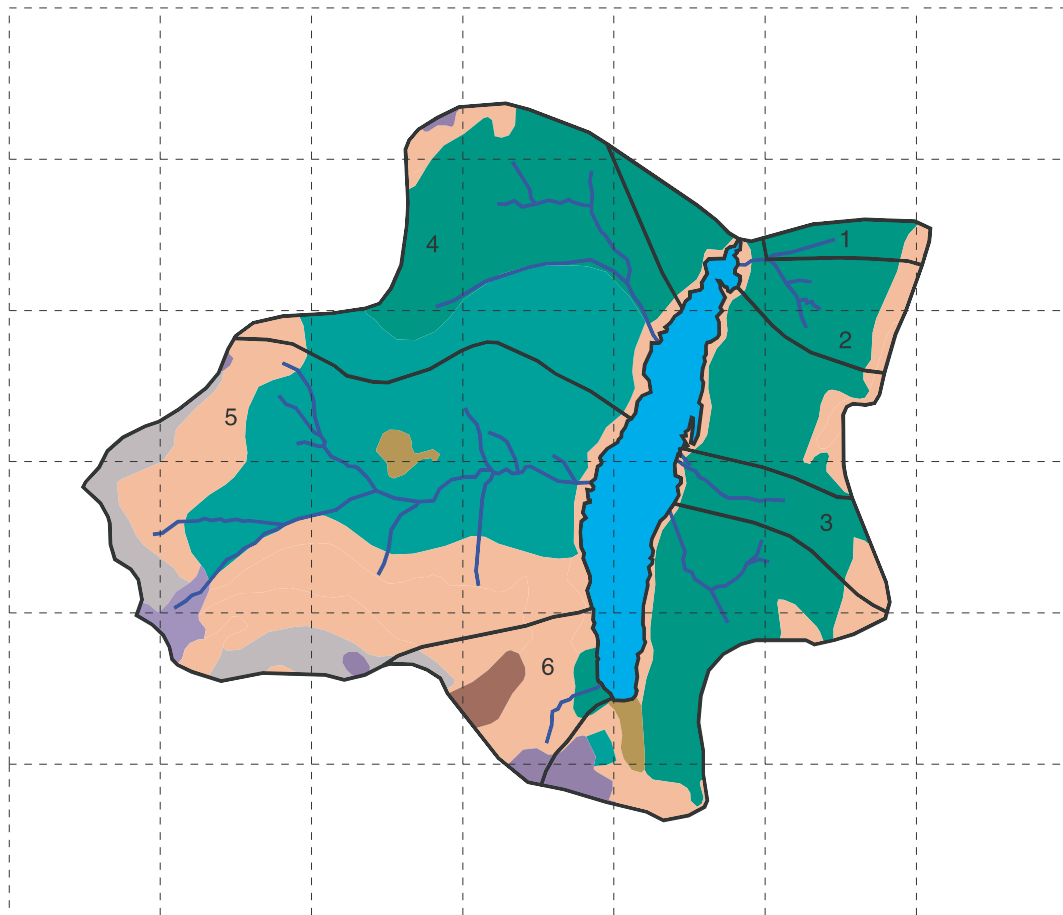
	N Input (Kgha <sup>-1</sup> y <sup>-1</sup> )			N Output (Kgha <sup>-1</sup> y <sup>-1</sup> )		Nitrogen Ratios (%)			
	Total N	NO <sub>3</sub>	NH <sub>4</sub>	NO <sub>3</sub>	T.Org.N	$\frac{\text{Total N (Out)}}{\text{Total N (In)}}$	$\frac{\text{NO}_3(\text{Out})}{\text{NO}_3(\text{In})}$	$\frac{\text{NO}_3(\text{Out})}{\text{Total N (In)}}$	$\frac{\text{NO}_3(\text{Out})}{\text{Total N (Out)}}$
Site 1	28	9.8	18.2	8.4	2.9	40	86	30	74
Site 2	28	9.8	18.2	11.4	2.8	51	116	41	80
Site 3	28	9.8	18.2	4.0	5.7	35	41	14	41
Site 4	24	8.4	15.6	1.5	6.1	32	18	6	20
Site 5	24	8.4	15.6	1.5	3.9	23	18	6	28
Site 6	24	8.4	15.6	2.4	4.4	28	29	9	15

### Catchment streams

A comparison of the general chemical properties of the six streams (Table 1.3.24) reveals major differences between catchments 1-3 on the east (mature forest) and 4-6 on the west (young forest/moorland) side of the loch. Streams 1-3 were generally more acid (mean pH range 4.63 - 4.79) than streams 4-6 (mean pH range 4.91 - 5.04) and consequently had higher

**Figure 1.3.19: Loch Grannoch catchment - land cover**

257 573

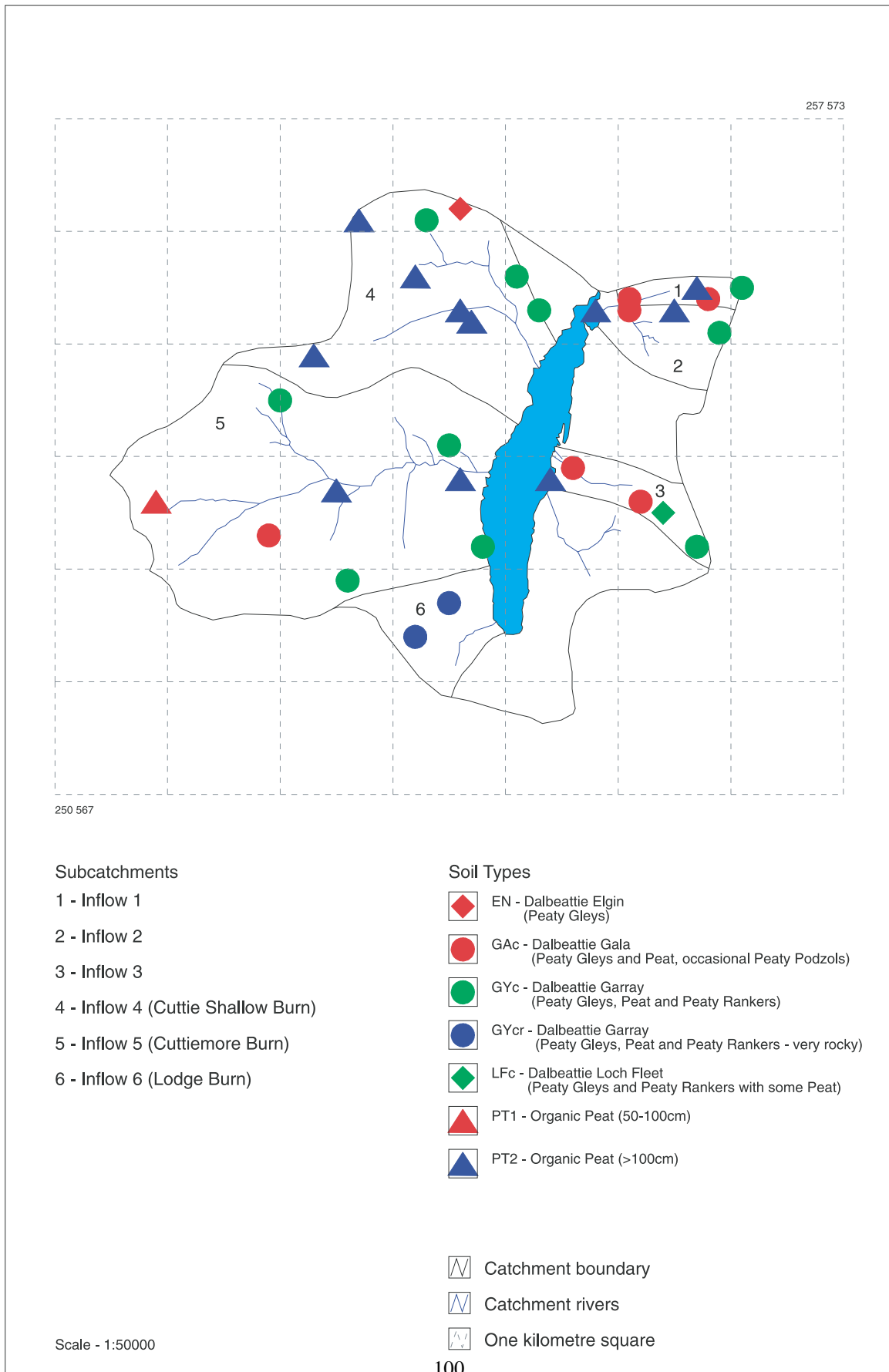


250 567

Subcatchments	Landcover	Hectares
1 - Inflow 1	Poor Rough Grassland	13.70
2 - Inflow 2	Peatland	20.48
3 - Inflow 3	Montane	60.51
4 - Inflow 4 (Cuttie Shallow Burn)	Recent Planting	381.60
5 - Inflow 5 (Cuttiemore Burn)	Conifer Plantation	525.79
6 - Inflow 6 (Lodge Burn)	Fresh Waters	111.48
	Cliffs	13.45
	Heather / Peatland Mosaic	13.15
	Poor Rough Grass / Heather Mosaic	404.57
		<hr/>
		1544.73
	Catchment boundary	
	Catchment rivers	
	One kilometre square	

Scale - 1:50000

Figure 1.3.20: Loch Grannoch catchment - soil sampling



concentrations of toxic forms of aluminium. Concentrations of marine derived salts (Na, Cl) were also greater at sites 1-3, reflecting the greater interception by mature trees. This mechanism is also mirrored in the comparison of sulphate concentrations.

Temporal trends in pH,  $\text{NO}_3^-$ , Total Organic N (TOrgN) and Total Organic Carbon (TOC) are presented in Figures 1.3.21-23. In all streams pH was generally correlated with flow (based on stage height measurements) with lowest pH recorded during highest flow. Nitrate concentrations followed a seasonal pattern in all streams, but winter peaks were significantly higher in streams 1-3 and were maintained over a longer period during the winter months. Evidence of significant nitrate leaching during summer months ( $5\text{-}20 \mu\text{eq l}^{-1}$ ) in streams 1-3 indicates that total N deposition at these sites ( $\sim 28\text{kg/ha/yr}$ ) exceeds tree uptake and immobilisation. In streams 4-6 the absence of nitrate in the summer suggests that all deposited N is utilised in the terrestrial system by the young trees, soil microbial activity and other immobilisation processes. Temporal trends in TOrgN closely matched those of TOC rather than  $\text{NO}_3^-$ , a situation typical of upland streams in Scotland (Harriman *et al.*, 1998). Peaks of TOrgN usually occurred during summer months when TOC concentrations were at their highest.

### 3. Nitrogen dynamics

#### *Nitrogen budgets*

Calculations of approximate input/output budgets (Table 1.3.25) reveal a number of interesting features. First, the extent of  $\text{NO}_3^-$  leaching follows the generally accepted pattern where high rates are found in the streams with mature forests (1-3) and low leaching rates are found in streams draining young forests. The moorland catchments showed a rate similar to, but somewhat higher than, the young forest sites. This pattern of nitrate leaching probably reflects the relative nitrogen requirements of the different vegetation types, but other factors may contribute to higher N availability, e.g. the combination of *Molinia* and flushed peat at site 6 (Pyatt *et al.*, 1979).

Secondly, apart from sites 1 and 2, leaching rates of TOrgN are significantly greater than for nitrate. This situation is typical of most Scottish streams with high TOC concentrations and low/medium N deposition. When these two factors are combined by comparing the ratio of nitrate output with total nitrogen output (nitrate + TOrgN), the differences between the low

TOC/mature forest sites (1-3) and the high TOC/ young forest sites are further accentuated (Table 1.3.25).

Thirdly, any estimates of the effects of N deposition on nitrate leaching depend on the assumptions made about the relative importance of soil and vegetation processes. For example, by incorporating all forms of N deposition into the budgets a 50-65% N-retention for catchments 1-3 is obtained, compared with a 67-78 % retention in catchments 4-6. Alternatively, by assuming that all the  $\text{NH}_4^+$  component of N deposition is utilised by vegetation or converted to Organic N, and that nitrification is relatively insignificant, there appears to be little nitrate retention at sites 1-2 but nearly 60% retention at site 3. For sites 4-6, nitrate retention ranges from 70-80%. A common assumption would be that both nitrate and ammonia in precipitation contributed significantly to nitrate leaching. From this scenario N retention rates around 90-95 % are obtained for sites 4-6 compared with rates of 60-85 % for sites 1-3.

From this analysis, site 3 appears to be a possible outlier when compared with sites 1 and 2. Nitrate leaching at site 3 is less than half that of sites 1-2 while TOrgN leaching is double the rate. This suggests that the extent of 'reactive' carbon in soils (as reflected by TOC concentrations in runoff) may determine immobilisation rates and ultimately, nitrate leaching. This process may also explain the similarity between site 4 and 5, where the expected greater nitrate leaching due to greater cover of old forest, is balanced by a higher immobilisation rate (mean TOC of  $12.4 \text{ mg l}^{-1}$  at site 4 compared with  $6.2 \text{ mg l}^{-1}$  at site 5).

#### *Predicting nitrate leaching*

Interpretation of the nitrogen dynamics in the six Grannoch catchments is problematic because over 60% of the N deposition is in the form of  $\text{NH}_4\text{-N}$  (16-18 kg/ha/yr) while <1 kg/ha/yr is lost as  $\text{NH}_4^+$  in runoff. Denitrification studies in peaty soils beneath the canopy and in open moorland plots indicate that N-losses by this process are unlikely to exceed 1-2 kg/ha/yr while soil solution measurements at other study sites indicate similar or lower estimates of nitrification rates. This implies a mean N-immobilisation/uptake rate of around 15 kg/ha/yr for sites 1-3 and one of around 20 kg/ha/yr at sites 4-6, even allowing for denitrification, nitrification and the incorporation of some of the N-deposition into the TOrgN component.

A widely used method for predicting nitrate leaching is to use C:N ratios in soils and waters where ratios of 25 or less are presumed to indicate the onset of nitrogen saturation (Gundersen *et al.*, 1998). Soil samples from over 30 plots, selected to cover all the major soil groups, vegetation types and elevation range, were analysed for carbon and nitrogen content and the results compared with similar data for water (Table 1.3.26). The soil C:N ratios revealed a considerable spatial variability within each sub-catchment and mean values were generally uncorrelated with nitrate leaching. Although C:N ratios in runoff water provide an integrated value for the catchment the data are subject to a degree of temporal variability. However the mean values give a somewhat better correlation with nitrate leaching as shown by the lowest C:N ratios at the sites 1 and 2 matching with highest nitrate leaching. Again, site 3 is an outlier, further emphasising the role of carbon in determining nitrate leaching.

Figure 1.3.21: pH in Grannoch streams

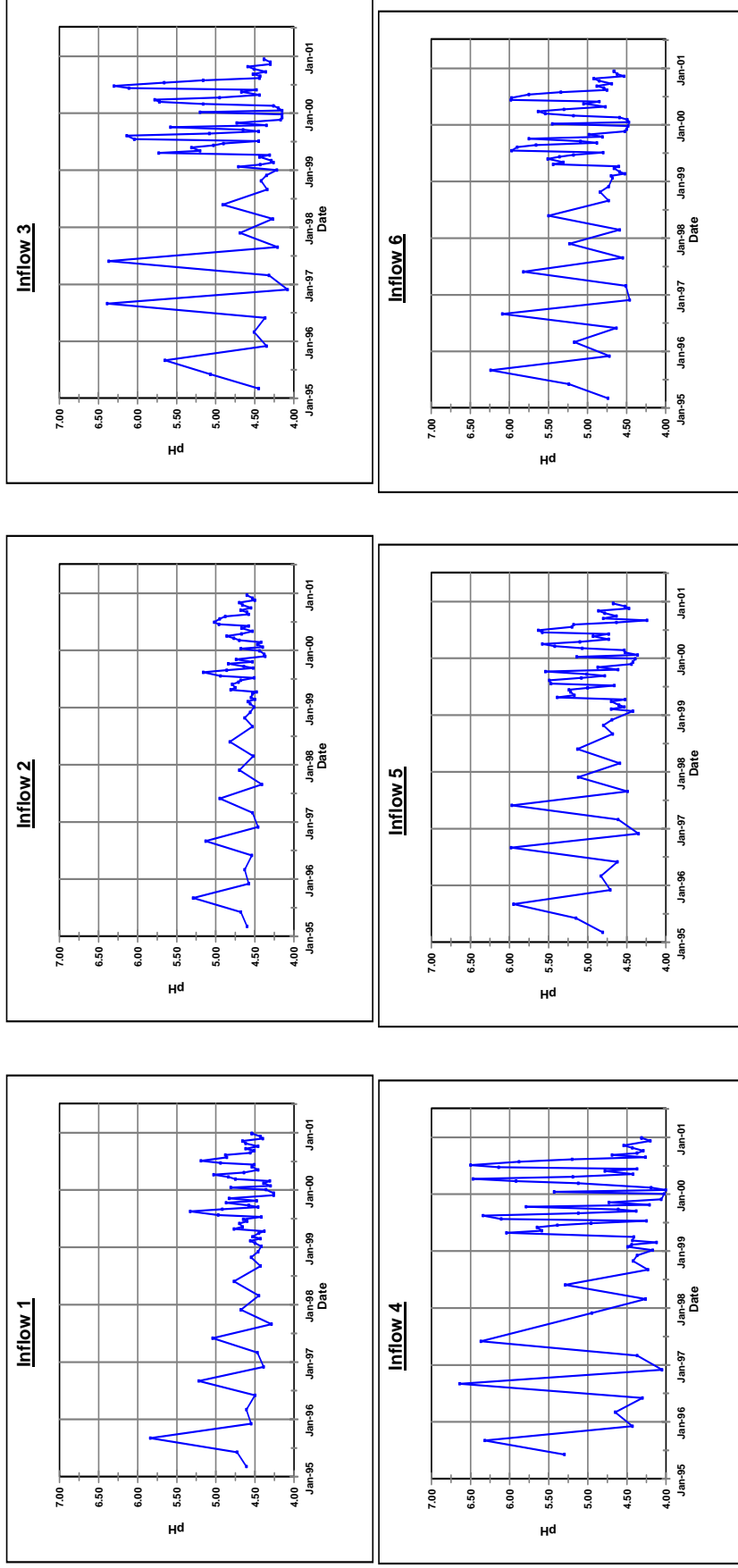




Figure 1.3.22: Nitrate and Total Organic N in Grannoch streams

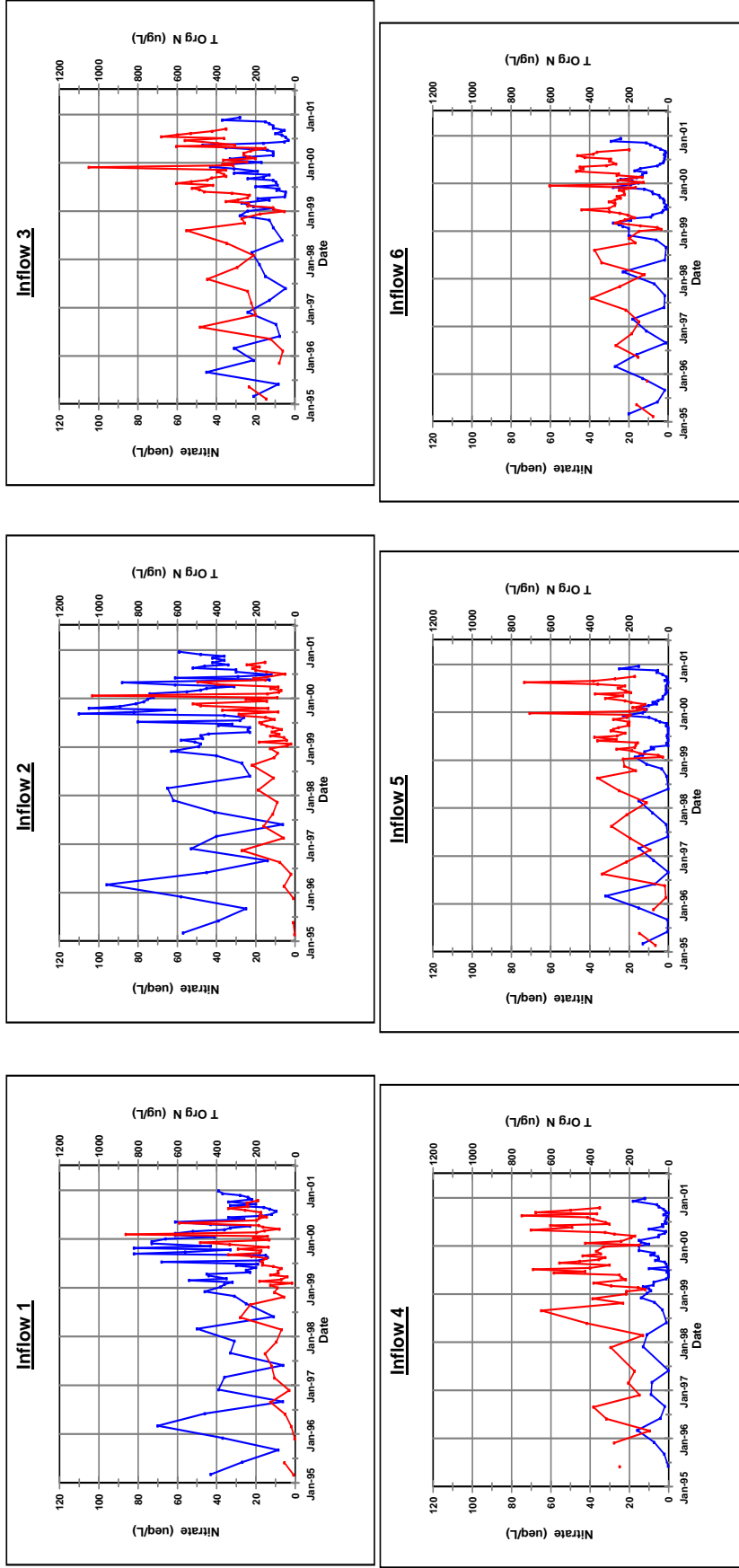


Figure 1.3.23: TOC and Total Organic N in Grannoch streams

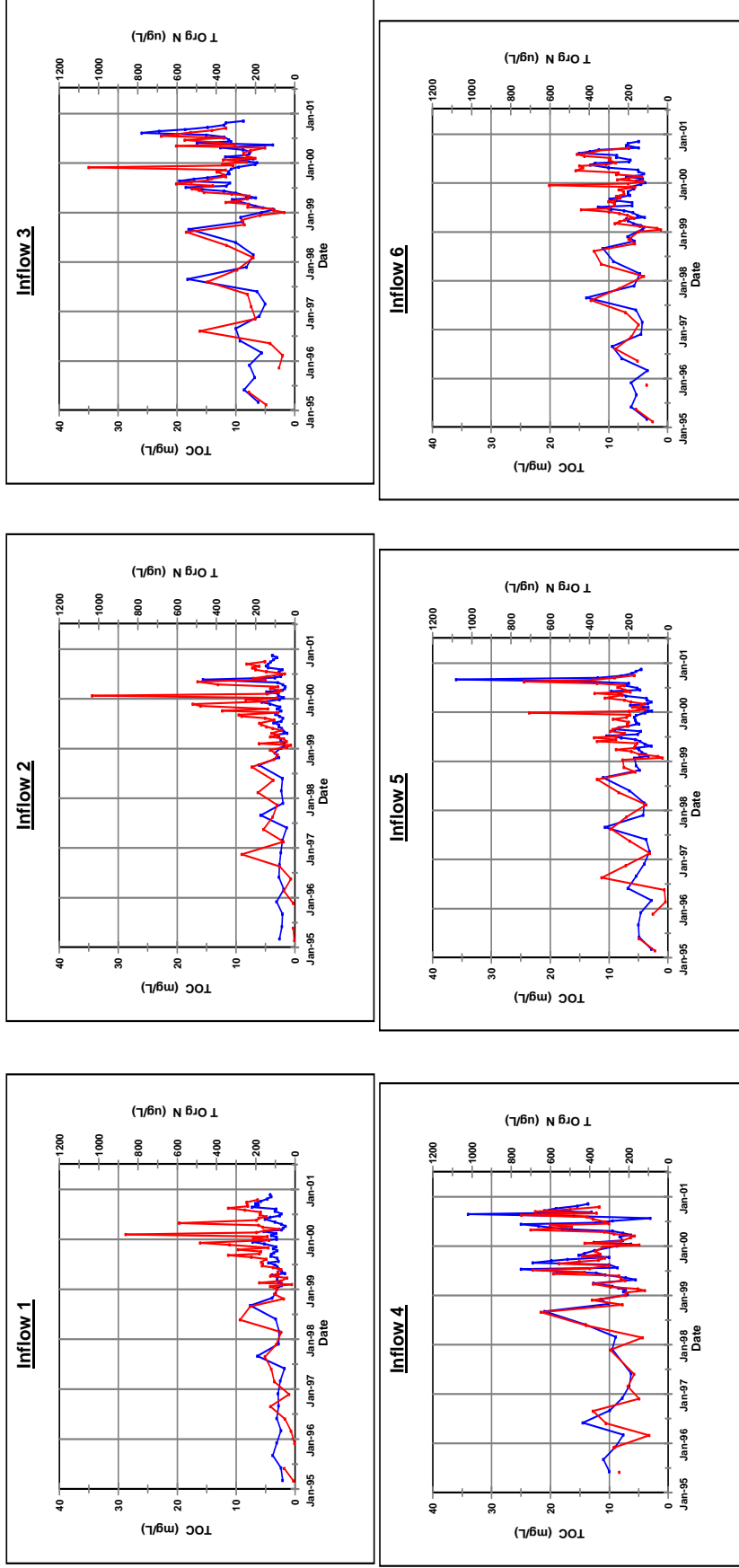


Table 1.3.26: Relationship between mean C:N ratios in soils and runoff and nitrate leaching in Grannoch catchments

Site	NO <sub>3</sub> <sup>-</sup>	T.org.N	TOC	C/N (water)	C/N (soils)	Range
Outflow	17	250	5.7	23	23	15-38
Burn 1	39	198	3.6	18	26	17-38
Burn 2	52	190	3.1	16	21	20-25
Burn 3	17	360	11.2	31	22	20-24
Burn 4	6	362	12.8	35	25	21-35
Burn 5	5	243	6.6	27	21	15-25
Burn 6	10	264	7.2	27	20	17-22

#### 4. Conclusions

These results highlight the major role of forest age and structure in controlling the rate of nitrate leaching from catchments receiving similar N deposition. In addition, immobilisation of deposited nitrogen appears to be relatively high (15-20 kg/ha/yr), although the sustainability of such a high immobilisation rate is uncertain.

There is no positive relationship between forest age and the leaching of organic forms of carbon and nitrogen while organic nitrogen constitutes the largest (and probably non-acidifying) component of the total N output from 4 of the 6 study catchments.

There may also be further benefit in evaluating the link between immobilisation rates and the proportion of the NH<sub>4</sub>-N component of deposition as an additional predictor of nitrate leaching.

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# Task1.4: Collection of data on soil N processes from extensive (regional) study sites

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## 1.4 Collection of data on soil N processes from extensive (regional) study sites

### 1.4.1. Data collection

Soil and surface water data for the purposes of MAGIC 7 development, testing and application were obtained for three regions (Pennines, Wales, and Galloway) during the current programme. In April 1998, organic soil and surface water samples were collected at sixty reservoir sites in the high deposition South Pennines region. At a further sixty stream catchments in Wales, previously sampled during the 1995 Welsh Acid Waters Survey, organic soil samples were collected during June 1998. In Galloway surface water sampling began in 1979, and included 49 lochs, which were re-sampled in March/April of 1988, 1993, 1994, 1996, 1997 and 1998. From 1993, 10 additional lochs were included in the survey. In 1997 and 1998 organic soil samples were collected from moorland and forested areas within the 59 catchments. Organic soil C and N content for the Pennine and Galloway samples were analysed at MLURI, and for the Welsh samples at CEH Merlewood. Data were then used to calculate catchment C/N ratios through a spatial weighting procedure. Pennine water samples were analysed at CEH Wallingford, and the Galloway loch samples were analysed at MLURI for a full set of chemical determinands.

Surface water data for the South Pennines (Table 1.4.1) show that this region is among the most acidified in the UK, with almost half of all sampled sites having a negative ANC, extremely high excess or non-marine sulphate ( $xSO_4$ ) concentrations and a high proportion of N inputs transferred to runoff.  $NH_4^+$  comprises a significant proportion of the total N export for a number of high elevation peat catchments. The results of the South Pennine reservoir survey, together with long-term data obtained from local water companies, have been described in Evans *et al.* (2000) and Evans and Jenkins (2000).

Table 1.4.1. Summary data for sixty sampled reservoirs, South Pennines Survey

	pH	ANC μeq/l	NO <sub>3</sub> μeq/l	NH <sub>4</sub> μeq/l	xSO <sub>4</sub> μeq/l	Ca μeq/l	DOC mg/l	NO <sub>3</sub> /xSO <sub>4</sub>
Minimum	3.96	-152	16	0.7	104	23	1.2	4%
25th Percentile	4.38	-55	33	2.2	171	106	3.5	17%
<b>MEDIAN</b>	<b>5.27</b>	<b>13</b>	<b>41</b>	<b>4.0</b>	<b>222</b>	<b>152</b>	<b>4.9</b>	<b>22%</b>
75th Percentile	6.11	64	54	6.3	270	218	5.9	27%
Maximum	7.12	220	97	32.0	402	332	9.8	48%

### 1.4.2. Testing of empirical C/N relationships

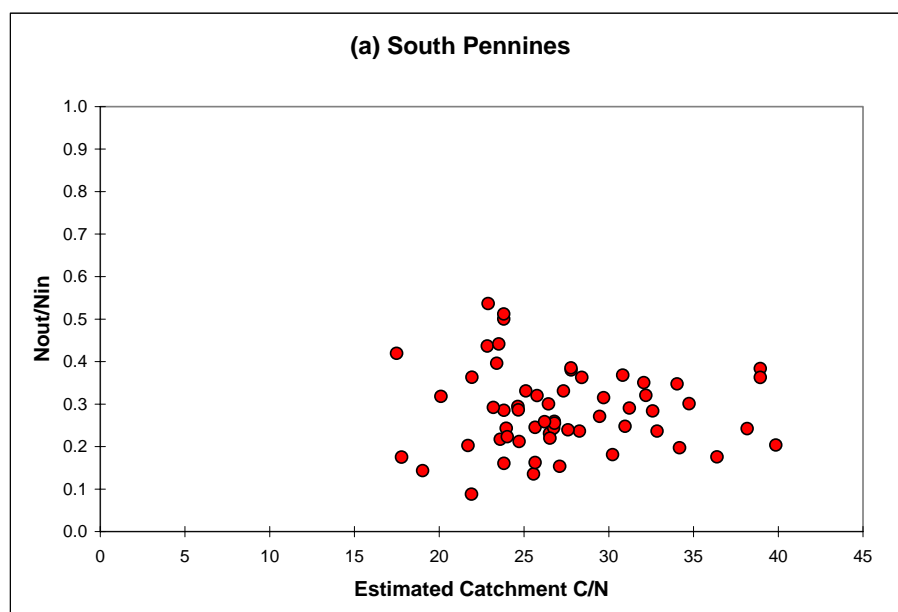
The key conceptual basis for the MAGIC 7 simulation of nitrogen is the empirical relationship between soil water N leaching and the C/N ratio of the organic soil obtained by Gundersen *et al.* (1998) (see following section). Gundersen *et al.* observed an inverse relationship between organic horizon C/N ratio and the ratio of

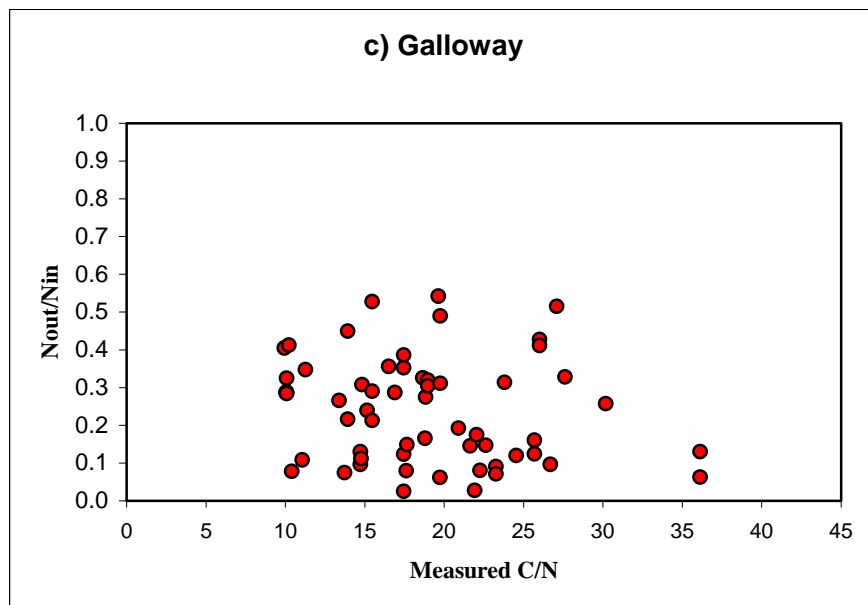
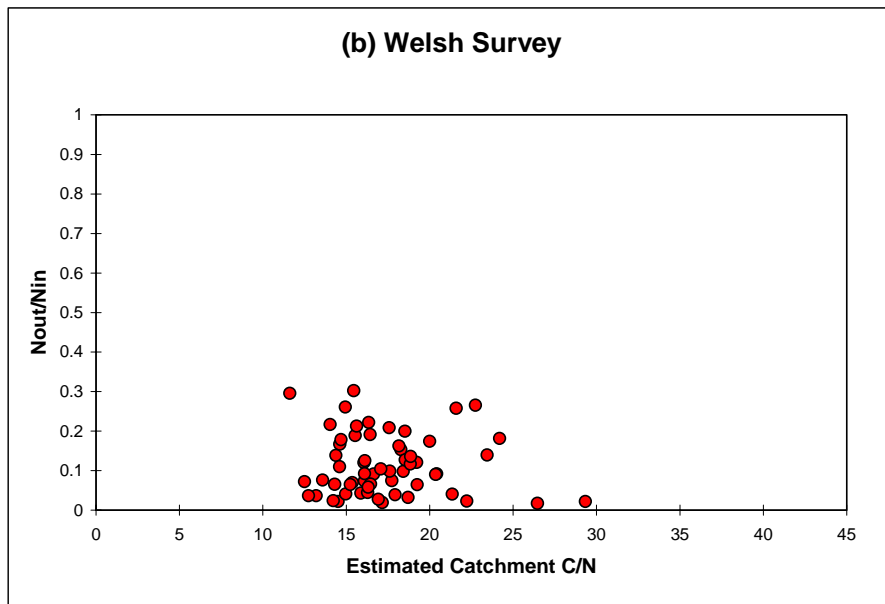
N leaching and N deposition ( $N_{OUT}/N_{IN}$ ) for a set of forested soil plots across Europe. In applying this empirical relationship to model stream N concentrations in the UK, it is assumed (i) that a similar relationship controls N leaching from UK upland soils in general (including moorlands); (ii) that this relationship can be extrapolated from soil plot to catchment scale; and (iii) that organic pools, and their C/N ratio, can be adequately quantified at the catchment scale.

To test these assumptions, estimates of catchment C/N for sites in the South Pennines, Wales and Galloway were compared to estimates of  $N_{OUT}/N_{IN}$  based on measured surface water nitrate ( $NO_3^-$ ), runoff estimates based on CEH 1km interpolated rainfall and evapotranspiration, and UK gridded  $NO_x$  and  $NH_x$  deposition. In practice, variations in  $N_{OUT}/N_{IN}$  within a region were a function primarily of  $NO_3^-$  concentrations. Results (Figure 1.4.1) suggest that, on a regional scale, it is difficult to detect the expected relationship between C/N and  $N_{OUT}/N_{IN}$ . It appears that, although the highest rates of N leaching in both regions do occur at lower C/N values, there is a high degree of scatter in leaching rates at any given C/N, and little evidence of an underlying inverse relationship.

A comparison of C and N measurements for individual soil samples (Figure 1.4.2), including samples collected at the Welsh UKAWMN sites and in the Lake District, show evidence of systematic differences in organic horizon composition between regions. In particular, data indicate that soil %N is consistently lower at a given %C in the Pennines, compared to other regions. Given that deposition and surface water N fluxes are much higher in this region, soils would be expected to show greater N enrichment in this region, and this result is surprising since it suggests the opposite. A possible explanation for this apparent contradiction is that much of the organic matter included in the samples collected is not actively involved in biological cycling, and the C and N content of this inactive pool does not therefore influence N leaching.

Figure 1.4.1. Observed relationships between catchment soil C/N and N input/output fluxes for regional surveys



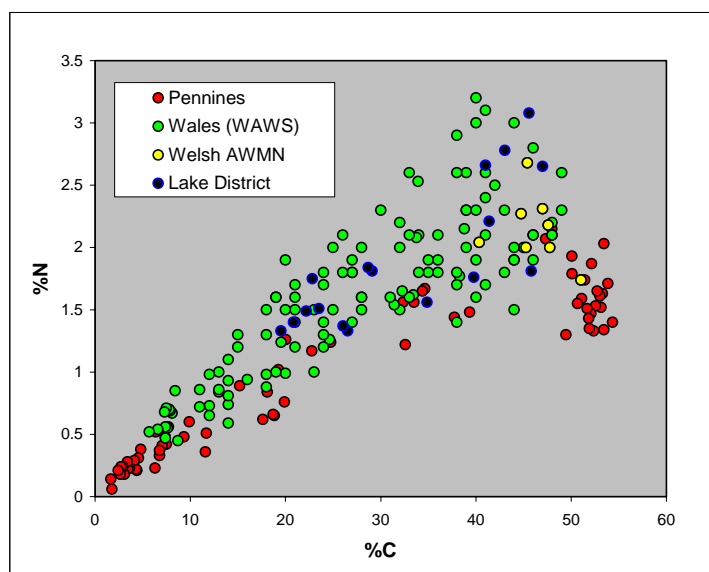


This hypothesis seems plausible given that the majority of samples collected in all regions were either peats, or the peaty horizons of mineral soils, and peats are formed specifically by the accumulation of non-decomposing (i.e. unreactive) organic matter.

The results of these assessments suggest that the extrapolation of a C/N control on N leaching from forest plot to whole-catchment is not straightforward. Although it remains likely that an active organic pool, and the nitrogen enrichment of this pool, plays a major role in determining ecosystem N leakage, two problems can be identified with respect to the modelling of nitrogen processes at the UK catchment scale.



Figure 1.4.2. Nitrogen and Carbon content of individual soil samples

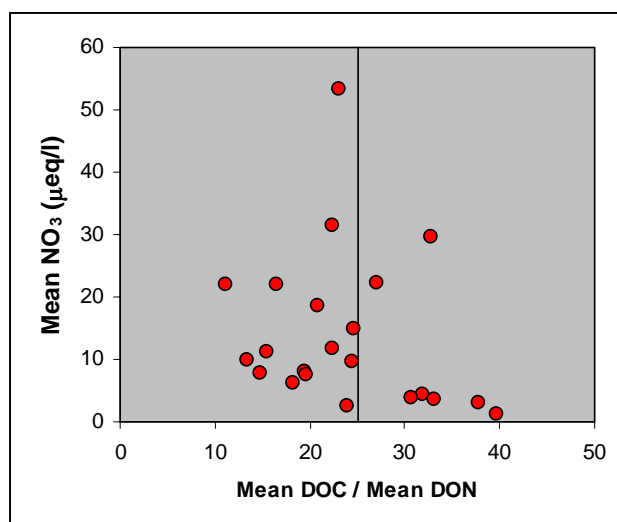


- 1) Data collected from comparable soil types at different locations in Wales and the South Pennines, and within a single catchment at Lochnagar (see following section), demonstrate a high degree of spatial variability in soil C and N content. This clearly raises problems for regional, and even site-specific, model applications in obtaining sufficient C and N data to accurately quantify the average catchment C/N ratio and total C pool at the catchment scale. Although a C/N control may operate on N leaching at the plot scale, therefore, it may be difficult to adequately account for, or quantify, spatial heterogeneity at the whole-catchment scale.
- 2) Current understanding of relationships between C/N and N leaching is largely based on forest soil organic horizons. In general, these horizons are well-defined, and undergo rapid biological cycling, so that the C/N ratio of the whole soil should provide an accurate indicator of ecosystem nitrogen enrichment. In the moorland environments that characterise much of the UK uplands, soils are often peaty and much of the organic matter within them may be chemically inert. As a result, the whole-soil C/N ratio may be a poor predictor of catchment N leaching.

These difficulties with the dynamic modelling of nitrogen have yet to be fully resolved, although several potential solutions may be noted. The problems noted in quantifying the active C and N pools within the soil could potentially be resolved by chemical separation of active (labile) and inactive (refractory) organic matter prior to C and N analysis. Alternatively, 'proxy' measures of soil nitrogen status may be applicable. The N content of vegetation has been shown to reflect levels of deposition and N leaching from forest systems (e.g. Gundersen *et al.*, 1998) and a similar relationship has been observed in UK moorland vegetation (Lee, *in press*). Harriman *et al.* (1998) have also demonstrated an inverse relationship between the DOC/DON ratio in runoff with mean  $\text{NO}_3^-$  concentration, and it is possible that runoff DOC/DON may reflect the 'active' C/N ratio of the catchment. This method also has the

advantage that runoff effectively integrates the C/N signal from the whole catchment, avoiding problems of soil heterogeneity. These advantages are however offset to some extent by the high temporal variability of DOC/DON ratios observed in runoff, requiring regular monitoring of runoff chemistry. A repeat of the analysis of Harriman *et al.* (1998) for sites in the UKAWMN (Figure 1.4.3) shows a somewhat weaker relationship between DOC/DON and  $\text{NO}_3^-$ . However, Harriman *et al.* also noted a threshold DOC/DON of 25 between leaching and non-leaching sites which, with the exception of the Bencrom River (high DOC/DON and high  $\text{NO}_3^-$ ), is apparently also observed within the AWMN dataset.

Figure 1.4.3. Relationship between runoff DOC/DON and  $\text{NO}_3^-$  concentrations, UK Acid Waters Monitoring Network sites.



Finally, problems with catchment heterogeneity may be addressed by an alternative method of calibrating MAGIC to ‘landscape types’, rather than whole catchments (Roberts *et al.*, 1998; Cooper *et al.*, 2000). Runoff concentrations from areas of homogenous soil and vegetation type are simulated based on multiple streamwater samples within a region, and a mixing model used to describe the runoff chemistry resulting from a mixture of landscape types at the catchment scale. Temporal changes in runoff from each landscape type can also be simulated using MAGIC. Since these defined landscape units should have more homogenous C and N characteristics than whole catchments, this approach has potential to provide a more accurate simulation of N leaching within MAGIC 7.

#### 1.4.3. Methodology to determine the carbon and nitrogen pools of an upland catchment

##### Background

The Lochnagar catchment (NO 252 859) is located in NE Scotland on the Eastern edge of the Cairngorm Mountains. It has a total area of 111 ha with an altitudinal range of 790-1150m, most of which is covered by montane vegetation including *Calluna vulgaris*, *Empetrium sp.*, *Vaccinium myrtillus*, *Lycopodium sp.* and some *Sphagnum* species near the loch edge. A particularly prominent feature of this

catchment is a steep north-facing corrie that comprises 31% of the total catchment area. Geologically the catchment is composed of biotite granite. The soils are derived from the Countesswells Association and range from poorly developed Alpine podzols on the steeper slopes to deep peats at lower altitudes surrounding the loch (Table 1.4.2). The estimated soil cover in the Lochnagar catchment is 40%.

*Table 1.4.2. Spatial extent of soil types in the Lochnagar catchment*

<b>Soil Type</b>	<b>km<sup>2</sup></b>	<b>% Area</b>
Rock and lithosols	0.351	31.45
Alpine Podzol	0.366	32.85
Peaty Ranker	0.013	1.21
Peaty Ranker and Boulders	0.057	5.12
Peaty Gley	0.048	4.31
Shallow Peat and Boulders	0.228	20.49
Deep Peat	0.051	4.57

Given the spatial extent of different soil types within the catchment and their individual characteristics, the aim of this study was to calculate the carbon and nitrogen pool sizes at a catchment scale. This provides important input parameters to dynamic models such as MAGIC7 where potential N saturation responses are represented by changes in C/N ratios. Given catchment variability in soil distribution, altitudinal ranges, and characteristics such as rockiness, two methods were utilised to calculate total carbon and nitrogen pools based on point data from a detailed soil survey.

#### Soil sampling Strategy

The sampling protocol was established prior to visiting the Lochnagar catchment by assessing several spatial datasets held at MLURI. This protocol was based on the assumption that the spatial distribution of soil is dependent upon altitude and slope. To ensure complete representation of soil types in the survey, a topographic model of the catchment was developed in a Geographic Information System (GIS). Eight classes were derived from this model based on various combinations of slope and altitude. The resemblance between this model output and the soil map drawn in the field is shown in Figures 1a and 1b. Spatial information from the model was used to highlight areas in the catchment that were considered important to sample.

An intensive soil sampling exercise took place in May 2000. A total of 60 samples were collected from specific areas identified on the soil map and topographic model from the top 10 cm of the organic horizon. Samples were analysed for carbon and nitrogen using the Carlo Erba NA1500 Elemental Analyser. The exact location of each sample was recorded with the aid of a GPS (Global Positioning System).

#### Assessment of observed soil C:N ratios in the Lochnagar catchment

The observed C/N ratios of catchment soils are highly variable and range from 21 to 50. There is no identifiable relationship between C/N ratio and soil type, although previous studies have reported lower C/N ratios in surface horizons of mineral soils

(lithosols, alpine podzols, and rankers) and higher ratios in organic soils from the same catchment.

#### Methodologies to calculate soil carbon and nitrogen pools

Two methods were developed to calculate carbon and nitrogen pools for the Lochnagar catchment. For each method the ‘total’ (entire organic compartment) and ‘surface’ (upper 10cm of the organic horizon) C and N pools were estimated in the catchment.

In the first method C and N data are simply averaged according to the number of samples collected from each soil type identified in the catchment (Figure 1.4.4a). The geometric mean and standard deviation for the different soil types are presented in Table 1.4.3. The greatest deviation in the C/N ratio is apparent for samples collected from organic soils (i.e. shallow and deep peat) (Table 1.4.3). In the absence of field measurements, the bulk density of the organic compartment is estimated ( $150 \text{ kgm}^{-3}$ ), whilst the depth the organic horizons are measured in the field. These data are spatially weighted according to the area of different soil types identified in Figure 1.4.4a. Carbon and nitrogen pools calculated by this methodology are shown in Table 1.4.4.

*Table 1.4.3. Geometric mean C:N data of seven soil types identified in the Lochnagar catchment*

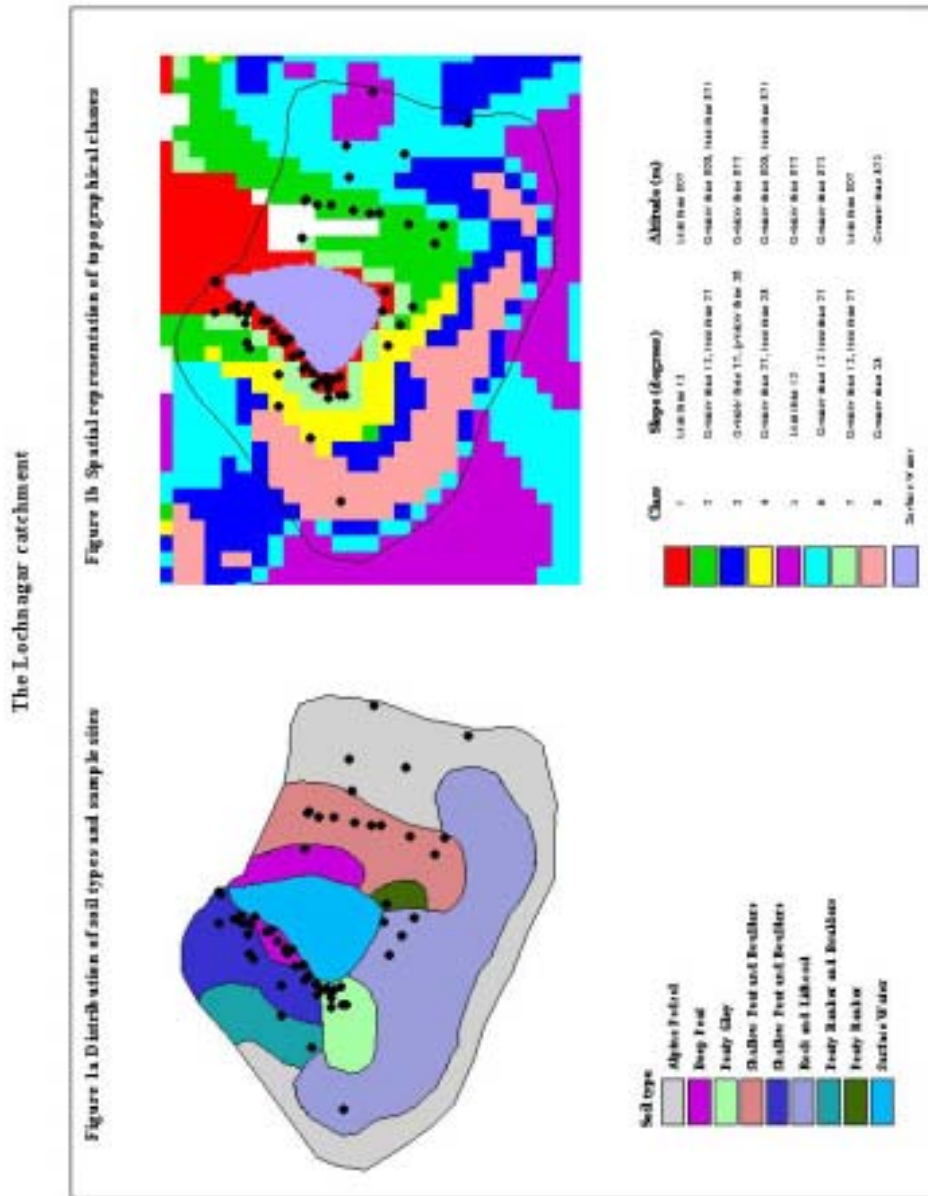
Soil Type	No.	C:N	Standard Deviation
Rock and lithosols	5	34.89	$\pm 2.35$
Alpine Podzol	5	30.71	$\pm 3.42$
Peaty Ranker	1	22.75	$\pm 0.00$
Peaty Ranker and Boulders	4	35.87	$\pm 2.13$
Peaty Gley	8	29.01	$\pm 4.32$
Shallow Peat and Boulders	27	32.49	$\pm 5.99$
Deep Peat	10	33.71	$\pm 9.28$

In the second method, the geometric mean of point C and N data are calculated based on the number of samples occurring within each class of the topographic model (Figure 1.4.4b). C and N pools are calculated using the same soil depth and bulk density information as described in the approach above. C and N pools calculated from this methodology are shown in Table 1.4.4.

#### Assessment of Carbon and Nitrogen pools

Given the range in catchment weighted C and N pools (calculated using different methodologies), the C/N ratios remain relatively constant ( $\sim 36$ ). One might expect a catchment with high C/N ratios to assimilate the majority of inorganic N (Gundersen *et al.*, 1998), but average summer  $\text{NO}_3^-$  concentrations of  $17 \mu\text{eq l}^{-1}$  have been measured in Lochnagar.

Figure 1.4.4. Soil types, topographic classes and sample sites for the Lochnagar catchment



While both methodologies gave rise to similar ‘surface’ organic pools (Table 1.4.4), the calculation of ‘total’ organic pools was greatest when the topographic model was utilised. The large ‘total’ C pool derived from the topographic methodology (967 mol/m<sup>2</sup>) is ‘representative’ of a catchment dominated by thin soils, and extensive areas of exposed rock. To validate this approach the estimated ‘total’ C pool from Lochnagar was compared with measured C pools derived from several European studies e.g. Risdalsheia, Norway (Wright *et al.*, 1993), Gardsjon, Sweden (Kjønaas *et al.*, 1998), and Speuld, Netherlands (Tietema *et al.*, 1998). Measured ‘total’ C pools from these studies are typically large (743, 1879, 1479 mol/m<sup>2</sup> respectively), and comparable to the C pool calculated using the topographical model. In particular, with the exception of catchment vegetation, catchment characteristics at Risdalsheia are similar to those observed at Lochnagar, in that the catchments have extensive areas of exposed rock and are dominated by organic soils. The ‘total’ C pool generated from the topographic model provides a more robust spatial representation of the distribution of organic soil properties in the Lochnagar catchment.

Table 1.4.4. Carbon and nitrogen pools derived from two methodologies

Methodology	C (mol/m <sup>2</sup> )	N (mol/m <sup>2</sup> )	C:N
1a) Soil map-surface organic pool	146	4	36.5
1b) Soil map-total organic pool	579	16	36.2
2a) Topographic model-surface organic pool	142	4	35.5
2b) Topographic model- Total organic pool	967	26	37.2

### Conclusions and Recommendations

This study has proven that large differences of organic soil C/N ratios occur both between and within different soil types at a small spatial scale. It is difficult therefore to assume that the C/N ratio of a single soil sample is representative of an entire catchment.

The total C pool of a catchment is one of the most important parameters controlling both the timing and magnitude of N leaching to surface waters, as predicted by the MAGIC7 model. Other soil parameters required for MAGIC applications such as depth, cation exchange capacity, and base saturation are subject to similar parameter estimation problems and are derived from a physico-chemical weighting classification (Helliwell *et al.*, 1998) developed for the Scottish uplands. It is recommended that a similar approach be utilised for the calculation of carbon and nitrogen pools. The total C pool of any catchment throughout Scotland can be determined with the aid of the topographical model which utilises national databases including a DEM (Digital Elevation Model), and the Soil Map of Scotland (1:250,000). In addition to the spatial analysis of catchment attributes performed with the topographic model, a set of representative soil samples from each topographic unit identified in the catchment is necessary to complete the assessment of C and N pools at catchment scale.

Task1.5: Use all data from appropriate experimental and monitoring sites to continue testing and developing both the mass balance model FAB and the dynamic model MAGIC 7

C.Evans, R.Ferrier, R.Helliwell, and A.Jenkins

1.5 Use all data from appropriate experimental and monitoring sites to continue testing and developing both the mass balance model FAB and the dynamic model MAGIC 7.

### *1.5.1. Development of MAGIC 7*

There were no process-based mechanisms for nitrogen retention in soils in MAGIC5 and first order uptake coefficients were calibrated to represent catchment immobilisation such that input matched output. These uptake coefficients were then assumed to remain constant into the future. This represents a 'best' case of N leakage since catchments that do not currently leak N will not leak in the future as N deposition is reduced. Jenkins *et al.* (1997) modified MAGIC to produce a new coupled S and N model (MAGIC-WAND) to address concerns over the interaction of S and N deposition on soil and surface water acidification. The model had no internal pool of stored N in the soil compartments. All of the nitrogen processes in MAGIC-WAND were rate-based and there was no internal state variable that could change the rates as N accumulated in the simulated systems (no feedback).

The new nitrogen dynamics included in MAGIC7 are based conceptually on an empirical model described by Gundersen *et al.* (1998). MAGIC7 simulates two species of inorganic N in soil and surface waters: nitrate and ammonium. The major processes affecting these ions in soils have been incorporated explicitly or implicitly into the model: atmospheric deposition, nitrification, denitrification, mineralisation, uptake by plants, immobilisation into soil organic matter and export in discharge water. Provision is made in the model for additions of nitrate or ammonium by processes not explicitly represented in the model (i.e. separate source and sink terms for simulation of fertilisation etc.). The inclusion of dynamic equations for nitrogen cycling within the model required the introduction of a soil organic matter compartment for each soil compartment being simulated. As with the acid/base components of MAGIC, the organic matter compartment is aggregated in space and time. The intention, however, is that this compartment be observable and/or interpretable at the plot or catchment scale. The nitrogen and carbon contents of this organic matter compartment are state variables simulated by the model in response to changing inputs or conditions in the soil solution.

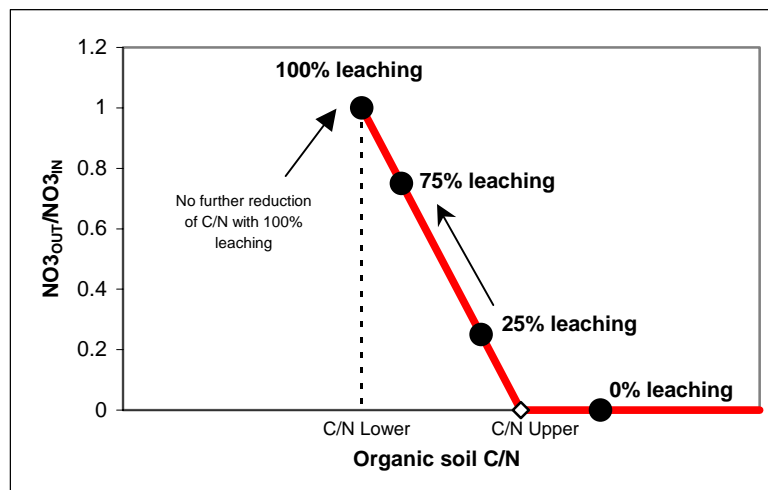
Atmospheric deposition of nitrate and ammonium, and denitrification rates must be specified as inputs in the model. Nitrification (conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ ) is modelled as a first order process and a rate constant must be provided. Plant uptake must be specified as an input and represents the net uptake of nitrogen by the plants (primarily the nitrogen stored in wood and large roots). Mineralisation in the model represents the net release of nitrogen that was formerly bound in organic matter. The mineralisation product is  $\text{NH}_4^+$ . Mineralisation rates depend on carbon decomposition rates and the C/N ratio of the organic matter compartment.

Immobilisation of inorganic N into the soil organic matter is controlled by the C/N ratio of the soil organic compartment (Figure 1.5.1). If the C/N ratio is above an upper threshold value ( $\text{CN}_{\text{UP}}$ ) immobilisation of inorganic N is complete. If the C/N ratio is below a lower threshold value ( $\text{CN}_{\text{LO}}$ ) there is no immobilisation of inorganic N. The



percentage of inorganic N immobilised varies linearly from 100% to 0% as the C/N ratio of the organic matter declines from  $CN_{UP}$  to  $CN_{LO}$ . This empirically based method for estimating immobilisation rates requires that the upper and lower threshold C/N values be calibrated for each site. Separate upper and lower thresholds for nitrate and ammonium are included to allow for preferential immobilisation of one ion over the other. The inorganic N immobilised from soil solution is added to the organic N in the organic matter compartment, lowering the C/N ratio of that compartment. In this manner there is a decline in the C/N ratio of the simulated soil organic compartment as N from deposition is accumulated. As the declining C/N crosses the upper threshold, leaching of inorganic N begins and gradually increases as C/N declines further.

Figure 1.5.1. Theoretical relationship between soil C/N and N leaching in MAGIC 7



The process equations affecting N occur sequentially at each time step. Ammonium and nitrate from deposition and ammonium from mineralisation are added to the soil solution. The current nitrification rate is then calculated and ammonium is removed (and nitrate added) to the soil solution. Next, the net uptake requirement of the plants is satisfied by removing inorganic N from soil solution (ammonium is removed first, followed by nitrate). If the available inorganic N concentration in soil solution is not sufficient to satisfy the plant requirement, the additional N needed is removed from the soil organic matter compartment. If inorganic N remains in soil solution following the plant uptake, immobilisation into the soil organic matter compartment is calculated and the appropriate amounts of nitrate and ammonium are removed from soil solution. Finally, after all biotic demands for inorganic N are satisfied, any nitrate or ammonium remaining in the soil solution is leached from the soil with the soil water drainage.

Time series inputs and outputs of organic C (and the C/N ratios of that organic matter) are required as inputs to the model. An initial value of both C and N in the organic matter compartment is also needed. If the organic inputs and outputs are set to zero for all time in the simulation, the organic C content of the organic matter

compartment will not change. The N content will, however, vary during the simulation as immobilisation and/or mineralisation occurs. In order for this aggregated representation of the N cycle to function properly in the model, the characteristics of the soil organic matter compartment must be properly identified in the field. Generally, the lumped organic matter compartment can be taken to represent the forest floor and upper organic soil horizons of a catchment, and the C content of these layers can be measured or estimated for use in the model. However, if only one soil compartment is included in a model application, the simulated C pool must represent the entire organic matter content of the soil column that is actively involved in N storage.

The highly aggregated approach to modelling N retention/release in soils is analogous to the approach used in MAGIC for modelling base cation exchange in soils. The overall catchment budgets of both types of ions (inorganic N and base cations) are important for simulating acidification responses. The base cation dynamics are controlled by a capacity factor (the total cation exchange capacity of the soils) and by an intensity factor (current base saturation of the soils). Both factors are crucial in determining the future (or past) responses of catchment soils to acidic deposition. The intensity factor determines the cation exchange and buffering that can occur at any time (low base saturation provides little base cation exchange, etc.). The capacity factor determines the length of time it takes for the intensity factor to change (number of years of leaching to produce lower base saturation).

The aggregated organic matter compartment functions similarly for N retention in that there are both capacity and intensity factors in the conceptual formulation. The intensity factor is the C/N ratio of the organic matter pool at any time (retention is complete for high C/N values etc). However, retention of N results in a lower C/N of the organic matter and as C/N declines, N saturation can begin to occur. The speed with which C/N changes is controlled by the capacity factor (the total pool of organic C available to immobilise nitrogen in the soils). The scales of aggregation and conceptual interpretation are essentially the same in MAGIC7 for the capacity and intensity factors of both the base cation exchange processes and N retention processes.

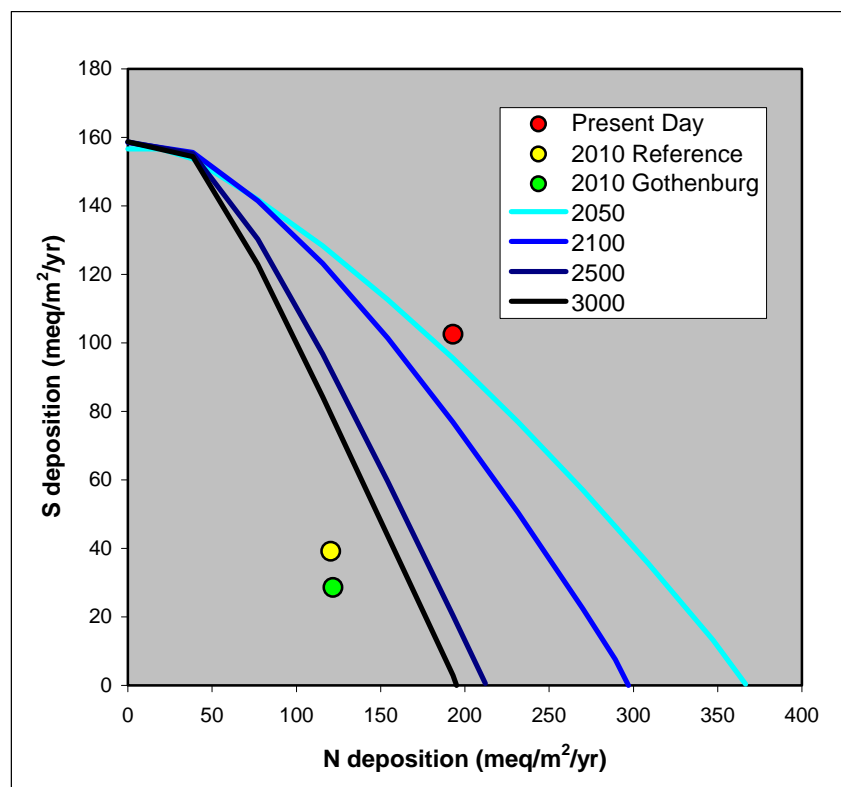
### ***1.5.2. Simulating critical loads for sulphur and nitrogen using MAGIC 7***

The key advantage of dynamic models, relative to the steady-state approaches used to determine critical loads, is their ability to simulate conditions at a given time. However, dynamic models have generally been used in a 'reactive' mode, in order to test the long-term effects of a defined emission scenario, rather than as tools in the initial development of emissions protocols (such as critical loads). To test the potential of MAGIC 7 for use in a more 'pro-active role', an application of MAGIC to the Afon Gwy, incorporating FAB-based estimates of immobilisation and denitrification (see following section) was used as the basis for the calculation of 'target loads' for S and N deposition. Target loads differ from critical loads in the inclusion of a specific target date by which the required chemistry threshold (e.g. ANC = 0) should be achieved. In the case of nitrogen, where time taken to reach

condition of total N saturation assumed by FAB may be very long, the conditions expected within shorter (e.g. 50 year) timescales may be of greater relevance in the development of emissions strategies.

For the Gwy, S and N target load functions were calculated for a threshold surface water ANC of 0 in 2050, 2100, 2500 and 3000 (Figure 1.5.2). Like critical load functions these show the combinations of S and N deposition with which zero ANC may be achieved at the target date, but unlike critical load functions are non-linear due to the time-dependence of N leaching. Interestingly, these results suggest that, while all four target dates require some deposition reduction relative to present day, the decreases required to obtain zero ANC by 2050 are much smaller than those required for longer periods; this is a reflection of extended period of time required to change soil C/N, and therefore to increase N leaching from this site. Future deposition predictions for both the Reference (HARM Second Sulphur Protocol emissions reductions only) and Gothenburg protocols (HARM 11.5 for S and NO<sub>x</sub>, FRAME for NH<sub>y</sub>, scaled to 1997 CEH deposition data – see NEG TAP Report) fall below the year 3000 target load function (which is approximately equivalent to the FAB critical load function), and will hence maintain ANC > 0 over the long-term. However it appears that a positive ANC could be achieved, if not permanently, then at least on a timescale of 100 years or more, with substantially smaller deposition reductions at this site.

Figure 1.5.2. MAGIC 7 Target Load Functions for the Afon Gwy



The significance of this simulation for the 'steady state' water chemistry concept used for critical load estimation is discussed in the following section. In general, the use of MAGIC 7 to derive target load functions for S and N deposition represents a significant step forward, whereby dynamic models may be used to aid the development, rather than simply assess the consequences, of emissions controls. An automated procedure for target load estimation is currently being incorporated in MAGIC 7, providing potential for this technique to be applied on a more extensive basis in future.

Task 1.6.1: Run the revised FAB model at all CLAG national mapping data set sites to map and re-assess critical load exceedance for total acidity for the UK

C.Curtis

### 1.6.1 Run the revised FAB model at all CLAG national mapping dataset sites to map and re-assess critical load exceedance for total acidity for the UK

#### ***FAB model revisions and new mapping***

The major revisions to the FAB national mapping dataset during the current CLAM contract period have been:

1. Incorporation of sites with missing soils data to complete the GB dataset (1445 site dataset increased to 1470 sites).
2. Omission of  $BC_{dep}$  data from critical load calculations and from exceedance calculation – with no net change in exceedance values (Max Posch, pers. comm.).
3. Inclusion of Northern Ireland for the first time (FAB modelling work done under separate contract with EHS, DOE NI).
4. Change to long-term mean runoff data (instead of previously used 1992-94 mean data) for consistency with soils critical loads work; used 1km catchment weighted data (1941-70) for all sites except 2 northern-most sites in Shetlands (CZHP51, CZHP61 – both not covered by longterm dataset) for which 1km weighted 1992-94 data were used.
5. Use of both  $ANC_{crit} = 0 \mu eq l^{-1}$  (previously used in UK) and  $ANC_{crit} = 20 \mu eq l^{-1}$  (widely used in Scandinavia) for comparison.
6. Screening of the mapping dataset to remove sites with evidence of non-atmospheric sources of pollution or analytical problems which could cause erroneous critical load exceedances (ion balance error >10%, non-marine sulphate > 500  $\mu eq l^{-1}$ , Na/Cl ratio <0.4); 337 sites removed from UK mapping dataset, mostly in the English lowlands.

With the inclusion of previously omitted sites in Great Britain, plus new sites (140) covering Northern Ireland for the first time with the FAB model, these maps are the first representation the full screened UK FAB mapping dataset (n=1273).

Contrary to the recommended method in the UNECE Mapping Manual, we have continued to use fixed rates of denitrification, calculated as a catchment weighted value determined by soil type, since the experimental work on denitrification rates in Section 1.3 confirmed that denitrification rates in the British uplands are much lower than those suggested by the recommended method (10%, increasing to 80% for peats, weighted by soil type).

Critical loads for total acidity have been calculated for both  $ANC_{crit} = 0 \mu eq l^{-1}$  and  $ANC_{crit} = 20 \mu eq l^{-1}$  using the SSWC model (Figs. 1.6.1 a-b). Exceedances of these critical loads have been calculated for the most recent national deposition dataset (mean 1995-97 values; Figs. 1.6.2 a-b) and for a revised 2010 (post Gothenburg Protocol) deposition dataset which uses reduced N deposition generated by the FRAME model in conjunction with HARM (version 11.5) modelled S and  $NO_x$  deposition (see NEG TAP Report; Figs. 1.6.3 a-b).

Similarly, the constraints on the critical load function using the FAB model for sulphur deposition ( $CL_{maxS}$ ) and nitrogen ( $CL_{maxN}$ ) have been calculated using both  $ANC_{crit} = 0 \mu eq l^{-1}$  and  $ANC_{crit} = 20 \mu eq l^{-1}$  (Figs. 1.6.4 a-b and 1.6.5 a-b).

Exceedances of FAB critical loads have been expressed in two ways. First, exceedance is calculated as the flux of acidity by which the critical load is exceeded (Figs. 1.6.6-1.6.7). This method gives an absolute measure of exceedance, but does not indicate whether S or N deposition is causing exceedance, and cannot therefore be used alone to determine the necessary emissions reductions. An alternative method is to express exceedance in terms of the options for reducing either S or N deposition, or some combination of the two, in order to achieve non-exceedance (Figs. 1.6.8-1.6.9). This method does not indicate the magnitude of exceedance, but shows which pollutants are causing it. With the FAB model, the maps have limited value when considered alone; for scenario testing, levels of both S and N deposition must be defined and run through the model together to determine the effect on critical load exceedance.

The effects of the choice of ANCcrit and the level of deposition (contemporary or 2010) in terms of the number of sites at which exceedance occurs and the acid species (S or N) requiring reduction, are summarised in Tables 1.6.1 a-b below.

Note that while screening of the mapping dataset has reduced the absolute number of mapping sites (from 1610 to 1273), the majority of sites removed were non-exceeded, lowland sites. The percentage of exceeded sites has therefore increased, but these figures only refer to the proportion of the mapping dataset and not to the whole lake populations in these regions.

In terms of the total numbers of mapping sites within the UK which are exceeded for a given deposition dataset, the figures vary depending on the static model (SSWC or FAB) and the critical ANC chosen. Table 1.6.2 summarises the results of SSWC and FAB model applications using both ANCcrit = 0  $\mu\text{eq l}^{-1}$  and ANCcrit = 20  $\mu\text{eq l}^{-1}$  for the two sets of deposition data described above. The SSWC model assumes that current nitrate leaching is at steady-state with N deposition and therefore represents the best case scenario with respect to N leaching. The mass balance used in the FAB model assumes that a large proportion of N deposition will ultimately leach (along with H<sup>+</sup>) and decrease ANC, even where current measured concentrations in surface waters are very low. In this respect the FAB model exceedances represent a worst case scenario. Similarly, the use of ANCcrit = 0  $\mu\text{eq l}^{-1}$  assumes that a greater depression of ANC is acceptable (best case) than if ANCcrit = 20  $\mu\text{eq l}^{-1}$  is used (worse case).

**Table 1.6.1a: FAB modelled deposition reduction requirements (number of sites) from mean 1995-97 levels**

Class	Species	ANCcrit=0 µeq/l					ANCcrit=20 µeq/l				
		ENG	WAL	SCO	NI	UK	ENG	WAL	SCO	NI	UK
0	Not exceeded	155	75	518	119	867	155	72	450	118	795
1	S only	0	0	5	0	5	0	0	10	0	10
2	S then S or N	6	2	51	1	60	2	1	79	1	83
3	S and N	89	30	31	7	157	97	38	101	9	245
4	N then S or N	5	2	2	2	11	5	7	4	1	17
5	Either S or N	31	34	101	7	173	27	25	64	7	123
<i>No. Sites:</i>		286	143	708	136	1273	286	143	708	136	1273
<b>Total exceeded:</b>		<b>131</b>	<b>68</b>	<b>190</b>	<b>17</b>	<b>406</b>	<b>131</b>	<b>71</b>	<b>258</b>	<b>18</b>	<b>478</b>
<b>% exceeded:</b>		<b>45.8</b>	<b>47.6</b>	<b>26.8</b>	<b>12.5</b>	<b>31.9</b>	<b>45.8</b>	<b>49.7</b>	<b>36.4</b>	<b>13.2</b>	<b>37.5</b>

**Table 1.6.1b: FAB modelled deposition reduction requirements (number of sites) beyond 2010 (post Gothenburg protocol) levels**

Class	Species	ANCcrit=0 µeq/l					ANCcrit=20 µeq/l				
		ENG	WAL	SCO	NI	UK	ENG	WAL	SCO	NI	UK
0	Not exceeded	180	92	602	126	1000	172	82	515	123	892
1	S only	0	0	1	0	1	0	0	5	0	5
2	S then S or N	2	0	5	0	7	1	0	11	0	12
3	S and N	54	4	15	2	75	73	21	81	6	181
4	N then S or N	38	29	22	6	95	25	24	31	4	84
5	Either S or N	12	18	63	2	95	15	16	65	3	99
<i>No. Sites:</i>		286	143	708	136	1273	286	143	708	136	1273
<b>Total exceeded:</b>		<b>106</b>	<b>51</b>	<b>106</b>	<b>10</b>	<b>273</b>	<b>114</b>	<b>61</b>	<b>193</b>	<b>13</b>	<b>381</b>
<b>% exceeded:</b>		<b>37.1</b>	<b>35.7</b>	<b>15.0</b>	<b>7.4</b>	<b>21.4</b>	<b>39.9</b>	<b>42.7</b>	<b>27.3</b>	<b>9.6</b>	<b>29.9</b>

**Table 1.6.2: Number and proportion of UK freshwater mapping sites showing critical load exceedance according to the SSWC and FAB models, for two values of ANC<sub>crit</sub> and two deposition scenarios.**

Model	Mean 1995-95 deposition				2010 (post Gothenburg) deposition			
	SSWC	SSWC	FAB	FAB	SSWC	SSWC	FAB	FAB
	0	20	0	20	0	20	0	20
England	103	110	131	131	64	83	106	114
Wales	38	45	68	71	12	29	51	61
Scotland	117	207	190	258	38	112	106	193
N.Ireland	9	11	17	18	3	8	10	13
<b>UK</b>	<b>267</b>	<b>373</b>	<b>406</b>	<b>478</b>	<b>117</b>	<b>232</b>	<b>273</b>	<b>381</b>
<b>%</b>	<b>16.6</b>	<b>23.2</b>	<b>25.2</b>	<b>29.7</b>	<b>7.3</b>	<b>14.5</b>	<b>17.1</b>	<b>23.8</b>



Figure 1.6.1.a SSWC critical load for ANC = 0 ueq/l.

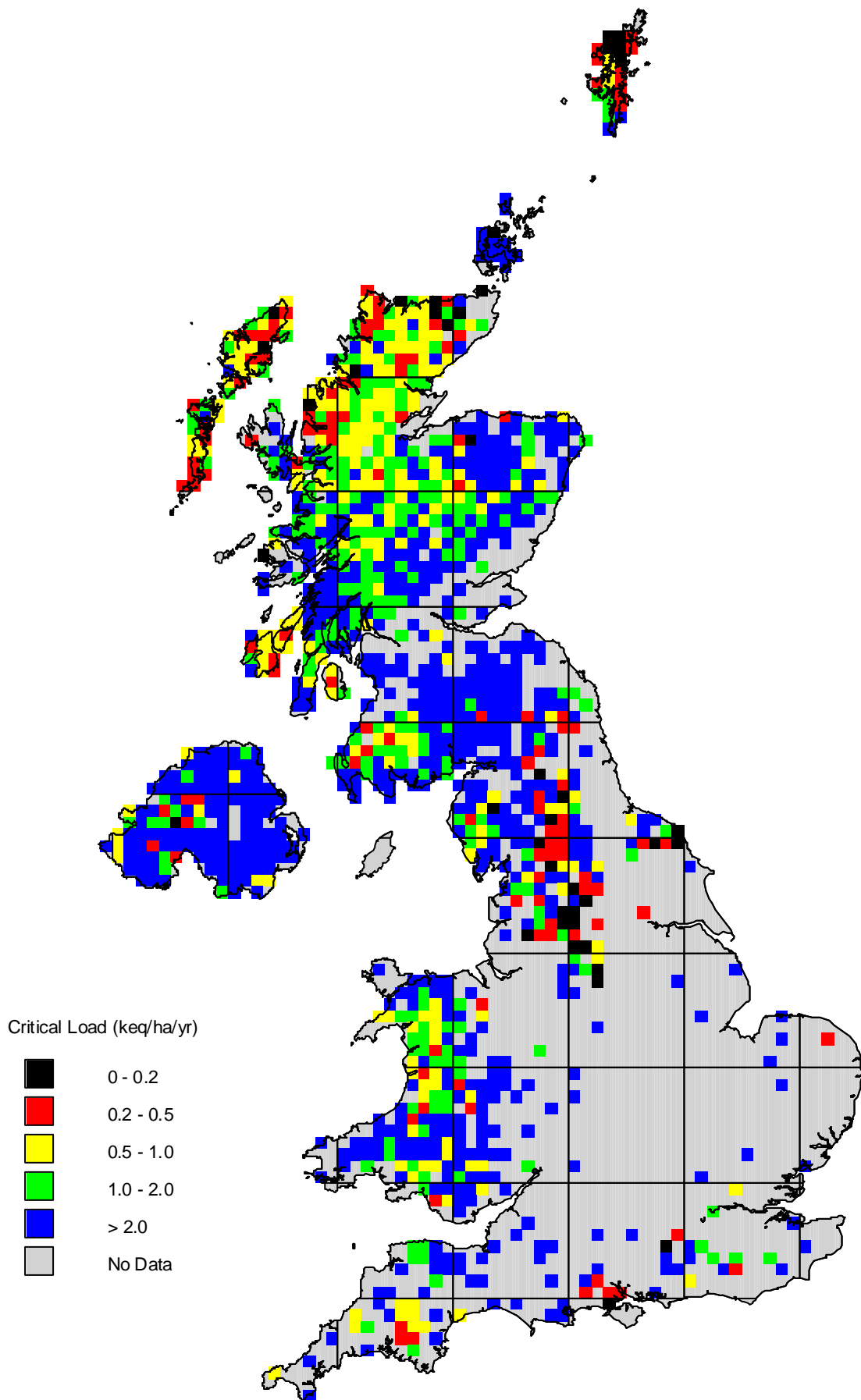


Figure 1.6.1.b SSWC critical load for ANC = 20 ueq/l.

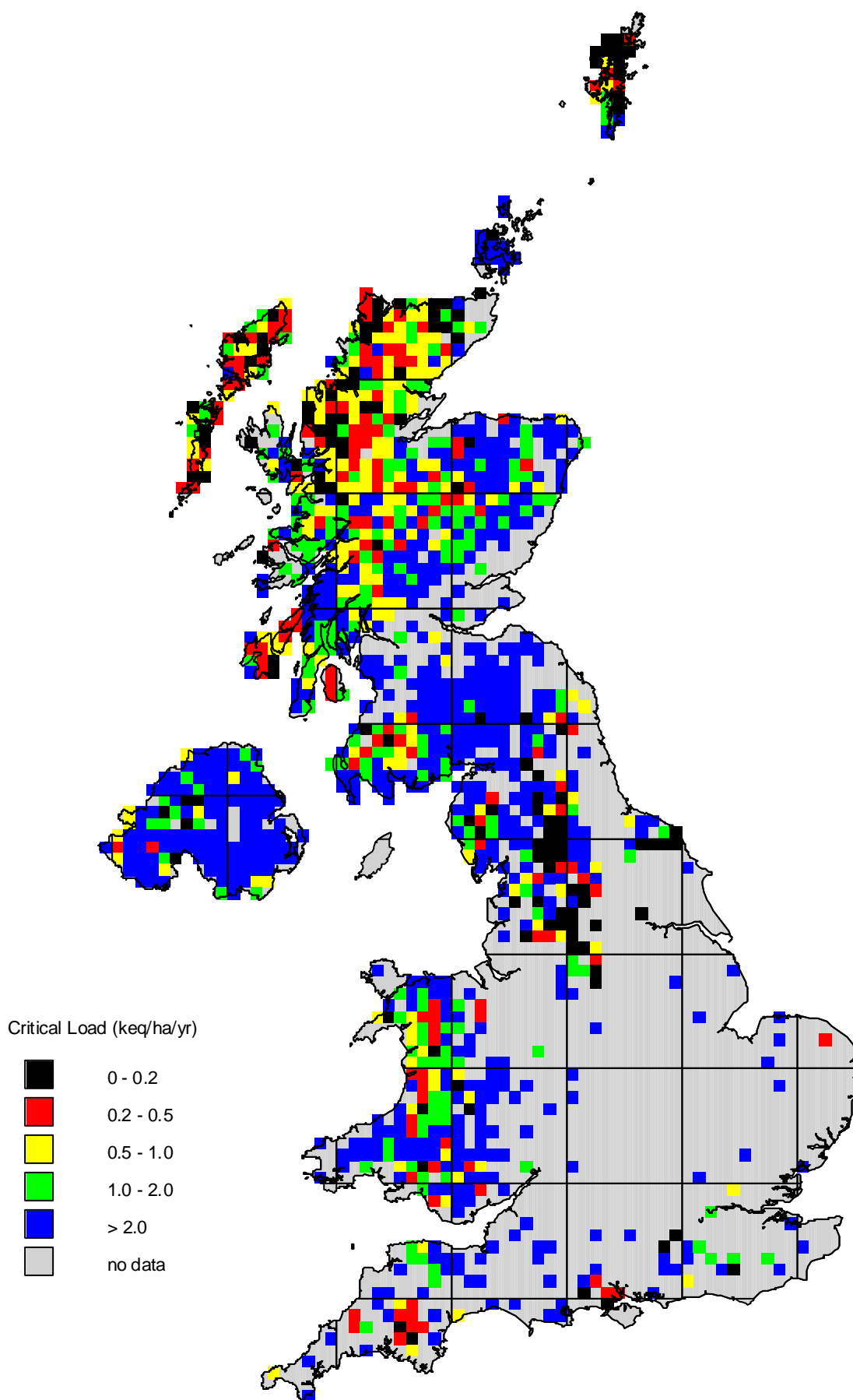


Figure 1.6.2.a SSWC exceedance under Current (95/97) scenario for ANCcrit = 0 ueq/l.

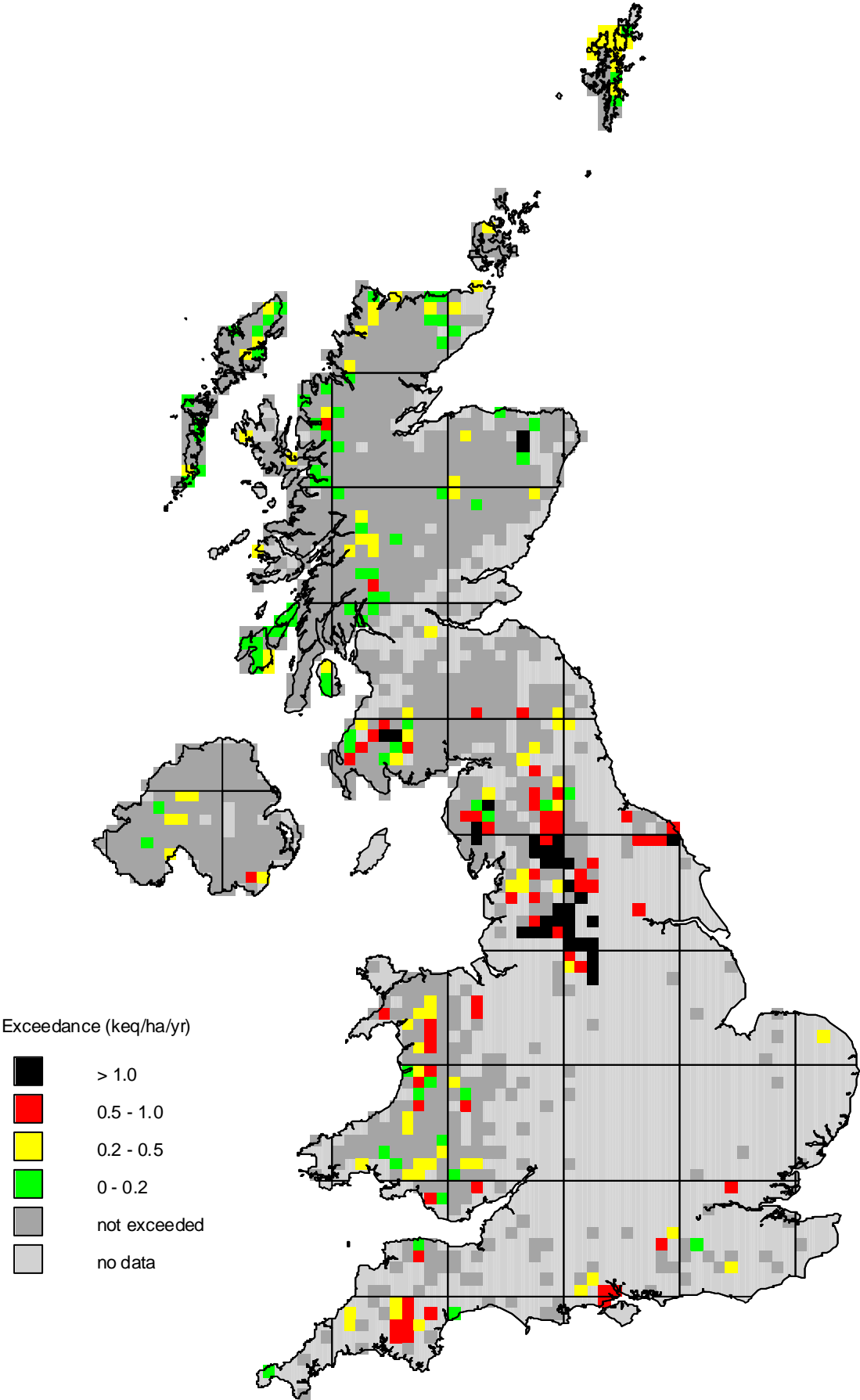


Figure 1.6.2.b SSWC exceedance under Current (95/97) scenario for ANCcrit = 20 ueq/l.

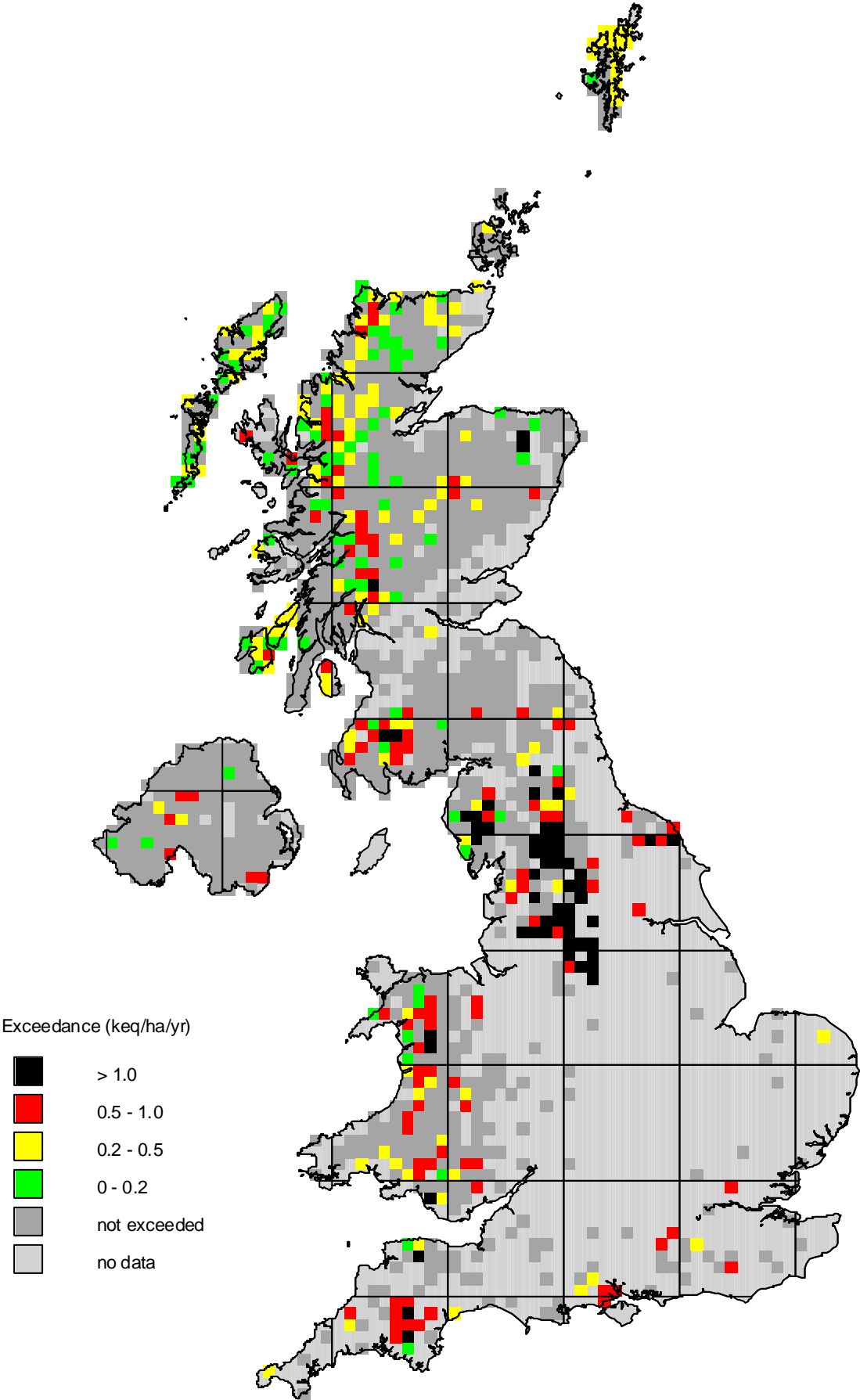


Figure 1.6.3.a SSWC exceedance under Gothenburg (2010) scenario for ANCcrit = 0 ueq/l.

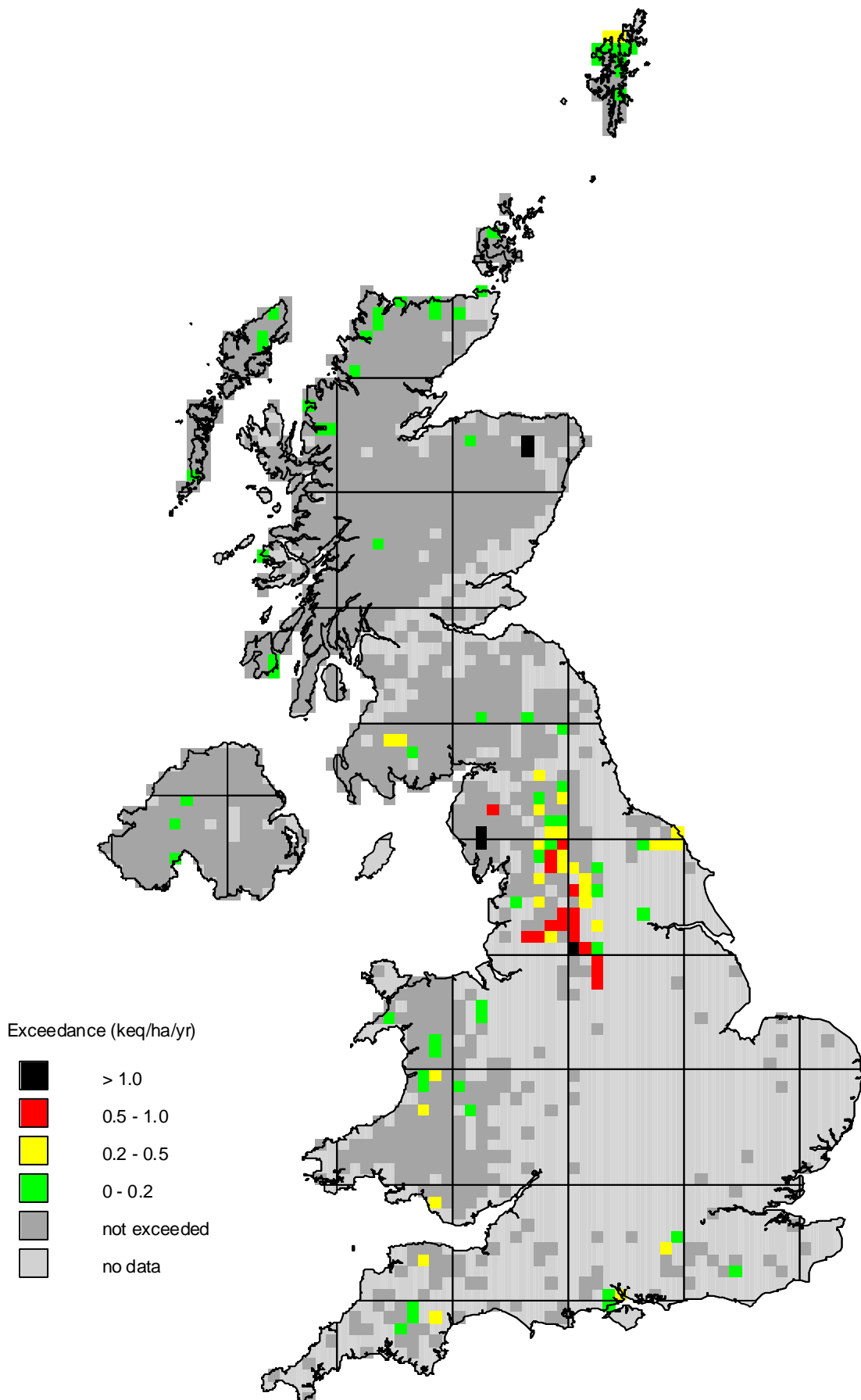


Figure 1.6.3.b SSWC exceedance under Gothenburg (2010) scenario for ANCcrit = 20 ueq/l.

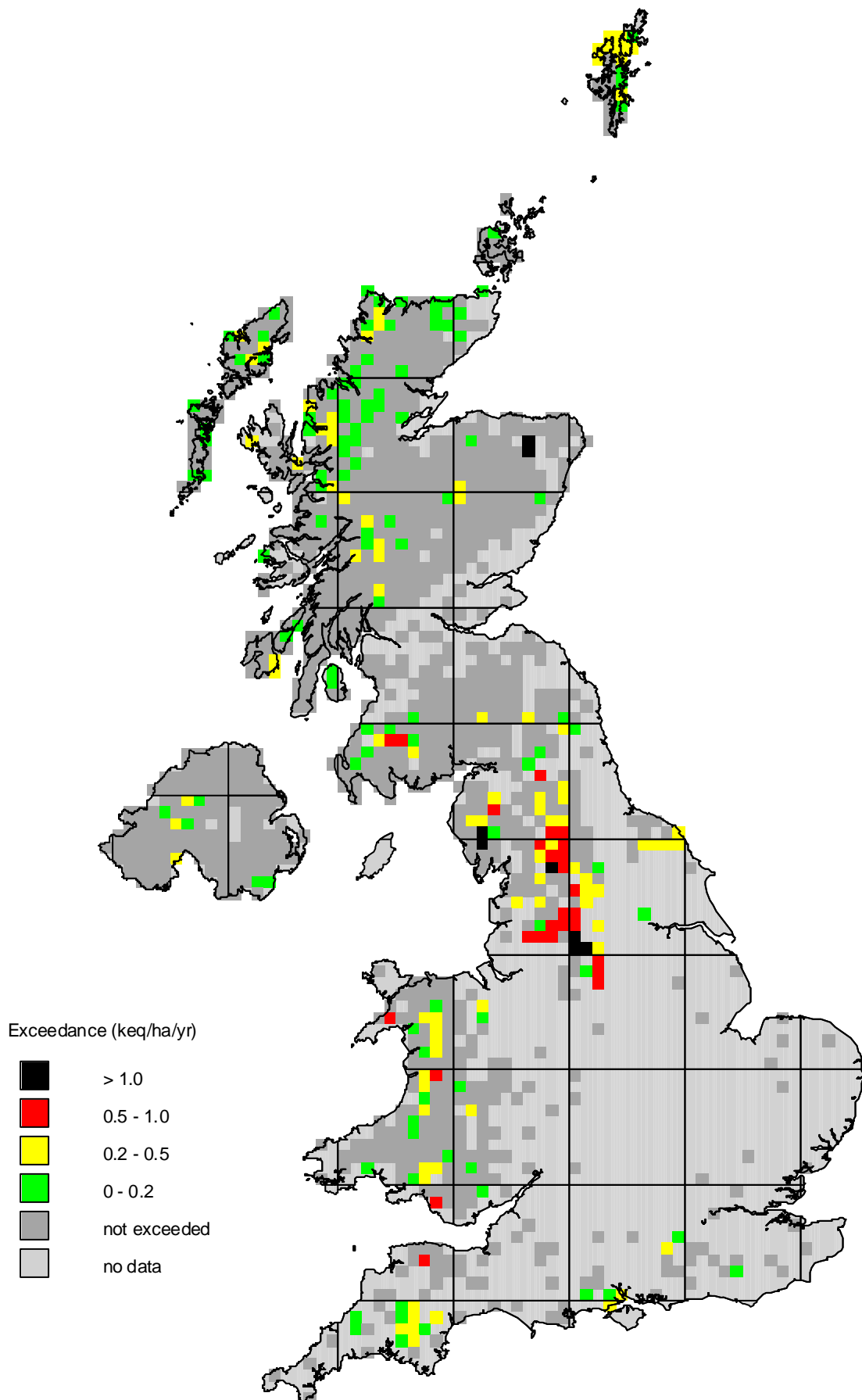


Figure 1.6.4.a FAB modelled CLmaxS for ANC = 0 ueq/l.

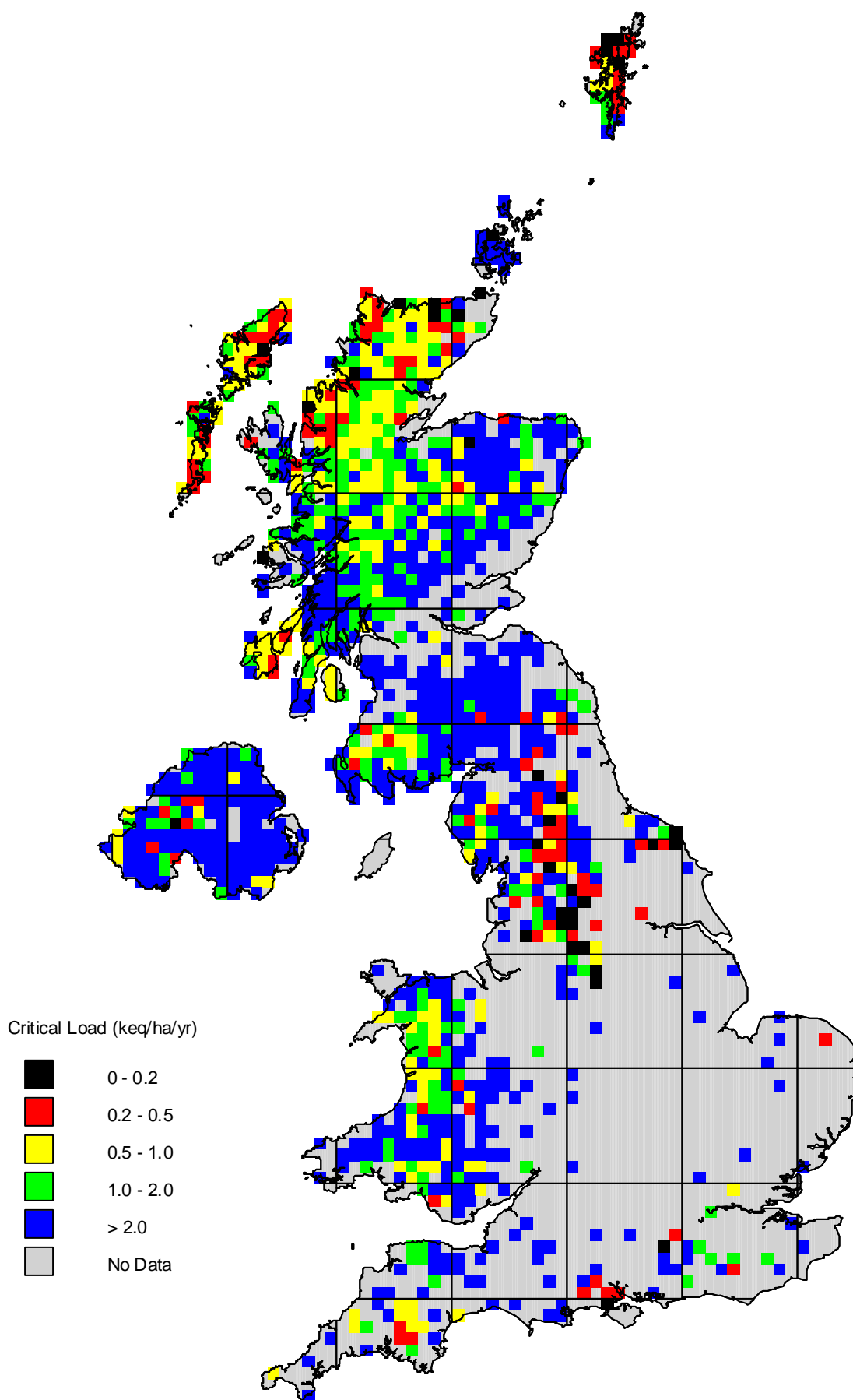


Figure 1.6.4.b FAB modelled CLmaxS for ANC = 20 ueq/l.

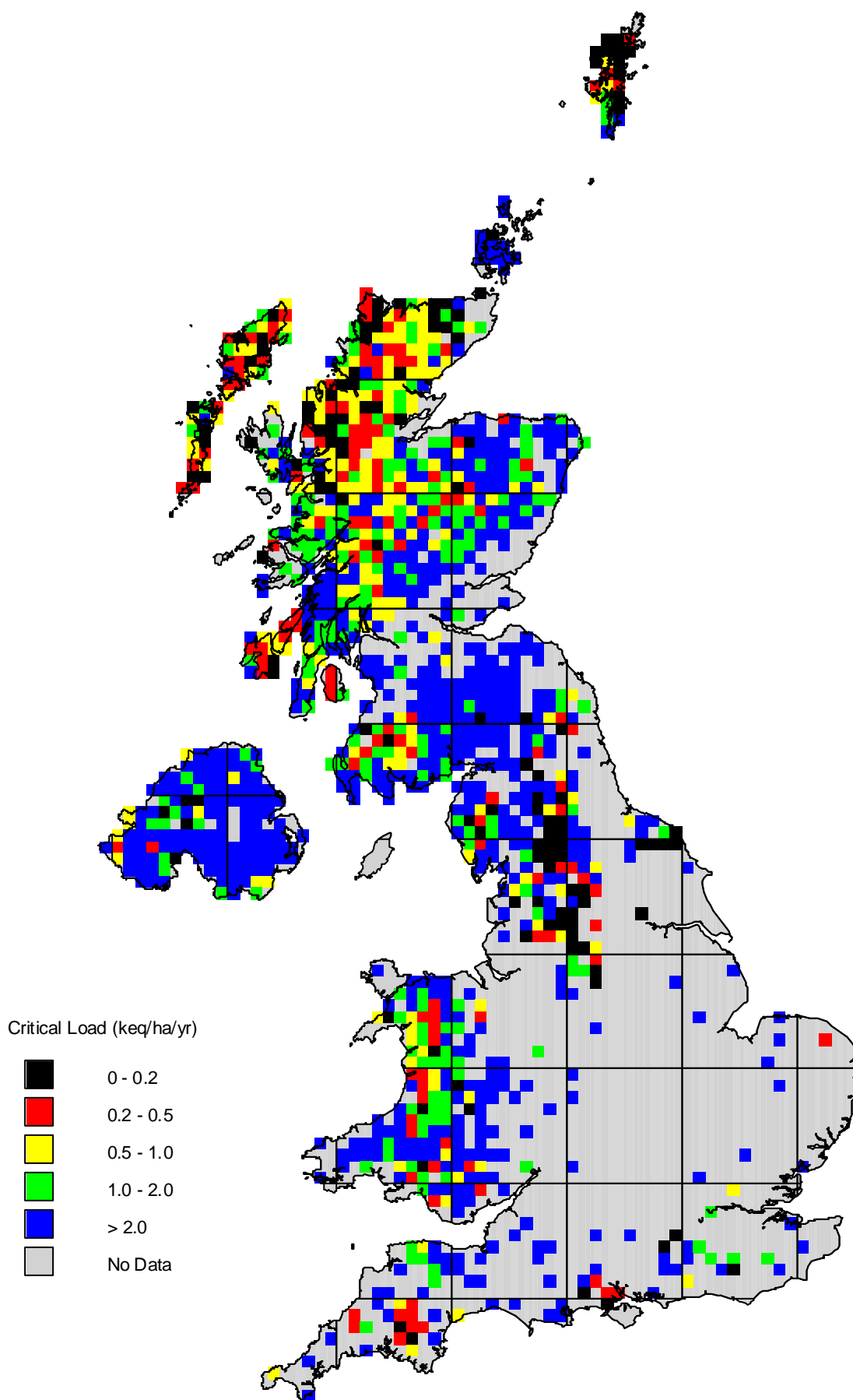




Figure 1.6.5.a FAB modelled CLmaxN for ANC = 0 ueq/l.

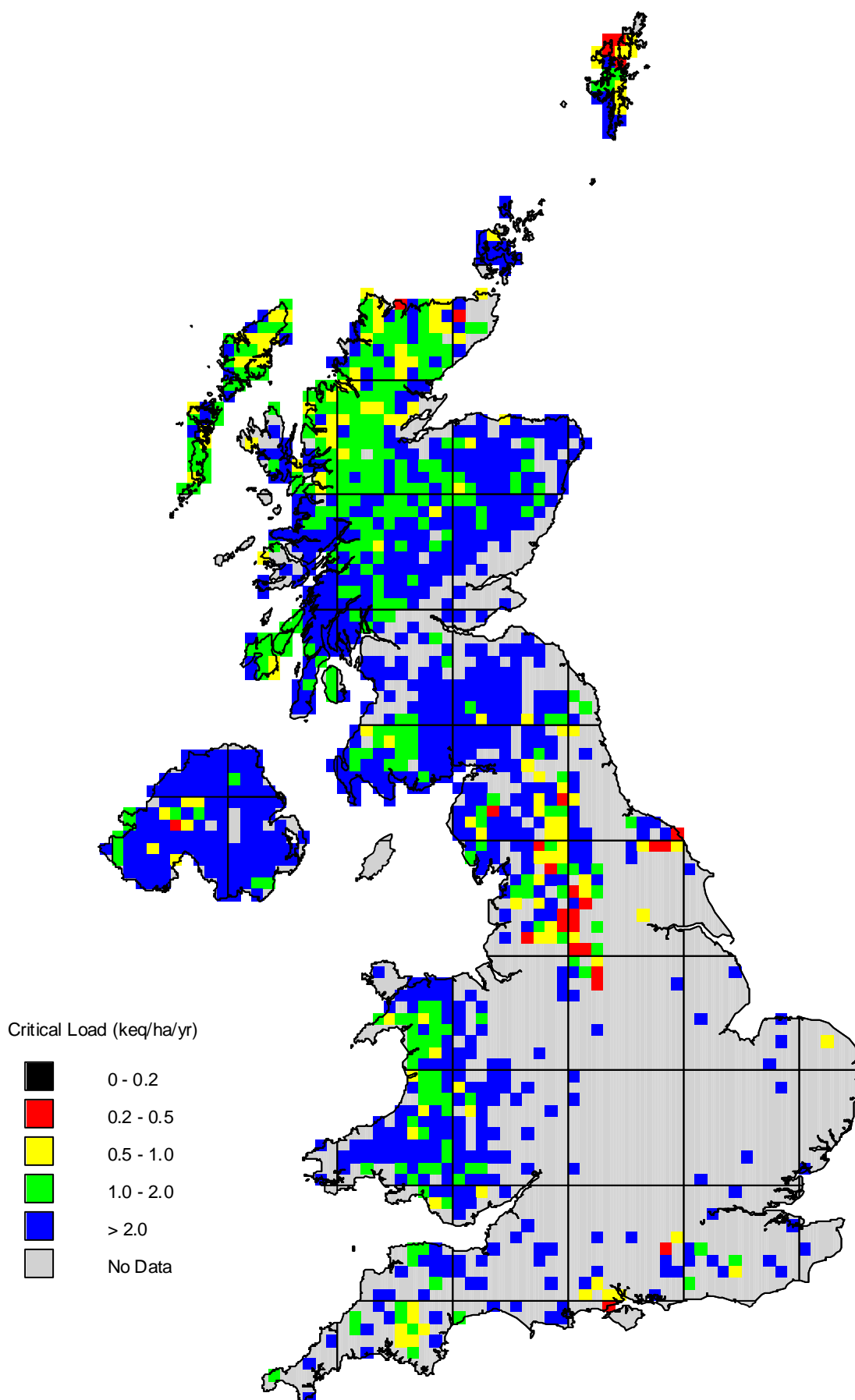


Figure 1.6.5.b FAB modelled CLmaxN for ANC = 20 ueq/l.

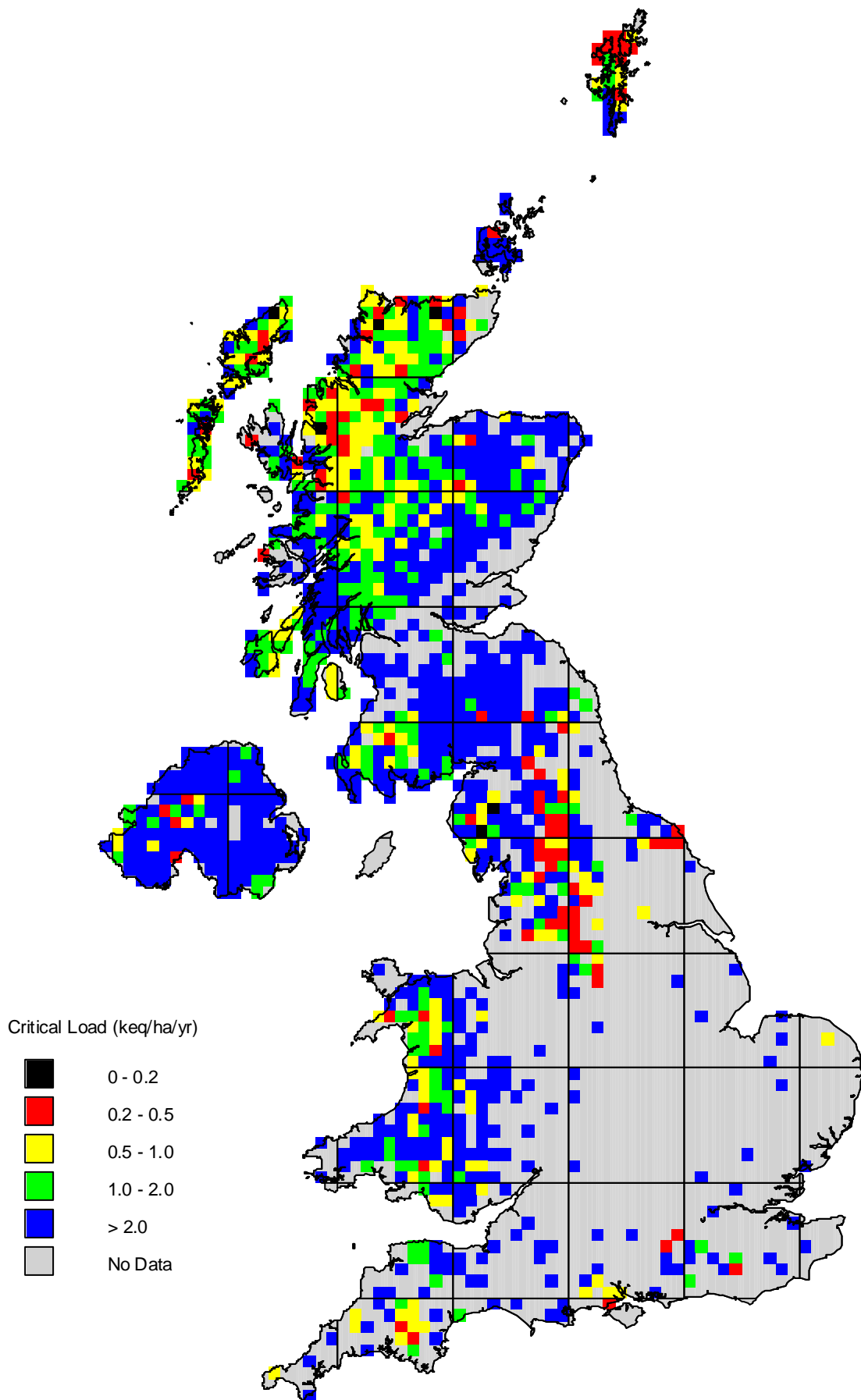


Figure 1.6.6.a FAB exceedance under Current (95/97) scenario for ANCcrit = 0 ueq/l.

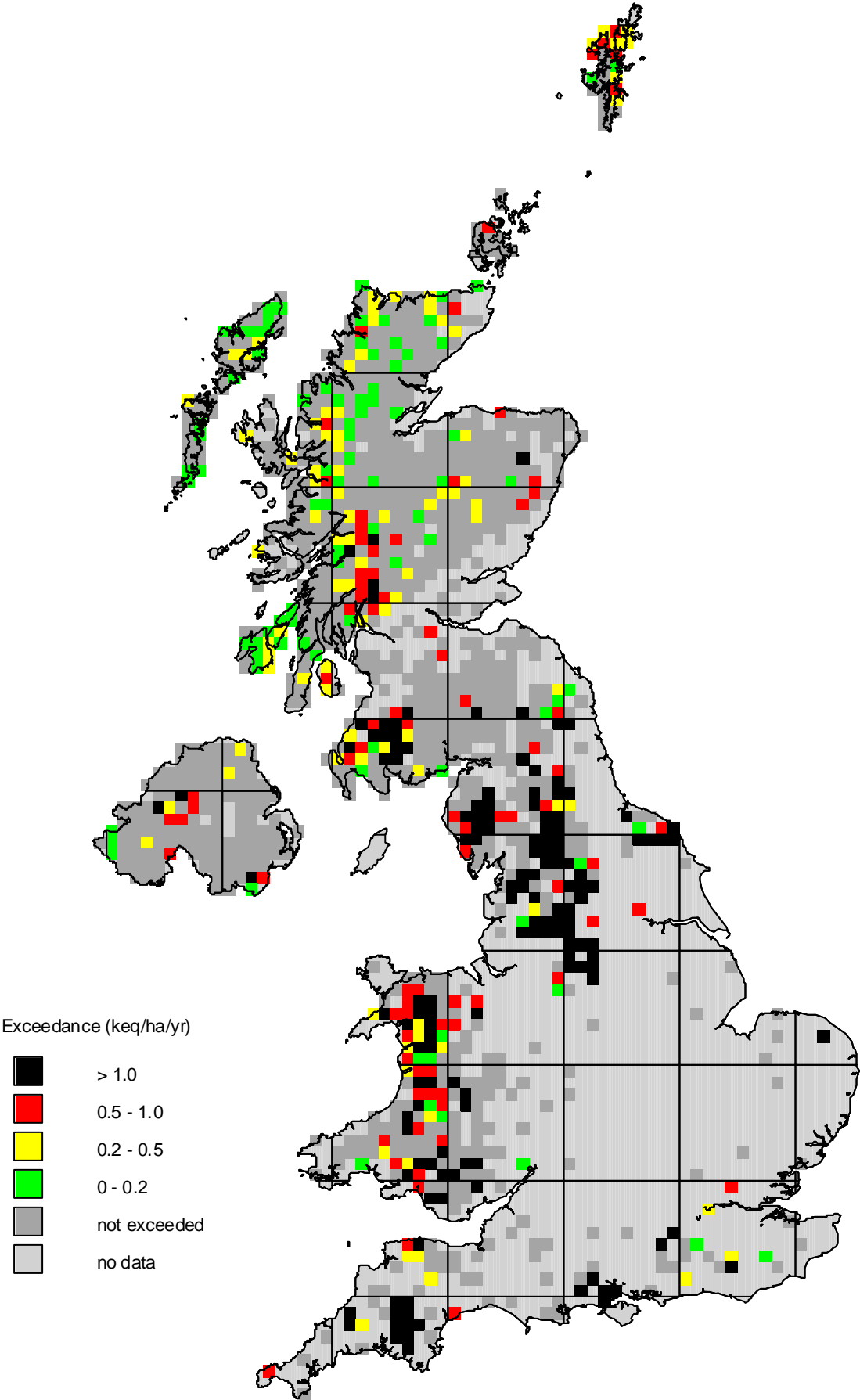


Figure 1.6.6.b FAB exceedance under Current (95/97) scenario for ANCcrit = 20 ueq/l.

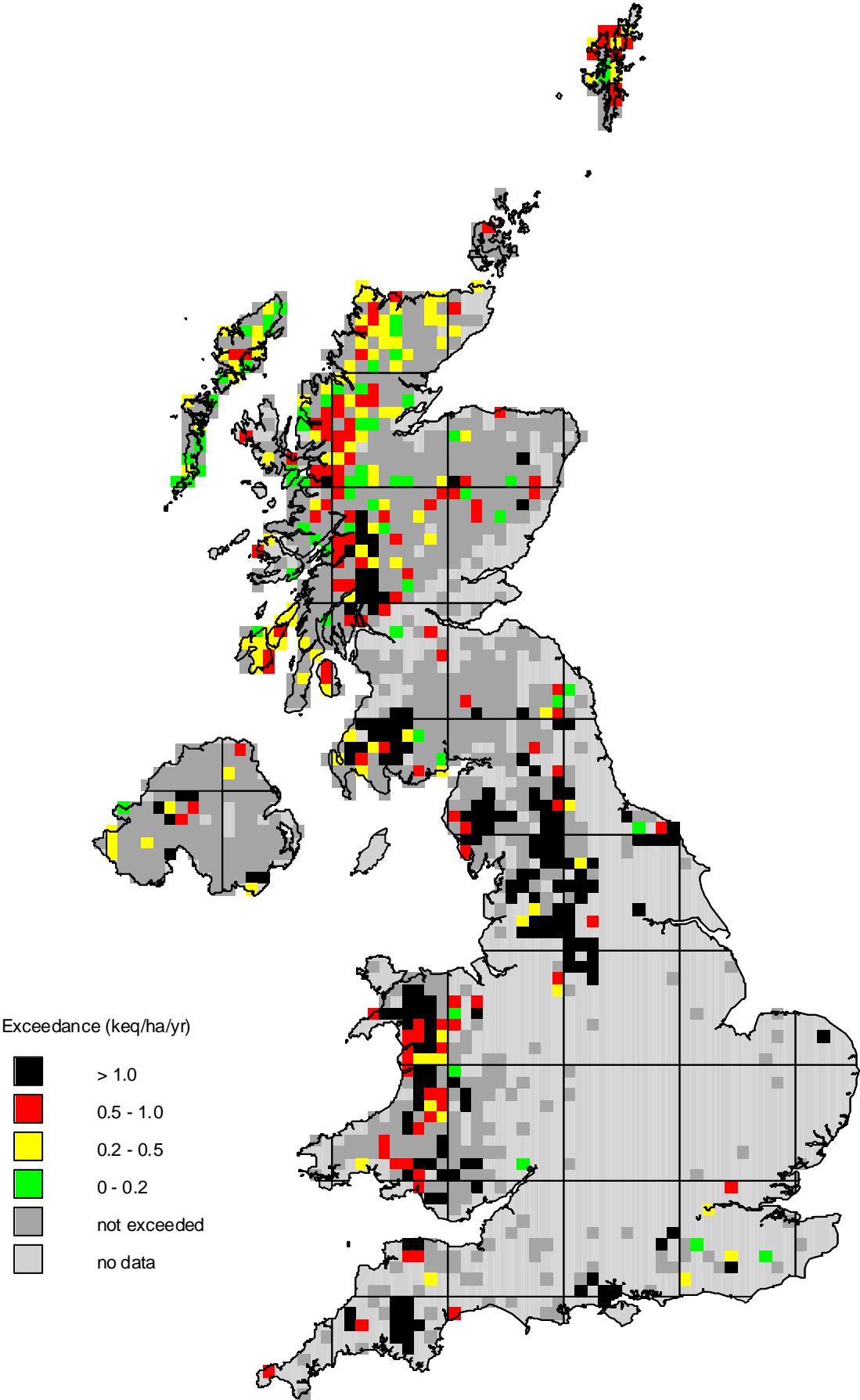


Figure 1.6.7.a FAB exceedance under Gothenburg (2010) scenario for ANCcrit = 0 ueq/l.

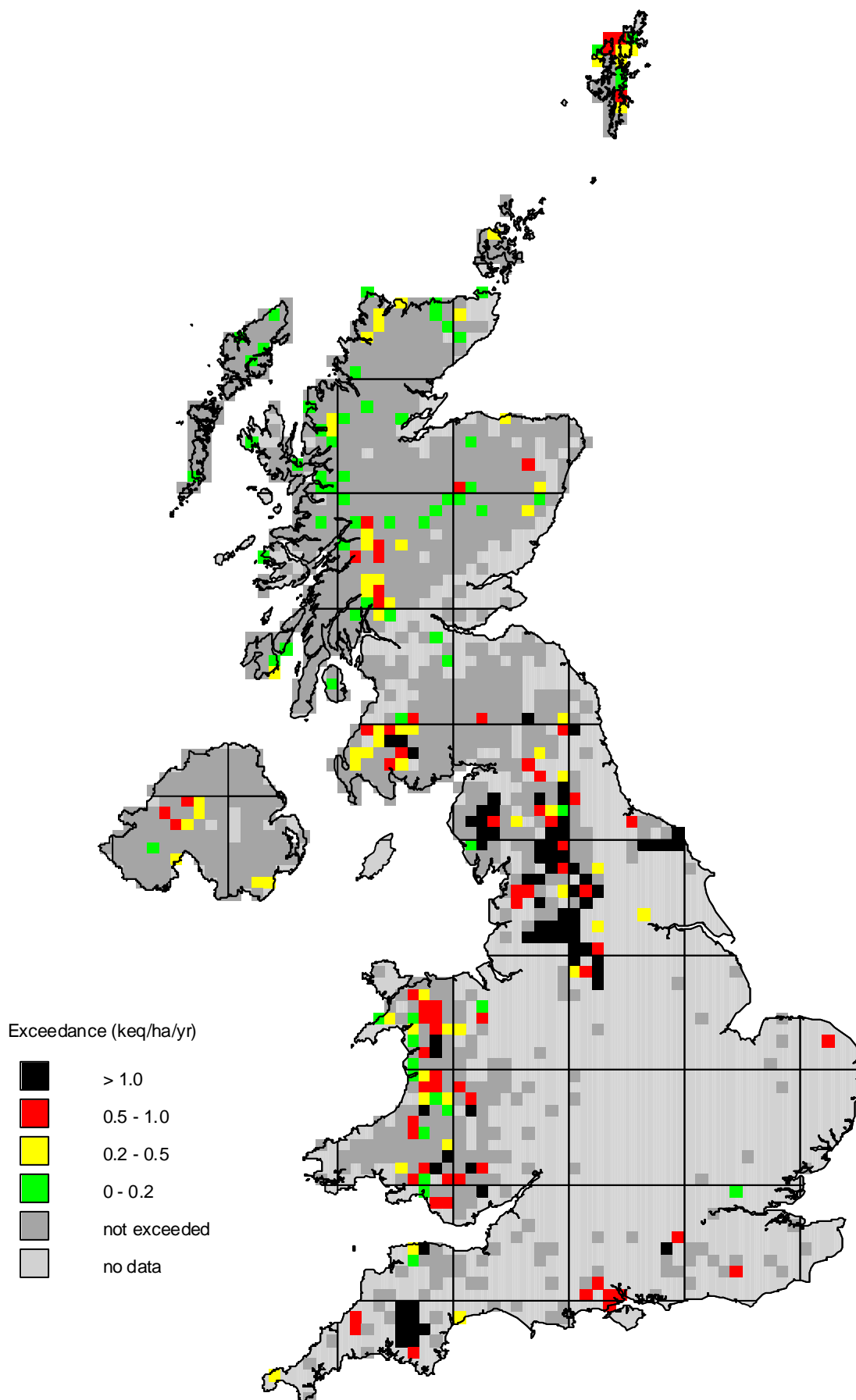


Figure 1.6.7.b FAB exceedance under Gothenburg (2010) scenario for ANCcrit = 20 ueq/l.

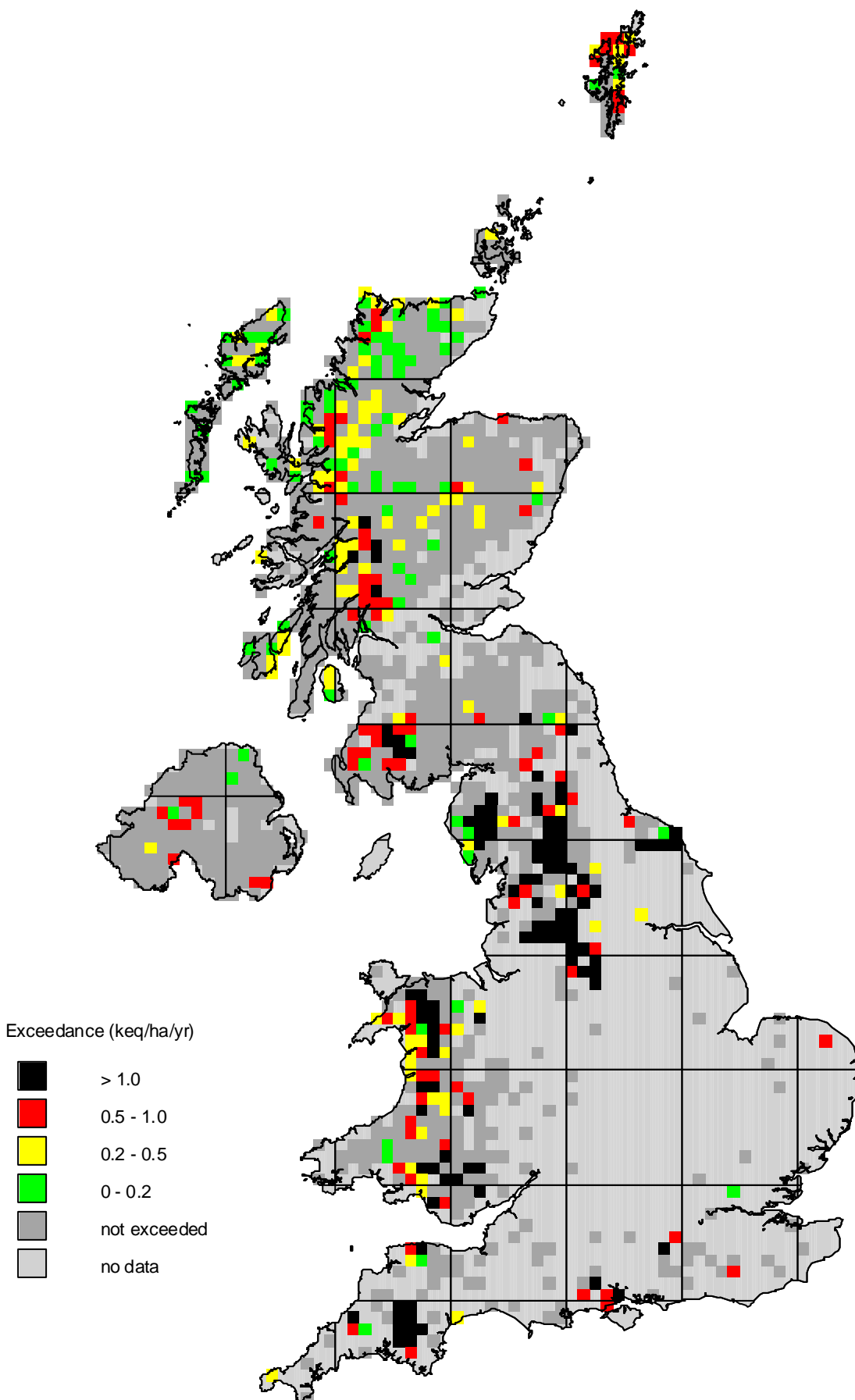


Figure 1.6.8.a FAB Class under Current (95/97) scenario for ANCcrit = 0 ueq/l.

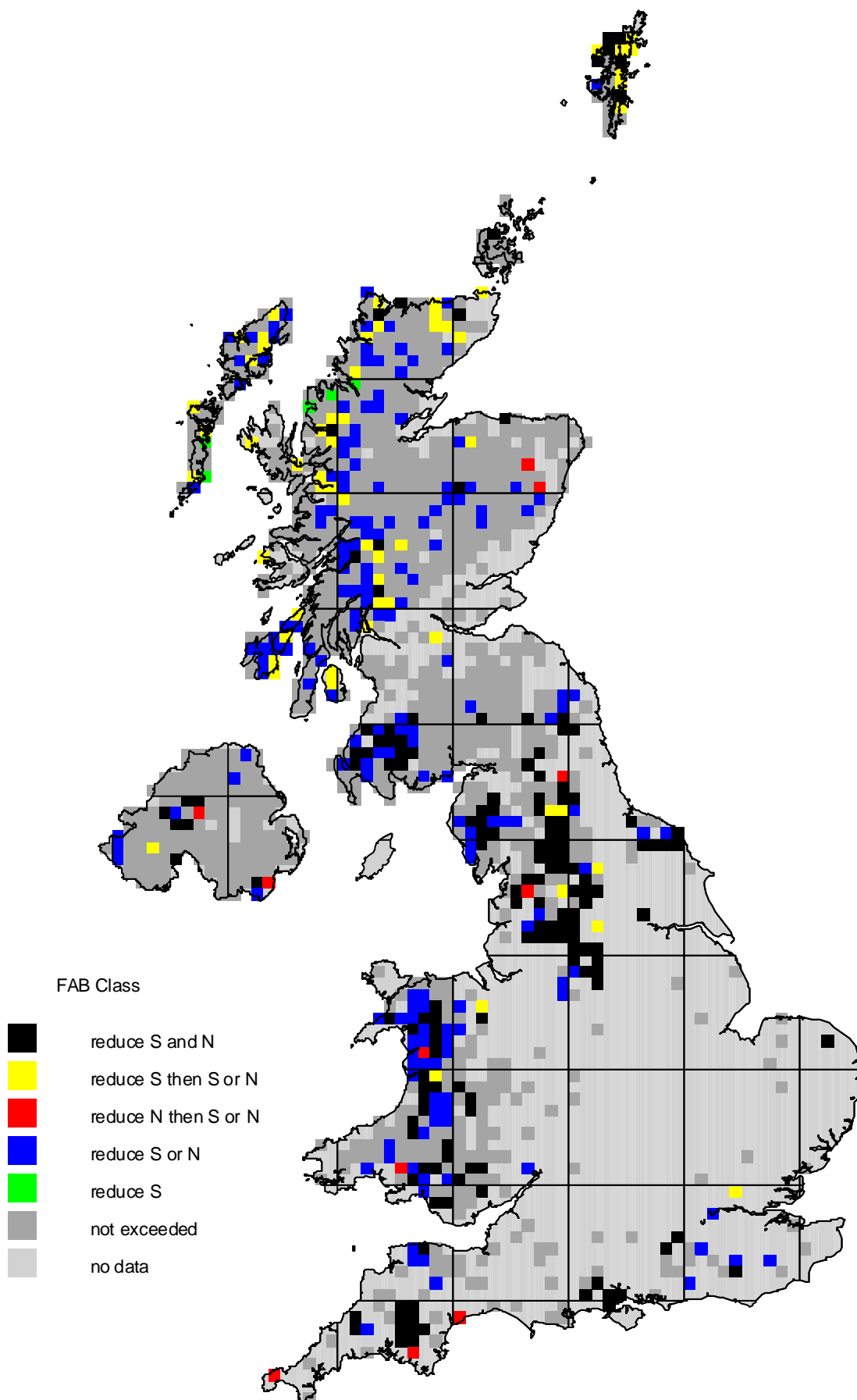


Figure 1.6.8.b FAB Class under Current (95/97) scenario for ANCcrit = 20 ueq/l.

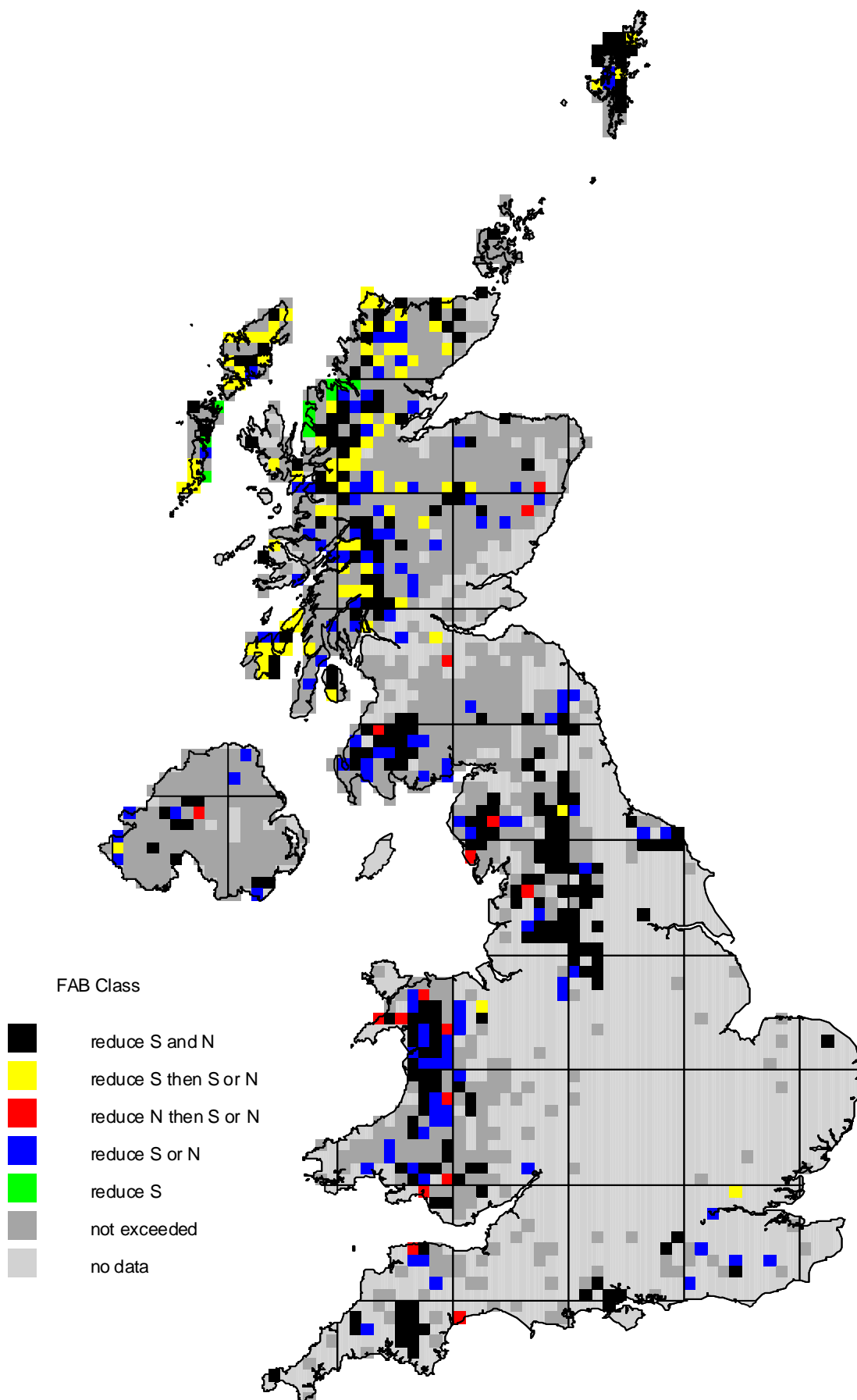




Figure 1.6.9.a FAB Class under Gothenburg (2010) scenario for ANCcrit = 0 ueq/l.

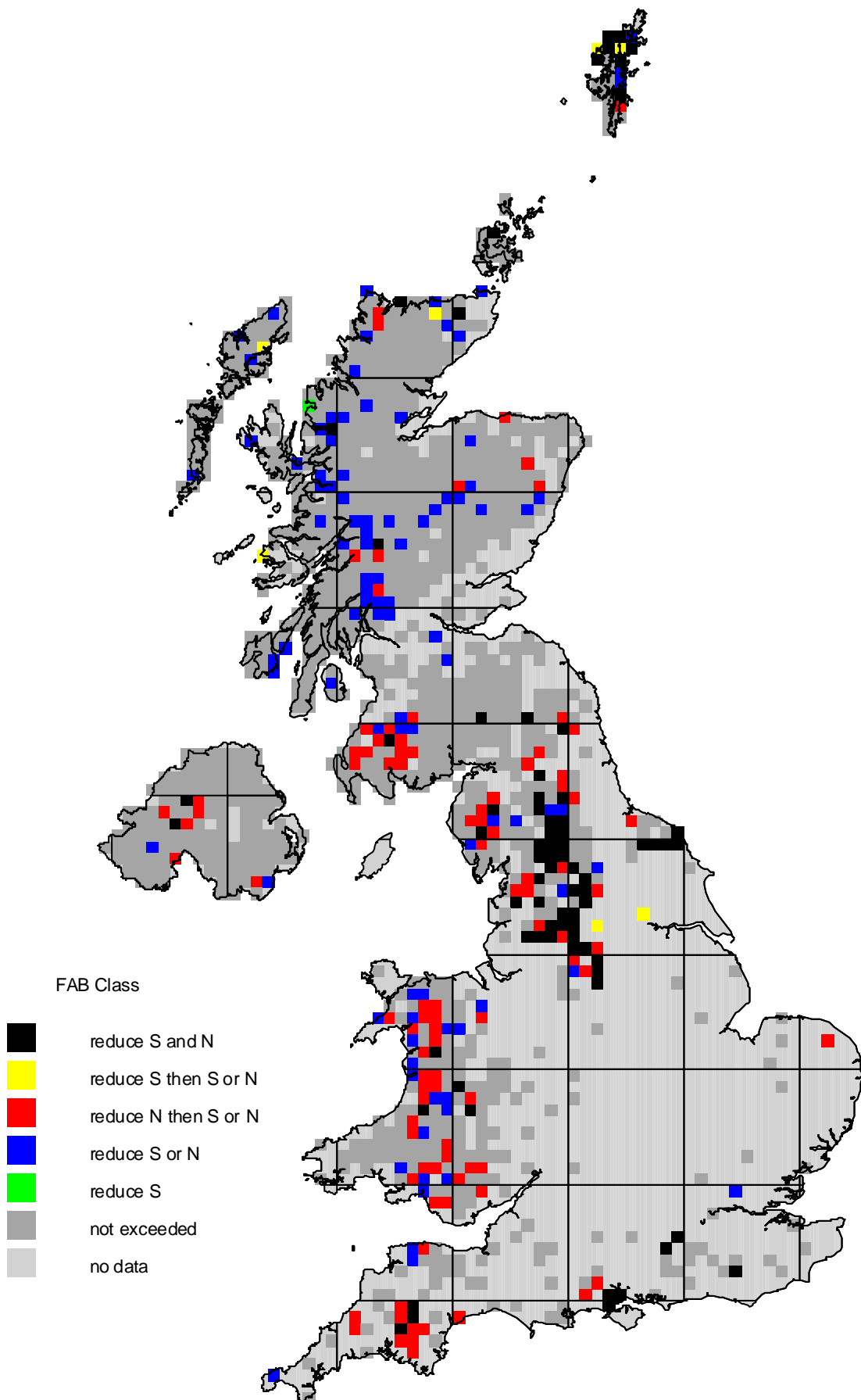
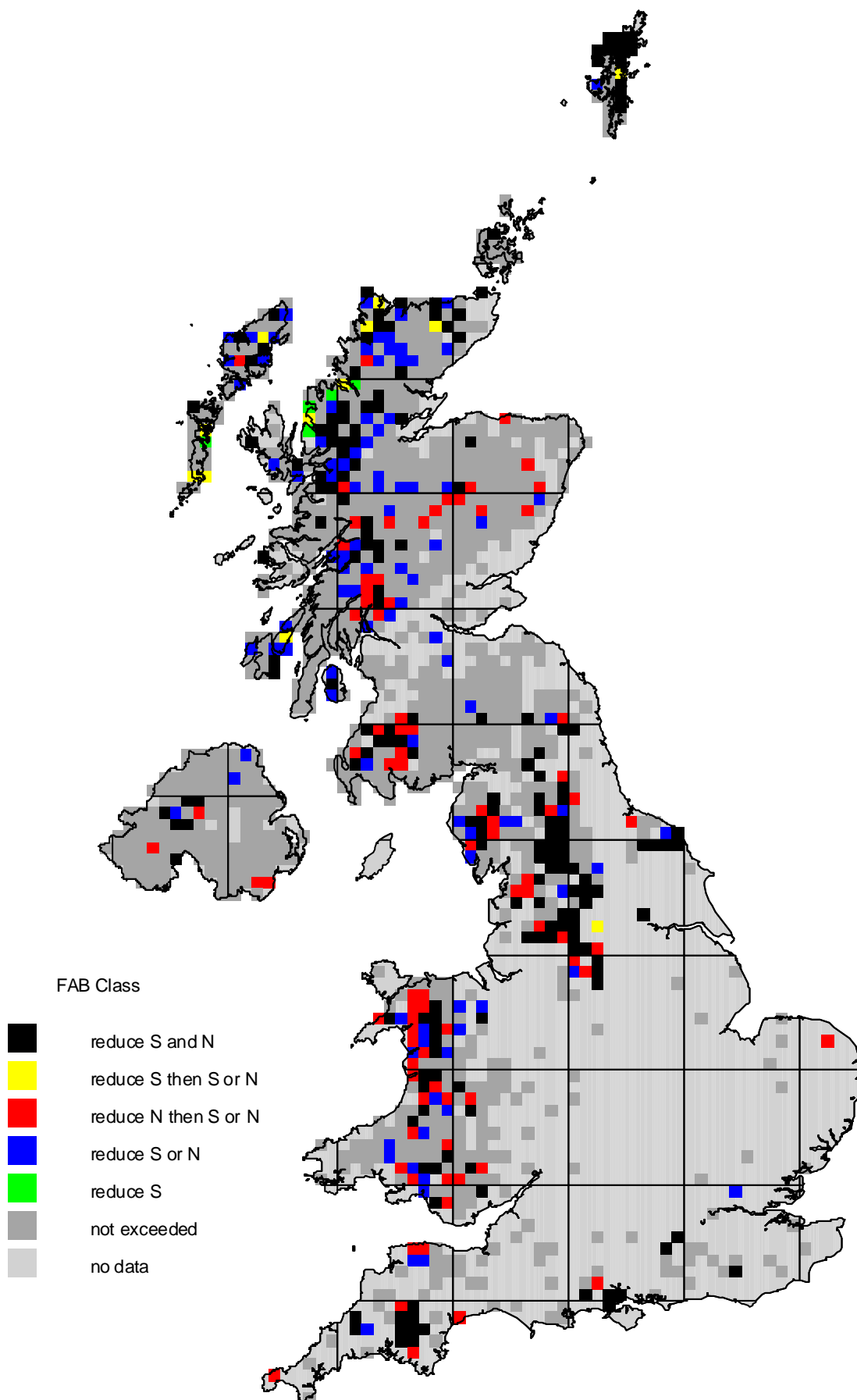


Figure 1.6.9.b FAB Class under Gothenburg (2010) scenario for ANCcrit = 20 ueq/l.



# Task 1.6.2: Linking MAGIC7 to FAB

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### **1.6.2 Linking MAGIC 7 to FAB**

Whilst MAGIC 7 was not used in the national mapping exercise, an application of MAGIC 7 at the Afon Gwy was used to examine the timescales involved in the attainment of steady state conditions within FAB. For this application, FAB terms for permanent N removal were incorporated in the MAGIC 7 calibration based on soil type (i.e. N immobilisation = 3 kg/ha/yr, denitrification = 1 kg/ha/yr). Other model parameters were based on detailed stream chemistry, rainfall, deposition and runoff data available for this site, and sampled soil C and N data. A forecast simulation was then run for 1000 years from present day based on HARM 11.5/FAME modelled S and N deposition for the Gothenburg Protocol (see Section 1.6.1 above; Figure 1.6.10). With no modelled sulphur adsorption/desorption,  $\text{SO}_4^{2-}$  concentrations fall rapidly to a steady state condition, but  $\text{NO}_3^-$  concentrations continue to rise, albeit at a declining rate, throughout the period of simulation. This continuous increase occurs as the C/N ratio of the large organic soil pool gradually declines, leading to increased  $\text{NO}_3^-$  leaching despite constant deposition. After an initial recovery following reductions in S and N deposition, therefore, ANC is predicted to slowly decrease in future as soils become more N-saturated.

This model application suggests that the ‘steady state’ condition of nitrate leaching assumed within FAB may take a very long time to attain, due to the requirement to change the N status of a very large organic pool. If correct, this result is significant in that it implies that FAB may provide a pessimistic prediction of surface water N concentrations (and therefore ANC) over shorter (e.g. < 100 year) timescales. This conclusion is obviously dependent on the accurate simulation of N leaching within MAGIC 7, and on the assumption that the C/N ratio of the entire surface organic pool must be substantially reduced before immobilisation falls to the low levels simulated by FAB. However, long-term stream monitoring data from across Europe (e.g. Wright *et al.*, in review) provide little evidence of changes in catchment N retention during the last 20-30 years, supporting the conclusion that it may be many years, or even centuries, before the nitrogen leaching from terrestrial ecosystems reaches the levels predicted by FAB.

**Figure 1.6.10 Long-term MAGIC 7 simulation for the Afon Gwy, incorporating FAB values for immobilisation and denitrification**

