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Critical Loads of Acidity and Metals

Interim Report to the Department of Environment, Transport and the Regions (contract no. EPG 1/3/117)

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CLAM Mid-term Report, December 1999

Introduction

The CLAM work programme commenced in April 1998 and is due for completion by the end of March 2001. All relevant aspects of the CLAM work programme are progressing in line with targets, with two minor exceptions. Several components are already completed (Sections 1.2, 1.4, 2.4 and 3.1) and routine sampling and experimental work is ongoing. Major field campaigns in summer/autumn 2000 will complete the sampling component of the work programme.

Two changes to the work programme have been implemented. Under Section 1.1, the literature review for catchment N sinks has been rescheduled since it became apparent that a very similar exercise was being carried out under the DETR soils umbrella contract. It is now intended to collaborate with the soils group in order to extend the scope of the review, which requires that reporting be delayed to the end of the contract period.

The second change to the work programme is related to recent analyses carried out on several datasets, including the Acid Waters Monitoring Network (AWMN), the Welsh Acid Waters Survey (WAWS) and Llyn Brianne, which have revealed that there seems to be a powerful climatic influence on both water chemistry and biology in certain parts of the UK which varies on a near-decadal timescale - the North Atlantic Oscillation. This cyclicity could have profound influences on the detection of longer term trends, for example in chemical or biological recovery following reductions in acid deposition. In the light of this new research emphasis, it was decided following discussons with DETR that resources from one part of the work programme (Section 2.1 - biennial sampling at c.30 "exceedance study" sites) would be better employed in increased efforts elsewhere, since the sampling resolution proposed would have been insufficient to address questions relating to episodic and climatic factors. Resources have therefore been diverted into additional work under the first part of Section 2.1, plus Sections 2.3 and 2.7. The scope of the literature review on biological recovery (2.3) and work on the importance of hysteresis, stochasticity and episodicity (2.7) has been expanded to incorporate climatic influences, while additional palaeolimnological work is proposed at two of the Galloway cluster sites (Section 2.1: Loch Enoch and Round Loch of Glenhead) to determine whether recovery of diatom communities has occurred since these sites were last cored several years ago.

EXECUTIVE SUMMARY

1 NITROGEN

1.1 *Ongoing*

Completion of the literature review for catchment N sinks has been postponed until the end of 2000 because it is now being written up in collaboration with the soils umbrella group.

1.2 *Complete*

The feasibility study for use of HOST to characterise catchment soil N dynamics has been completed using an integrated approach comprising HOST classification, Soil Wetness Classification and literature review based values. Each soil type has been allocated a Soil Wetness Class and a corresponding range of denitrification values, with a maximum range of 4-6.2 kgN ha^{-1} yr^{-1} which is up to 50% higher than the previously employed value used for peat and gley soils. Catchment denitrification rates for Scottish sites have been derived, weighted by soil type. The revised denitrification data will be used in the parameterisation of MAGIC7 in a regional application to Galloway.

1.3 *Ongoing*

The field programme for evaluation of N dynamics at the catchment scale began with the construction and installation of instrumentation in March 1999 and has been fully implemented since October 1999. At the four selected sites (Allt a'Mharcaidh, Afon Gwy, Scoat Tarn and River Etherow) the following samples/measurements are being taken: bulk deposition, soilwater chemistry, soil temperature, soil moisture, grazing offtake, denitrification fluxes (with and without N additions), ^{15}N (natural abundance and post-additions), surface water chemistry (streams or lake inflows and outflows) and flow. The full N budget sampling year will be complete by the end of September 2000. Ongoing supplementary work at Loch Grannoch over the same timescale will compare C/N status and denitrification fluxes in forest and moorland subcatchments.

1.4 *Complete*

Regional studies entailing both surface water and organic soil sampling have been completed in the Pennines, Galloway and Wales. Data from these surveys have been utilised in the development of dynamic models (Section 1.5).

1.5 *Ongoing*

Data from the regional studies (Section 1.4) have been used to test the assumption that N leaching is controlled by soil C:N ratios. The poor relationships found so far may be due to insufficient soils data for the measurement of C:N status on a catchment basis (spatial variability) and/or the unsuitability of C:N as a control for non-forest systems. Ongoing work at N-budget catchments (Section 1.3) should help to clarify these issues and improve MAGIC model parameterisation.

1.6 *To be addressed in last 6 months of programme*

2. RECOVERY

2.1 *Ongoing*

Monthly sampling of 10 Galloway lochs has continued throughout the present contract, and an evaluation of trends in the data will be completed by Spring 2000. Further sampling at 30 "exceedance" sites has been abandoned and resources diverted into studies of new issues, including sea-salt impacts and climatic (North Atlantic Oscillation) effects on chemistry and biology.

2.2 *Ongoing*

Site specific MAGIC7 applications are currently being undertaken for the AWMN sites, and will also include the N budget sites (Section 1.3) when sampling and data analysis is complete at the end of 2000. Regional MAGIC7 applications are already complete for the Wales, Galloway and Pennine datasets, but recalibrations may be required if MAGIC7 is modified to incorporate the findings of the intensive N budget work.

2.3 *Ongoing*

A draft review on biological recovery in freshwater ecosystems affected by large-scale disturbances has been completed, but new findings have revealed additional complications regarding recovery so it is anticipated that the desk review will be subject to further revisions over the remainder of the contract period.

2.4 *Complete*

A desk study assessing the value of analogue matching techniques has been circulated.

2.5 *Ongoing*

Site selection for this part of the work programme is currently ongoing, and field sampling will take place during spring/summer 2000.

2.6 *Ongoing*

The existing CLAG chemical-biological database, comprising data from the Scottish Baseline Survey, UK AWMN, Welsh Acid Waters Survey/Resurvey and CLAG, has been used in the analysis of relationships between water chemistry and biology (diatoms and invertebrates). Biological communities were first classified using TWINSPAN, which identified five diatom and five invertebrate assemblages, showing strong relationships with several chemical parameters, including pH, alkalinity and aluminium. A generalised additive model (GAM) and classification and regression tree (CART) techniques were successfully used to predict communities from single or multiple chemical and physical parameters. Work is ongoing on the harmonisation of biological data and the further development of these biological predictive models.

2.7 *Ongoing*

Analyses of various datasets have revealed that year-to-year variations in the stability of invertebrate communities in upland freshwaters, initially thought to represent stochastic variations, may be driven largely by climatic factors (the North Atlantic Oscillation) over an approximately decadal timescale. Such cyclical patterns can have a major consequences for the detection of longer term trends, in particular recovery from acidification. Experimental work to investigate the effects of episodicity on two mayfly species (*Ephemerella ignita* and *Baetis rhodani*) has been carried out, and the results showed a contrasting tolerance to wet-weather flow, with stream chemistry rather than food quality being the limiting factor. The reasons for inter-specific variation are not understood, but may be influenced by severity and frequency of episodes. Several papers are currently in preparation for submission to major journals.

2.8 *Ongoing*

A statistical method has been developed for incorporating episodes into biological models, and MAGIC7 will be used to provide biologically relevant indicators for linkage to these models in the next phase of this work.

2.9 *Ongoing*

Regional MAGIC7 simulations have been carried out under different forestry scenarios for Wales and Galloway. Under the "best case" scenario where forest is removed and the land is allowed to revert to moorland, there is a significant recovery in surface water ANC relative to the more realistic "replanting after harvest" scenarios. Work is ongoing to incorporate effects of different non-forest vegetation and temperature regimes, and will take account of results from N-budget sites (Section 1.3).

2.10 *Scope to be reconsidered by DETR.*

3. HEAVY METALS

3.1 *Complete*

A scoping study has been completed and submitted to DETR. It is intended to synthesise the report into a paper for journal submission.

3.2 *Ongoing*

Measurement of metals in bulk deposition and lakewater at Lochnagar is continuing, while the final annual sampling under the current contract of sediment traps, epilithic algae, zooplankton, catchment vegetation and aquatic macrophytes will be carried out in summer 2000.

WORKPACKAGE 1: NITROGEN

1.1 Review values for catchment nitrogen sinks reported in the literature

This part of the work programme has now been tied in to an ongoing exercise within the Soils Umbrella group to compile a literature database of N process rates. A literature review on denitrification carried out under Section 1.2 of this programme has contributed to this work. Representatives of the Soils and Freshwaters Umbrella groups will continue to liaise and collaborate in the development of the database.

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_2O 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						
	<40		40-60 cm	60-80 cm	>80 cm Drainage outfalls		
Average FCD	Mineral soil	Peaty soil			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 kg ha^{-1} 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 kg ha^{-1} yr^{-1}) (Fig 1).

Conclusion

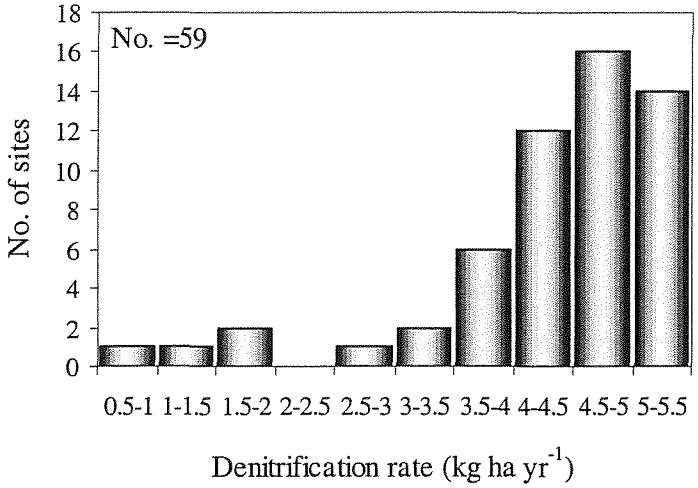
It is likely that denitrification may alleviate some of the effects of excess N in catchments dominated by peat and gleyed soils. In the UK, measurements of denitrification in undisturbed, semi-natural ecosystems are rare. It is therefore important that the results from this study are validated with denitrification data collected from the "Nitrogen Budget" sites (Workpackage 1.3). and it is feasible that these data will substitute the estimates of denitrification from the literature. 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 podzol	0-0.8	Emmett and Reynolds, 1996 (Measured: Aber, Wales)
II	1. Imperfectly drained brown earth 2. Imperfectly drained humus iron podzol	0.28	Ashby *et al*, 1998 (Well drained upland soil with low organic matter (C is the limiting factor))
III	Peaty gleyed podzol 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 podzol Peaty gley	4	Hall *et al*, 1997 (Gley soil)
VI	Peaty gley Basin peat Blanket peat Peaty ranker	4-6.2	Hornung *et al* 1995 (Peat with high pH) Melin and Nommik, 1983 (Mature Scotspine, Sweden) Freifelder *et al*, 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



1.3a Evaluate the nitrogen dynamics at a catchment scale for at least four catchments across a gradient of N leaching relative to deposition

Four sites were selected for intensive N-budget study (N-budget sites) along gradients of N deposition and N saturation (Table 3, Figure 2). Total N deposition ranges from low levels of 0.37 keq ha^{-1} yr^{-1} (5.2 kgN ha^{-1} yr^{-1}) at the Allt a'Mharcaidh, Cairngorms, up to 2.26 keq ha^{-1} yr^{-1} (31.6 kg ha^{-1} yr^{-1}), at the River Etherow in the Pennines, one of the regions of highest deposition of both S and N in the country.

Table 3: Deposition data (ITE annual mean data for 1992-94, catchment weighted)

Deposition (keq ha^{-1} yr^{-1})	**Allt a' Mharcaidh**	**Afon Gwy**	**Scoat Tarn**	**River Etherow**
S (non-marine):	0.401	1.189	1.27	2.482
Total N:	0.371	1.69	1.7	2.258
Runoff (mm):	1093	2476	2526	1192

The various stages of N saturation, as defined by water chemistry, are represented in these four sites (Figure 2). 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 4.

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 is being 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 3), 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 has been 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 are also taken 2-weekly for chemical analysis. The two main tributaries of Scoat Tarn are sampled in the same way, and will 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 has been installed. Stage measurements obtained will be calibrated to discharge through periodic dilution gauging. Stage data obtained so far indicate a high degree of temporal flow variability at both sites.

Table 4: Selected water chemistry data (AWMN annual mean data for 1997)

	Allt a'Mharcaidh	Afon Gwy	Scoat Tarn	River Etherow
pH	6.52	5.35	5.05	4.58
ΣBC* (μeq/l)	93	71	45	300
SO4* (μeq/l)	33	45	42	206
NO3 (μeq/l)	2	15	18	57
ANC (μeq/l)	58	12	-15	37
Cl (μeq/l)	107	149	174	323
TOC (mg/l)	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 4-8). Each soil type constitutes a study area on which replicated experimental plots were set up (Table 5).

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) comprises:

1. soilwater suction sampler located below rooting zone
2. static denitrification chamber
3. ^{15}N additions area
4. adjacent grazing exclosure

Table 5: 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 podzol
Allt a'Mharcaidh	M4	Shallow peat
Afon Gwy	G1	Hilltop peat
Afon Gwy	G2	Peaty gley
Afon Gwy	G3	Podzol
Afon Gwy	G4	Valley peat
Scoat Tarn	S1	Podzol
Scoat Tarn	S2	Peaty gley
Scoat Tarn	S3	Deep peat
River Etherow	E1	Deep peat (recently burnt *Calluna*)
River Etherow	E2	Deep peat (unburnt *Calluna*)

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. Sampling is done fortnightly and the samples are analysed for NH_4^+, NO_3^- and organic N at MLURI.

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 are sampled with syringes and airtight glass vials 4-weekly and analysed for CO_2, CH_4 and N_2O on a GC at ITE Bangor.

Figure 2: Long-term nitrate concentrations at CLAM intensive study sites (AWMN data)

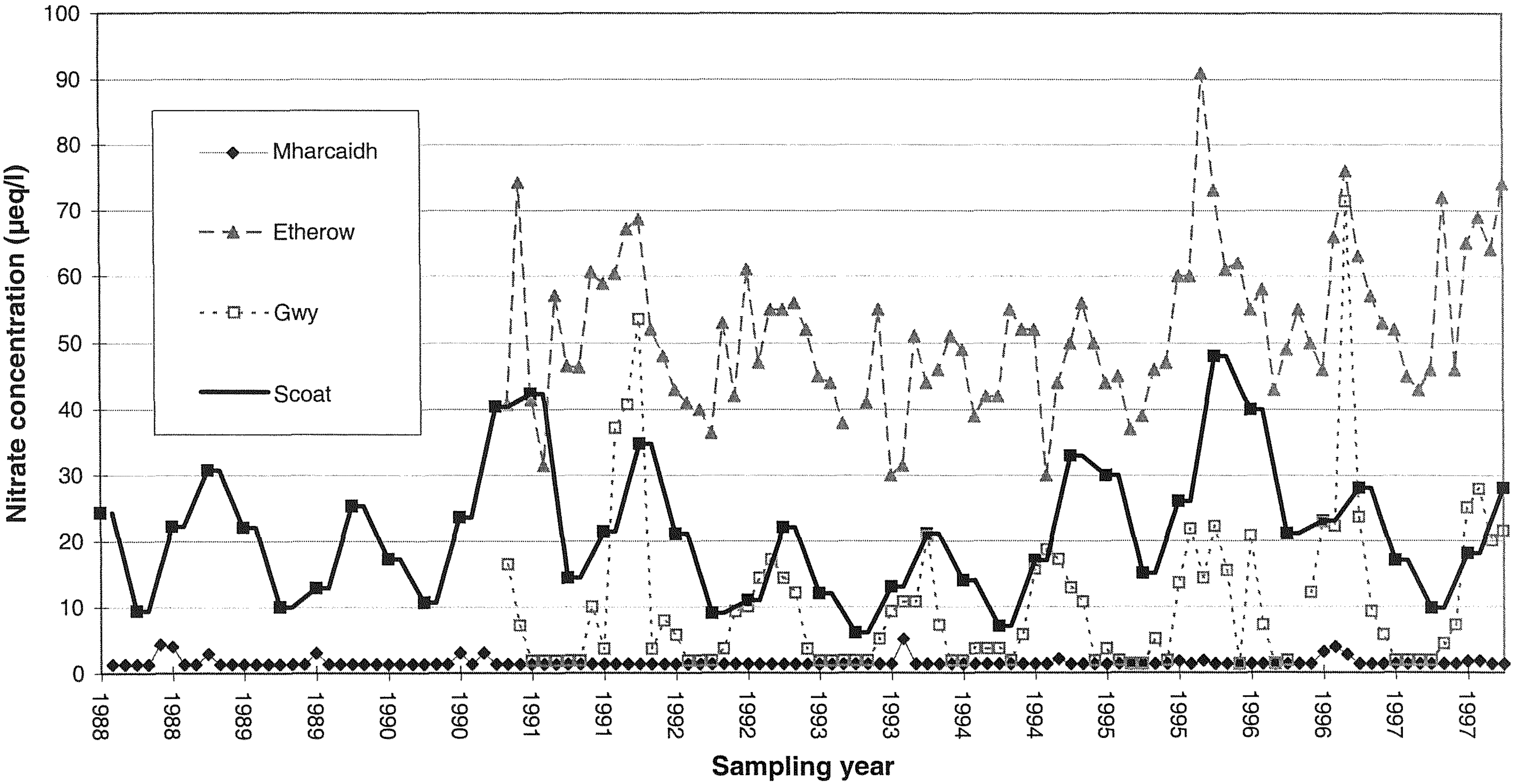
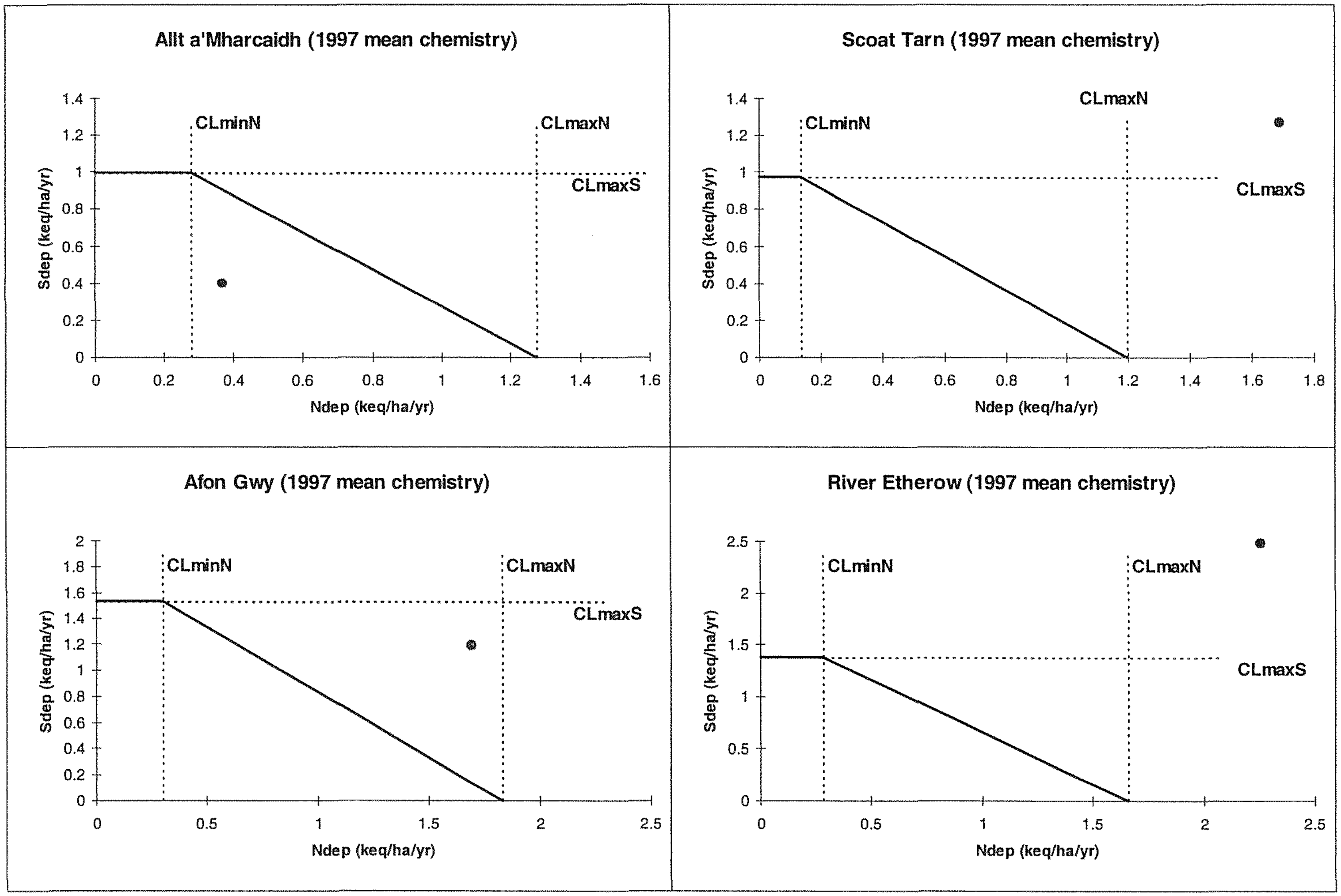


Figure 3: FAB Model Critical Load Function for N-budget sites



^{15}N additions

Funding for the ^{15}N additions work was finally secured from National Power in November 1999. The addition of ^{15}N labelled solution will provide data on N immobilisation and uptake through destructive sampling of soils and vegetation in the plots at the end of the sampling period. ^{15}N additions commenced in October 1999 and will be continued for a period of 12 months.

Grazing exclosures

Grazing exclosures ($1m^2$) 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 ($0.5m^2$ plots in the centre of the $1m^2$ fenced exclosures) were then removed from within the fenced plots and from adjacent unfenced areas. These samples are currently being processed to provide the following information:

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

Comparison of these data from inside and outside the fenced exclosures will provide figures for grazing offtake.

In addition, root layer samples were collected along with soil cores separated by horizon. The soil, root layer and above-ground biomass dried samples will be analysed for ^{15}N at ITE Merlewood in order to provide natural abundance figures and a baseline for comparison with post-addition values of ^{15}N.

Soil moisture

Soil moisture is measured 2-weekly at 3 points within each plot using a theta-probe.

Soil temperature

In each of the 13 study areas a temperature datalogger was buried at 5-10cm depth and takes soil temperature measurements at 2 hour intervals. The loggers were installed in early September when soilwater chemistry and denitrification measurements started and will be downloaded quarterly.

Secondary experimental plots

Secondary experimental plots (identical to the primary plots) were paired with the primary plots in 7 selected soil study areas (Table 6: 3 replicates per soil type = 21 plots).

The secondary plots include soilwater suction samplers which serve 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 are used for fertiliser addition experiments in which NH_4NO_3 solution is added fortnightly at a rate equivalent to 20 kgN ha^{-1} yr^{-1} in

10% of annual estimated runoff (see Table 3). The fertiliser is added in identical amounts every 2 weeks directly into the static chambers after gas sampling has been carried out. The experiment will provide data on the effect of N additions on denitrification rates when the results are compared with denitrification data from paired plots without N additions. Soil moisture is measured 2-weekly (3 replicates) by theta-probe, but no ^{15}N additions are carried out at these plots.

Table 6: Secondary experimental plots at N budget sites

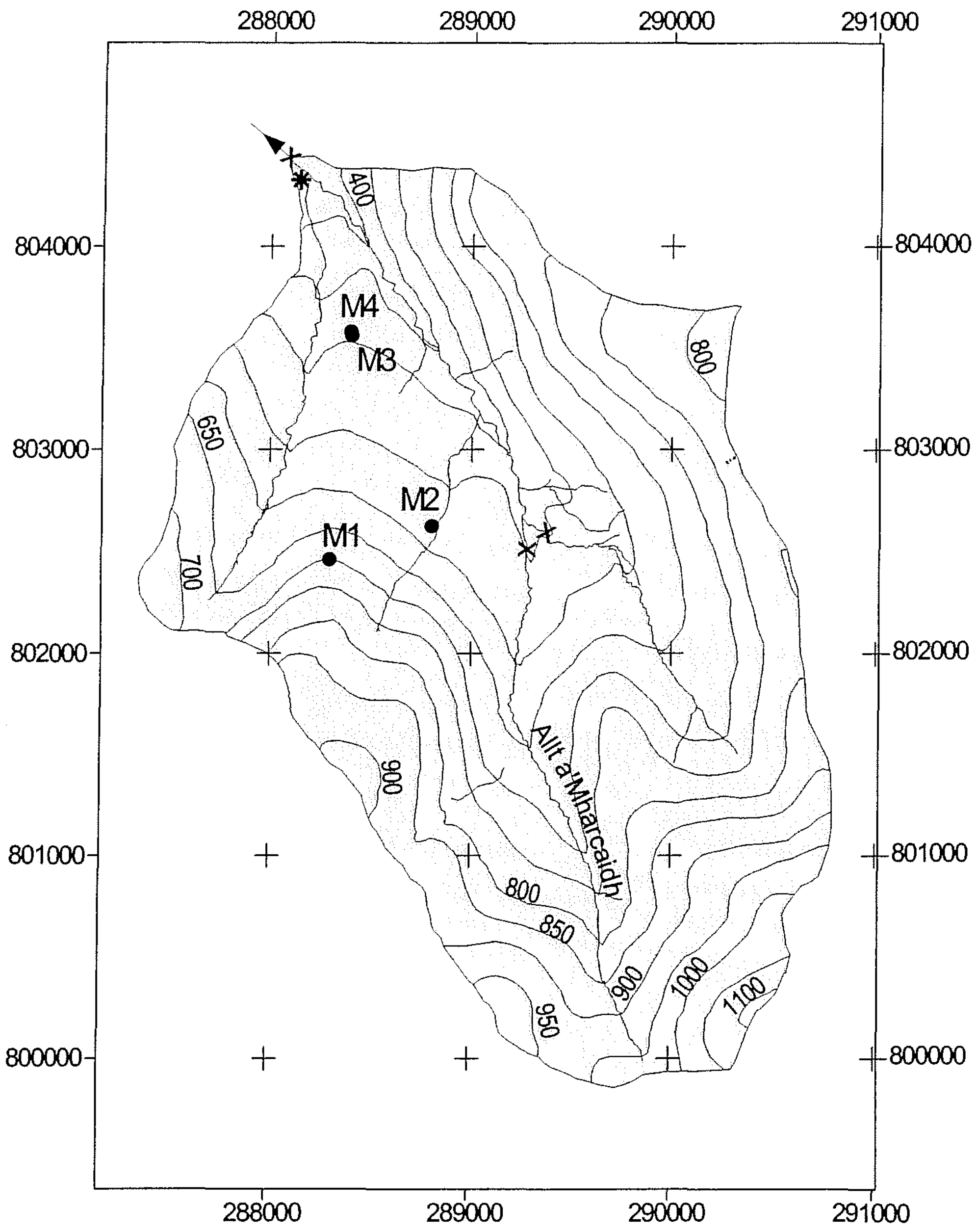
Site	Soil code	Soil type
Allt a'Mharcaidh	M3	Peaty podzol
Allt a'Mharcaidh	M4	Shallow peat
Afon Gwy	G1	Hilltop peat
Afon Gwy	G2	Peaty gley
Afon Gwy	G3	Podzol
River Etherow	E1	Deep peat (recently burnt *Calluna*)
River Etherow	E2	Deep peat (unburnt *Calluna*)

A summary of all the ongoing sampling work in the N-budget study catchments is provided in Table 7.

Table 7: Measurements at N-budget catchments

Measurement	Location	Sampling frequency	Method	Start date
Water chemistry	Catchment outflow	At least 2-weekly	Dip sample	Mar. 1999
Bulk deposition	Within catchment	At least 2-weekly	AEA Bulk Collector	Mar. 1999
Soilwater chemistry	Primary plots	2-weekly	Suction sampler	Sept. 1999
Denitrification	All plots	4-weekly	Static chamber + vials	Sept. 1999
Soil moisture	All plots	2-weekly	Theta probe	Aug. 1999
Soil temperature	Study area (soil type)	2 hourly	Tinytalk datalogger	Sept. 1999
^{15}N natural abundance	Exclosures + adjacent areas	One-off	Destructive soil+vegn.	Sept.1999
^{15}N post additions	Primary plots	One-off	Destructive soil+vegn.	Sept. 2000
Grazing offtake	Exclosures + adjacent areas	One-off	Veg. year's growth	Sept.1999
N additions & N_2O	Secondary plots	Monthly	Static chamber	Oct. 1999
Flow	Catchment outflow	30 minutes	Pressure transducer	Sept. 1999

Figure 4: Experimental Plots at Allt a'Mharcaidh



Allt a'Mharcaidh

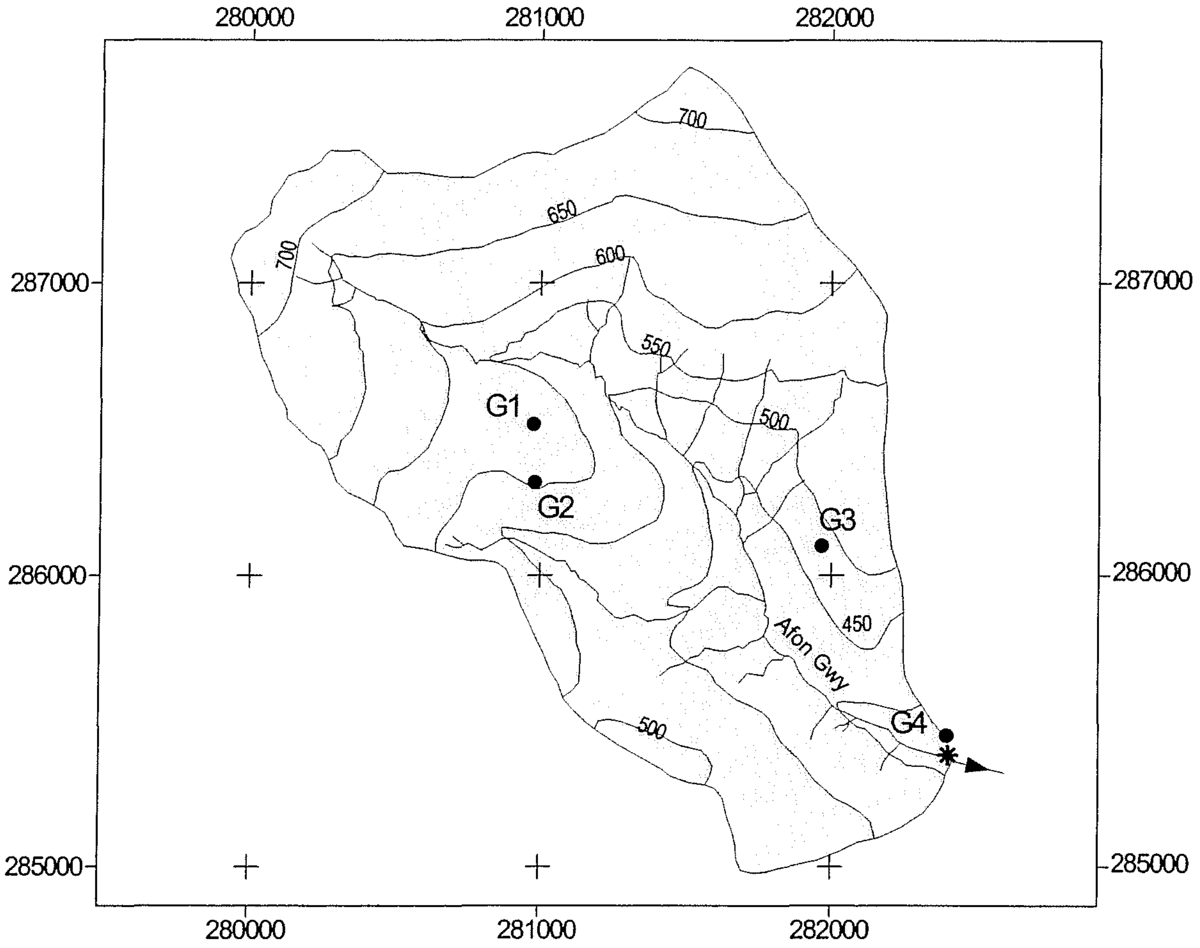
✱ Bulk deposition collector

● Experimental plots

X Stream water sample point

Name	Soil	Exclosure	N Budget & 15N	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 5: Experimental Plots at Afon Gwy



Afon Gwy, Wales

- ✱ Bulk deposition collector
- ● Experimental plots

Name	Soil	Exclosure	N Budget & 15N	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

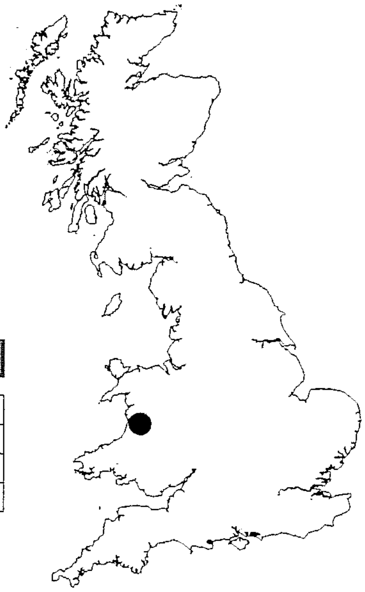
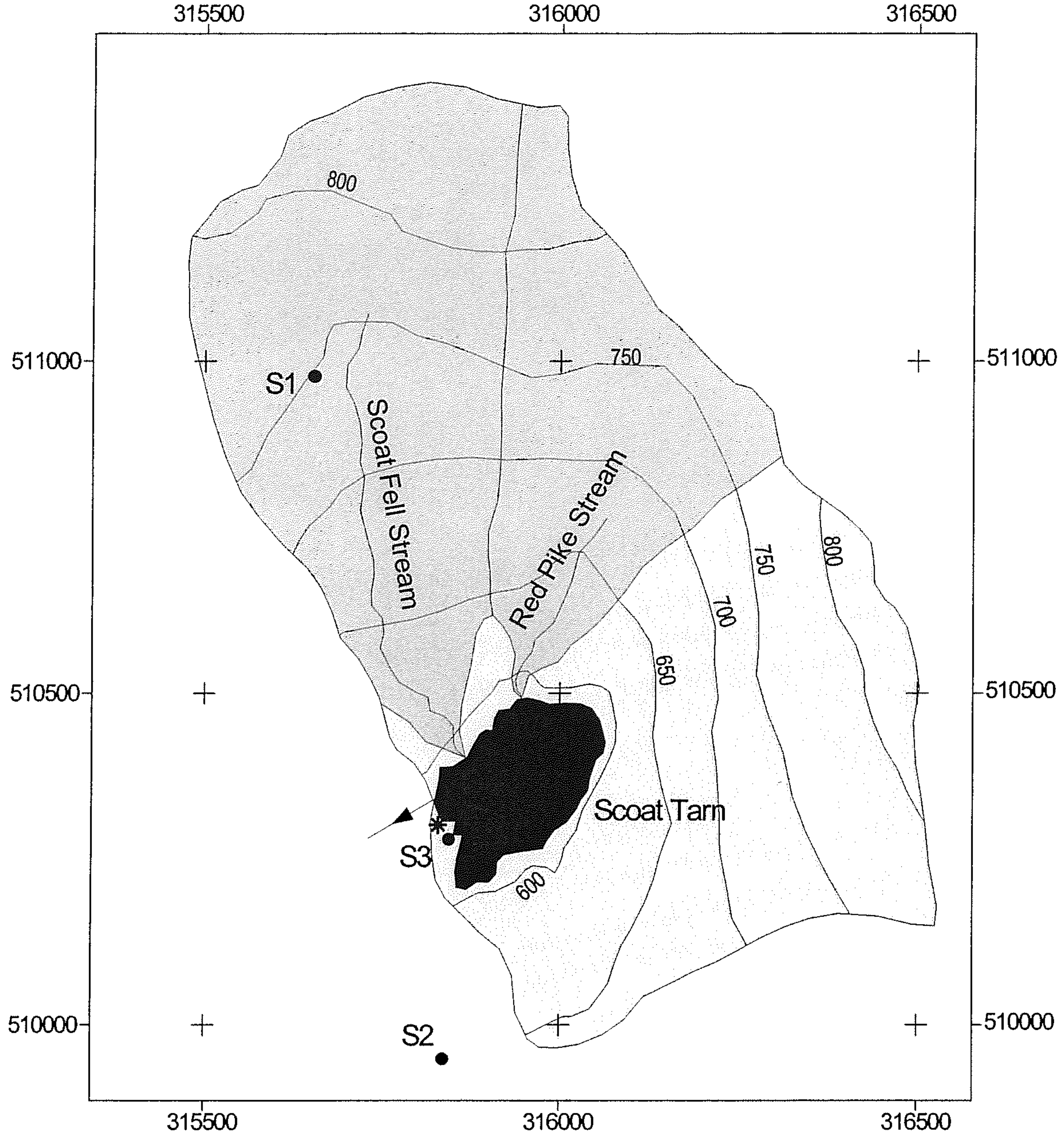
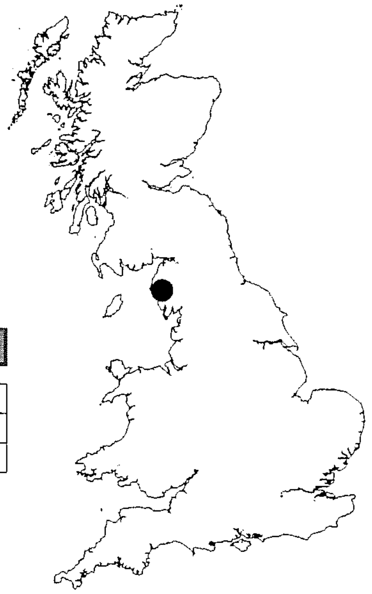


Figure 6: Experimental Plots at Scoat Tarn



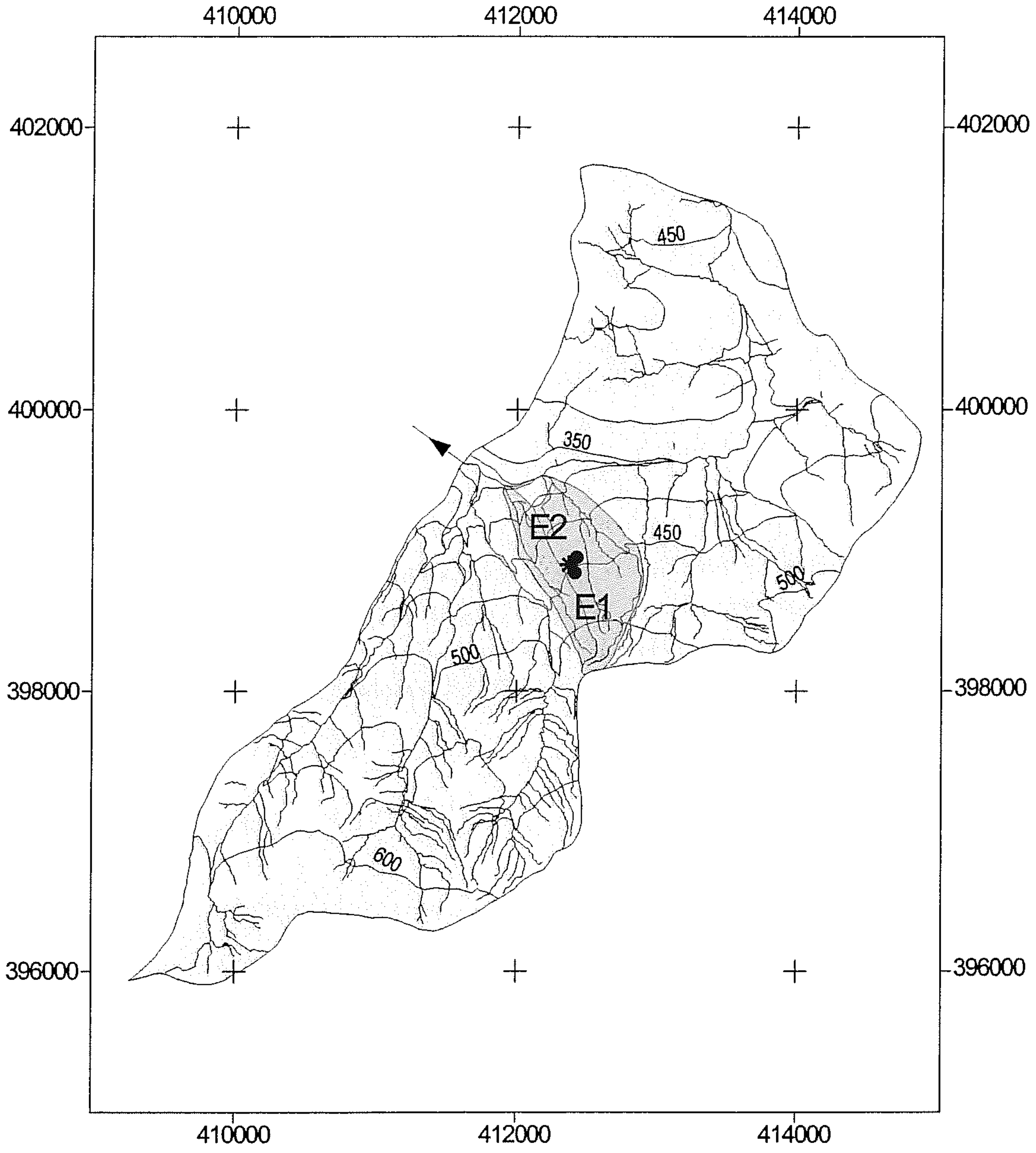
Scoat Tarn, England



- ✱ Bulk deposition collector
- ● Experimental plots

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

Figure 7: Experimental Plots at River Etherow



River Etherow, England

* Bulk deposition collector

● Experimental plots

Name	Soil	Exclosure	N Budget & 15N	N Additions
E1	Burnt Calluna	Yes	Yes	Yes
E2	Calluna	Yes	Yes	Yes

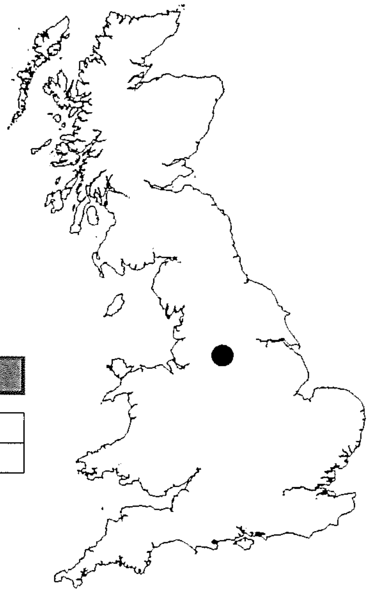
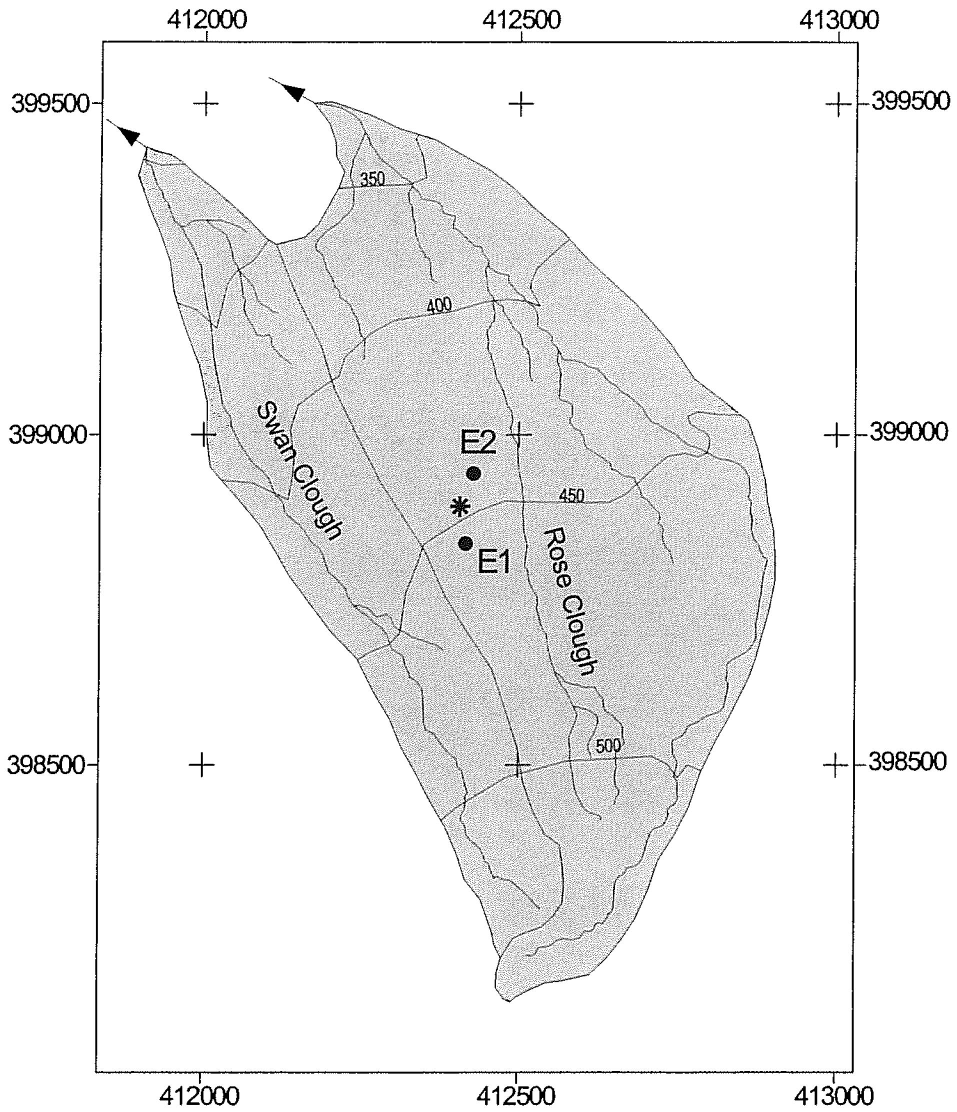


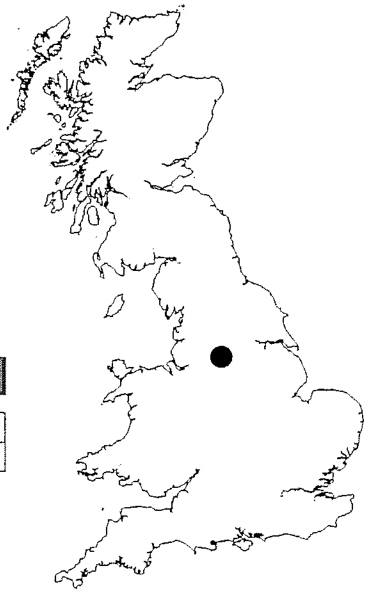
Figure 8: Experimental Plots at River Etherow relative to Swan and Rose Clough



River Etherow, England

- ✱ Bulk deposition collector
- ● Experimental plots

Name	Soil	Exclosure	N Budget & 15N	N Additions
E1	Burnt Calluna	Yes	Yes	Yes
E2	Calluna	Yes	Yes	Yes



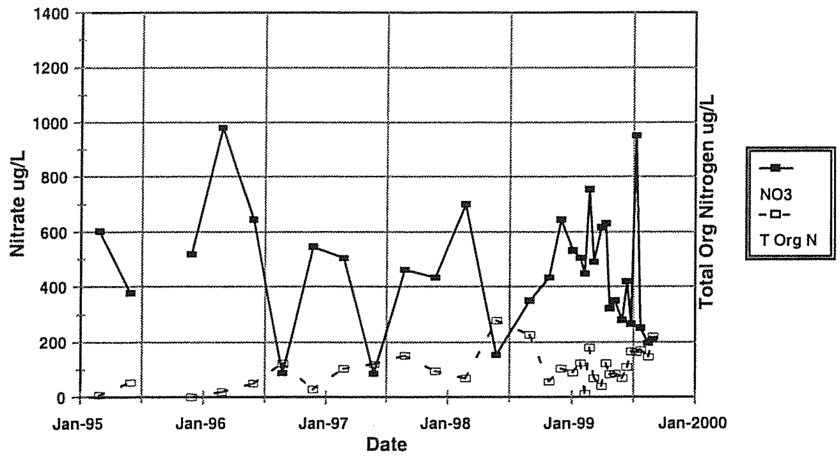
1.3b Forested non-forested comparison

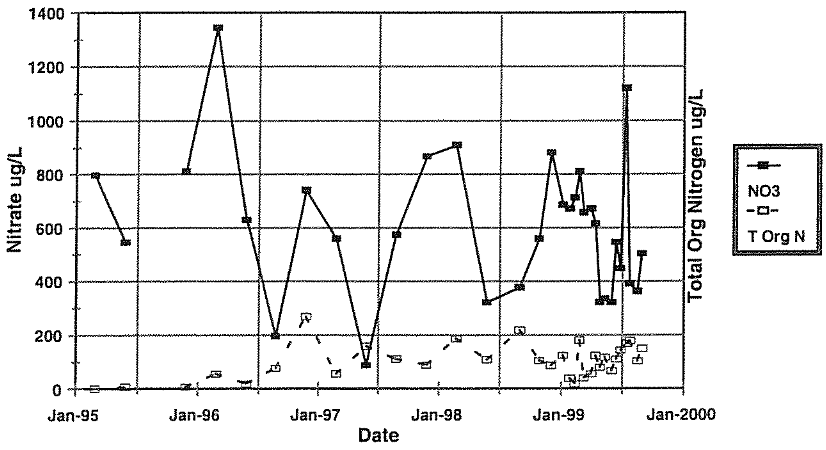
A comparison of nitrate leaching between forested and non-forested sub-catchments is being undertaken in the Loch Grannoch catchment (N deposition - 24-28 kg ha^{-1} yr^{-1}). Twice monthly sampling and chemical analysis of samples from six sub-catchments, at different stages of forest development, and 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 99 for C/N analysis by MLURI. A further 9 sites were selected for denitrification studies and the N- chambers installed in August 99.

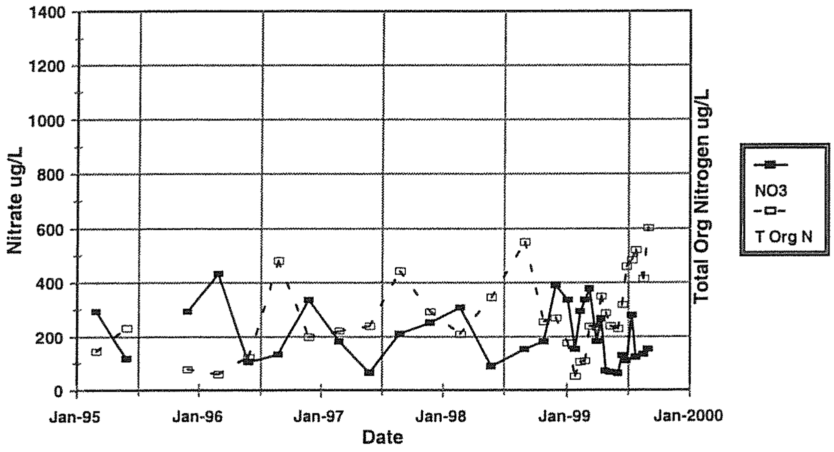
Water sampling sites identified as; Grannoch O/F and Grannoch 1-6. Sampling of rain and mist for chemistry and carbon particles in the Grannoch catchment has continued on a twice monthly basis during 1999.

Preliminary results (Figure 9) show that nitrate leaching from the mature forest catchments (1-3) is three to four fold greater than the adjacent moorland catchment (6). By contrast, nitrate leaching from the relatively young forest catchments (4/5) is about half that from site 6. Concentrations of dissolved organic N (DON) are generally well correlated with dissolved organic carbon (DOC) concentrations which varied with season and flow. However, the relationship/ratios of DOC/DON varies within catchments and between catchments.

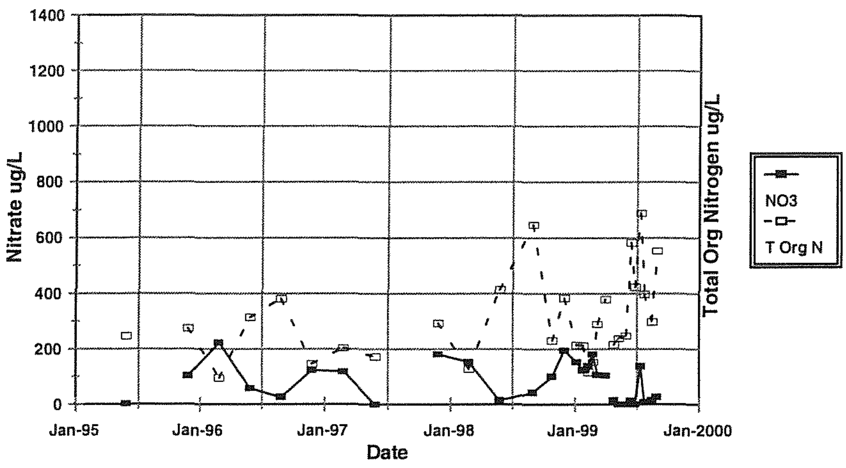
Figure 9: Seasonal variation in NO_3^- and organic N for Loch Grannoch study sites


Loch Grannoch Inflow 1

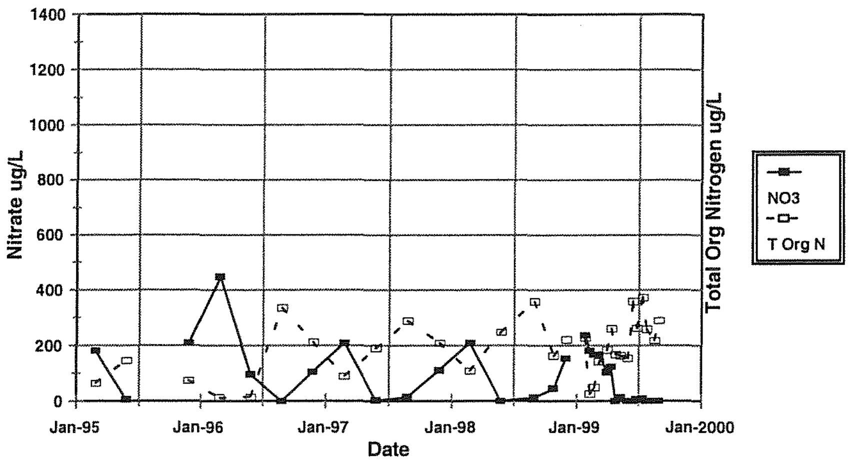

Loch Grannoch Inflow 2


Loch Grannoch Inflow 3

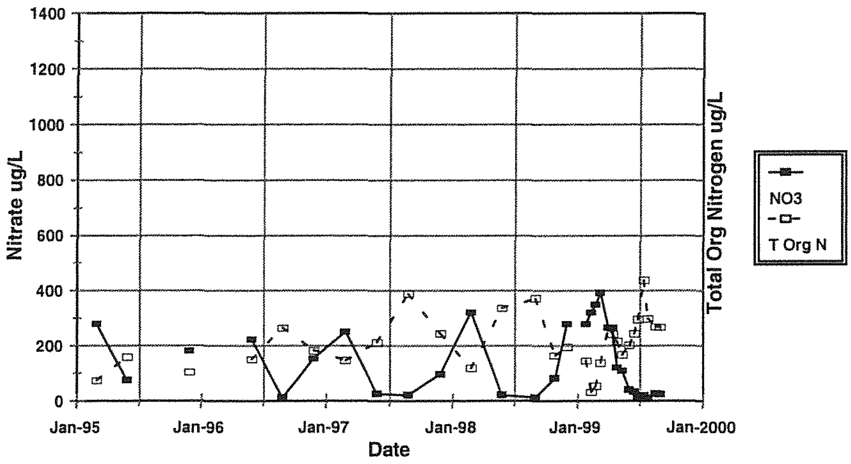
Loch Grannoch Inflow 4



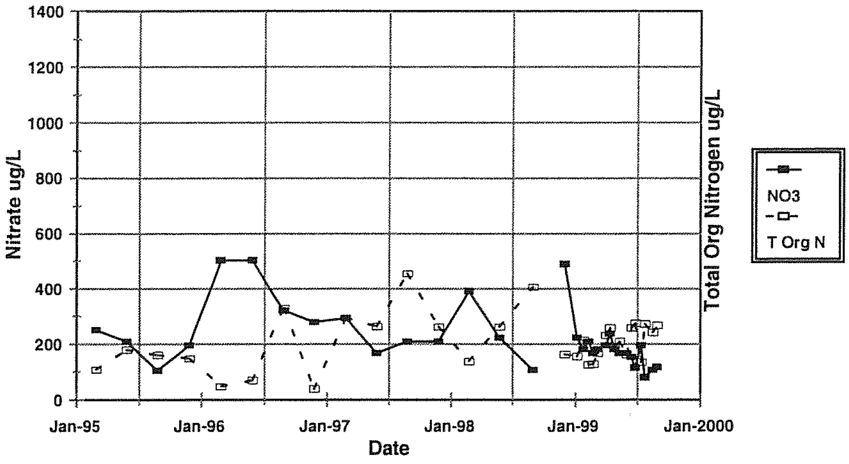
Loch Grannoch Inflow 5



Loch Grannoch Inflow 6



Loch Grannoch Outflow



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

Soil and surface water data for the purposes of MAGIC 7 development, testing and application have been compiled 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 South Pennines, a high deposition region. At a further sixty catchments in Wales, for which stream water chemistry has previously been measured as part of the Welsh Acid Waters Survey, organic soil samples were collected during June 1998. In Galloway, surface water sampling began in 49 lochs in 1979. These lochs 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 (where applicable) 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 ITE Merlewood. Data were then used to calculate catchment C/N ratios through a spatial weighting procedure. Pennine water samples were analysed at IH, and the Galloway loch samples were analysed at MLURI for a full set of chemical determinands.

Surface water data for the South Pennines (Table 8) indicate that this region is among the most acidified in the UK, with almost half of all sampled sites having a negative ANC, extremely high 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.* (in press) and Evans and Jenkins (in press).

Table 8. Summary data for sixty sampled reservoirs, South Pennines Survey

	pH	ANC	NO_3	NH_4	xSO_4	Ca	DOC	NO_3/xSO_4
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%
MEDIAN	**5.27**	**13**	**41**	**4.0**	**222**	**152**	**4.9**	**22%**
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%

The data collected in Galloway were used to investigate the significance of N deposition on the potential acidification of surface waters. Relationships between N deposition, soil C:N ratios, land use and surface water NO_3 concentrations were assessed. From these data it is apparent that a large number of catchments in this region were at a high risk from N leaching primarily due to low soil C:N ratios. High surface-water NO_3 concentrations in afforested catchments were associated with soil C:N ratios below 20. This relationship was not evident in moorland catchments where NO_3 leaching was strongly related to N deposition and the loch:catchment ratio, rather than the soil C:N ratio (Helliwell *et al.*, in press).

1.5 Use all data from all appropriate experimental and and monitoring sites to continue testing and developing both the mass balance model FAB and the dynamic model MAGIC7

The current formulation of MAGIC 7 assumes the relationship between N_{OUT}/N_{IN} and catchment C/N shown in Figure 10; Stored N deposition causes soil C/N to decline to a threshold value, C/N_{UPPER}, below which N begins to leak. As C/N falls further, N_{OUT}/N_{IN} increases linearly until it reaches a value of 1 (i.e. zero N retention) at C/N_{LOWER}. This relationship is based on plot-scale studies of European forest soils (Gundersen *et al.*, 1998), which also suggest a range of 10 between C/N_{UPPER} and C/N_{LOWER}. During MAGIC 7 calibration therefore, this range is held constant, and C/N_{UPPER} and C/N_{LOWER} allowed to vary, in order to match present day observed N_{OUT}/N_{IN} and C/N.

C/N and surface water chemistry data collected under Component 1.4, together with ITE Bush gridded N deposition estimates, have been used to assess the validity of the MAGIC 7 calibration procedure. Analysis of the Pennines and Welsh data (Figure 11) suggest that, on a regional scale, the relationships between N_{OUT}/N_{IN} and C/N do not reflect those derived from the plot-scale experiments. Neither region shows the clear inverse relationship expected, with a wide scatter in values of N_{OUT}/N_{IN} at any given C/N. There are indications that maximum values of N_{OUT}/N_{IN} do tend to occur at low C/N ratios, but since other low C/N sites retain virtually all N input there are clearly additional factors influencing N leaching.

The observed relationships between N leaching and catchment C/N raise concerns about the current calibration of MAGIC 7. In particular, there appear to be several potential problems with the extrapolation of C/N dynamics from forest plot scale to catchment scale:

(a) Data so far available suggest high spatial variability in C/N ratios. C/N estimates for the Pennine and Welsh sites are based on a small number of samples, and may not adequately reflect the true catchment C/N status.

(b) Most study catchments contain two or more soil types, each of which may have a different C/N – N leaching relationship. Combining these will generate a more complex relationship than that observed at the plot scale for a single soil type.

(c) Whereas the N content of forest organic horizons tends to be rapidly cycled, in some moorland soils (e.g. peats) much of the organic matter may be chemically inert. N contained in this inert material may not be involved in N cycling, in which case the C/N ratio of the bulk peat will not provide a suitable measure of the reactive N available for leaching.

Ongoing work at intensive study sites should help to clarify these issues. Organic soil sampling at a high spatial resolution will address within catchment variability in C/N, and measurements of poorly quantified fluxes such as denitrification and vegetation uptake will allow these to be better incorporated within the model. Work is in progress with regard to the calibration procedure, which will be altered and refined in light of results obtained during the programme.

This part of the programme will be completed after the field sampling period when data analysis has been carried out (Winter 2000/01). The results from the field programme will feed directly into FAB model development.

Figure 10. Theoretical relationship between soil C/N and N input/output used for MAGIC 7 calibration

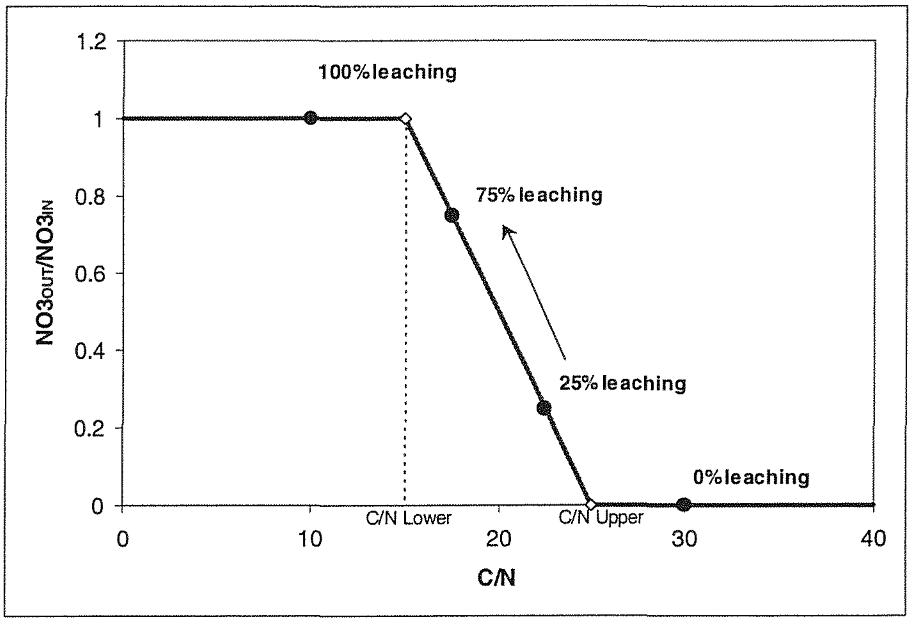
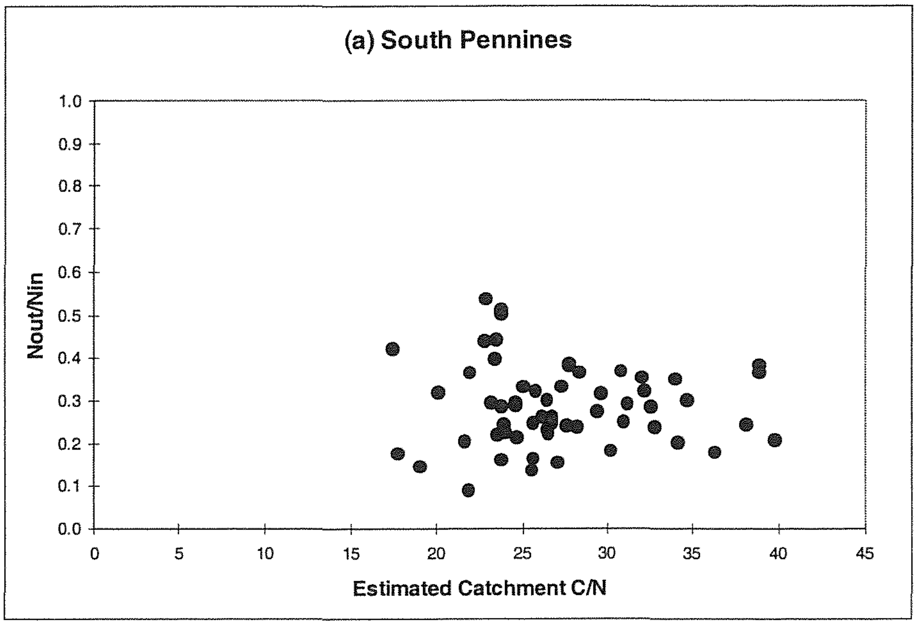
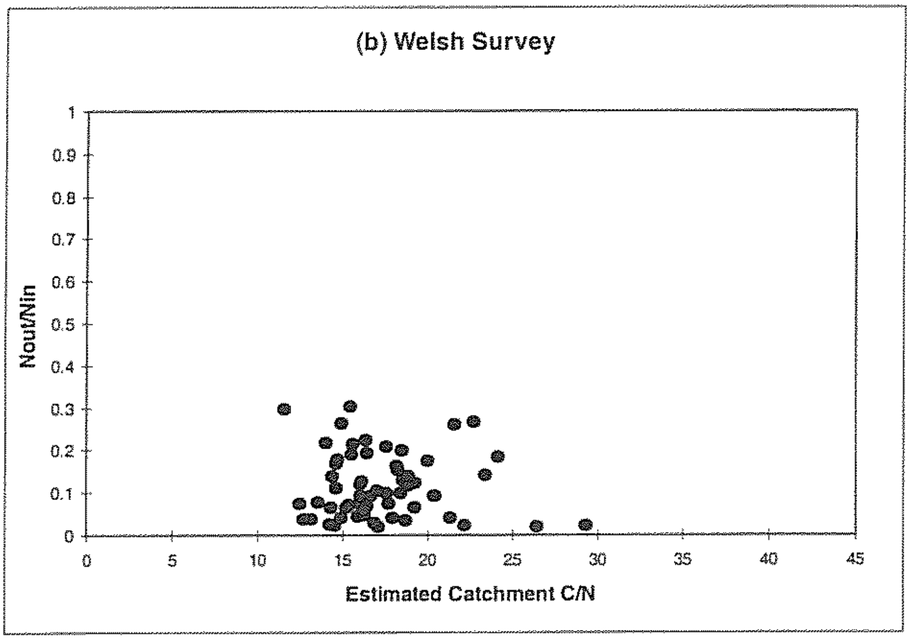


Figure 11. Observed relationships between catchment soil C/N and N input/output fluxes, South Pennines and Wales.




(b) Welsh Survey
Nout/Nin
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
5
10
15
20
25
30
35
40
45
Estimated Catchment C/N

1.6 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

This part of the programme will be completed after the field sampling period when data analysis has been carried out (Winter 2000/01). The results from the field programme will feed directly into FAB model development.

Additionally, work linking FAB and MAGIC 7 will commence following the completion of Work Package 1.5. MAGIC 7 parameterisation will be matched to that of FAB in order to provide an estimated timescale for attainment of FAB steady state conditions.

2.2 Run MAGIC7 on both a site specific and regional mode

Site specific MAGIC 7 applications are currently being undertaken for the Acid Waters Monitoring Network sites following the collection of site C/N data during the last twelve months. The model will also be applied to the N budget sites (Work package 1.4), utilising detailed information on N fluxes to refine the calibration procedure once these data become available.

Regional MAGIC 7 applications have been undertaken for the Welsh, Pennines and Galloway datasets. For calibrated sites in each region, future changes in surface water chemistry have been modelled using HARM deposition forecasts based on the Second Sulphur Protocol. Modelled ANC and NO_3 for the present day and 2050 are shown in Figures 12-14. In the South Pennine region, modelling suggests that NO3 concentrations will rise substantially. However, large concurrent decreases in SO4 are expected to lead to an overall recovery in ANC. In Wales, where deposition levels are currently lower, increases in NO3 are expected to be smaller, and again reductions in SO4 should lead to some ANC recovery. In Galloway some recovery in surface water ANC across the region is predicted. There is a distinct spatial pattern with the more acidified, low ANC sites clustering in high altitude areas dominated by base poor granitic geology. However, it is these high altitude sites with low ANC which show the greatest recovery in 2047. Although a recovery in surface water NO3 was apparent in 2047, this subtle change from 1997 to 2047 was not evident for the majority of sites in the Galloway region (Figure 14). HARM scenarios for the recently signed UNECE multi-pollutant protocol have recently become available, and will be used for further MAGIC 7 applications within the next six months.

Given the uncertainties in model calibration identified under Work Package 1.5, current MAGIC 7 forecasts are likely to be refined as work progresses. However, a parallel application of the original MAGIC model to the Pennine region provides support for the underlying assumption of nitrogen breakthrough in MAGIC 7. MAGIC uses a fixed ratio of N_{OUT}/N_{IN} to determine NO_3 runoff at each time step, and thus does not include a breakthrough term. This results in generally higher hindcast NO_3 simulations compared to those in MAGIC 7 (e.g. Figure 15). The increased historic N loss under MAGIC requires an associated high level of soil base cation desorption, but at many acidic, high nitrogen sites in the Pennines this is inconsistent with present day observed soil and surface water base cation levels. As a result, 14 of the most acidic Pennine sites could not be calibrated using MAGIC. Similar problems were encountered with the application of MAGIC to acidic high-N sites in the national CLAG dataset (Evans *et al.*, 1998), and these results demonstrate the necessity for a breakthrough component in the dynamic modelling of nitrogen. It is therefore essential that the more advanced nitrogen simulation in MAGIC 7 should continue to be developed.

Figure 12: MAGIC 7 Application to the South Pennines

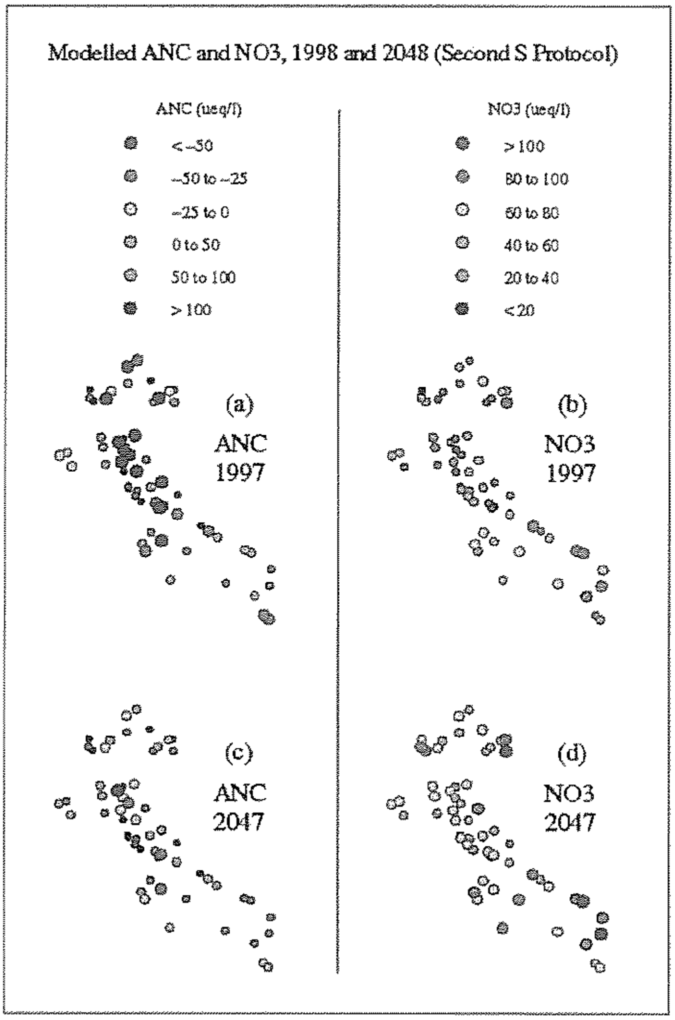


Figure 13: MAGIC 7 Application to Wales.

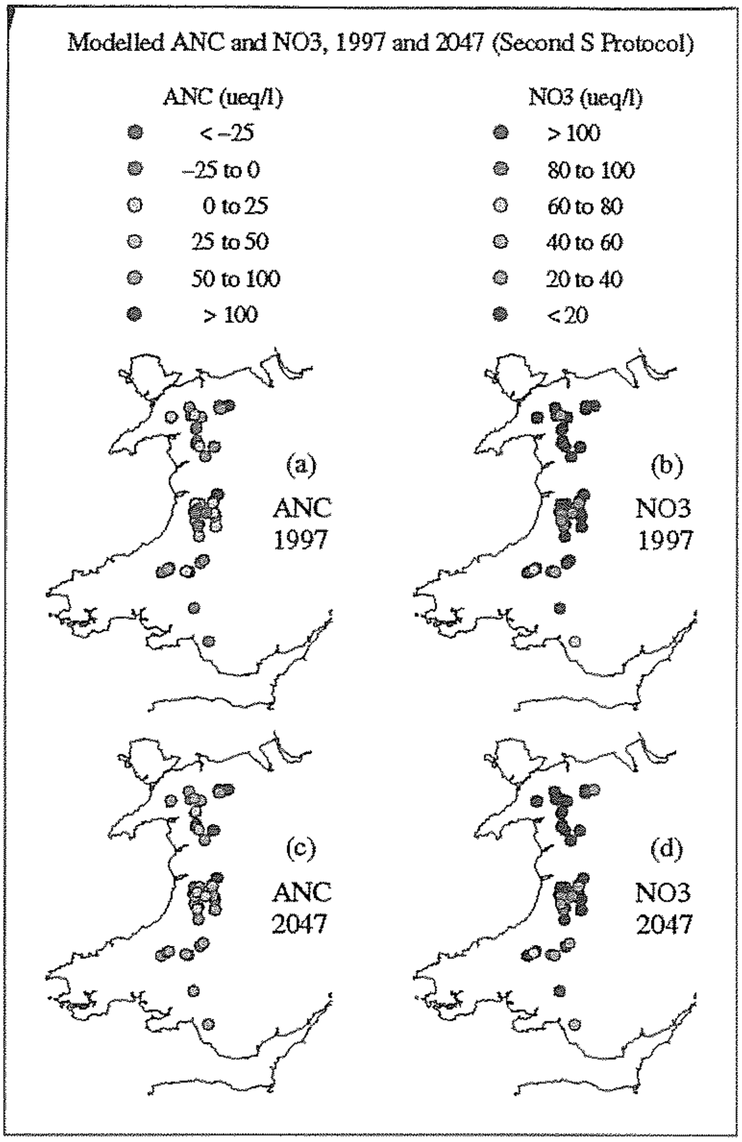


Figure 14. MAGIC 7 application to Galloway

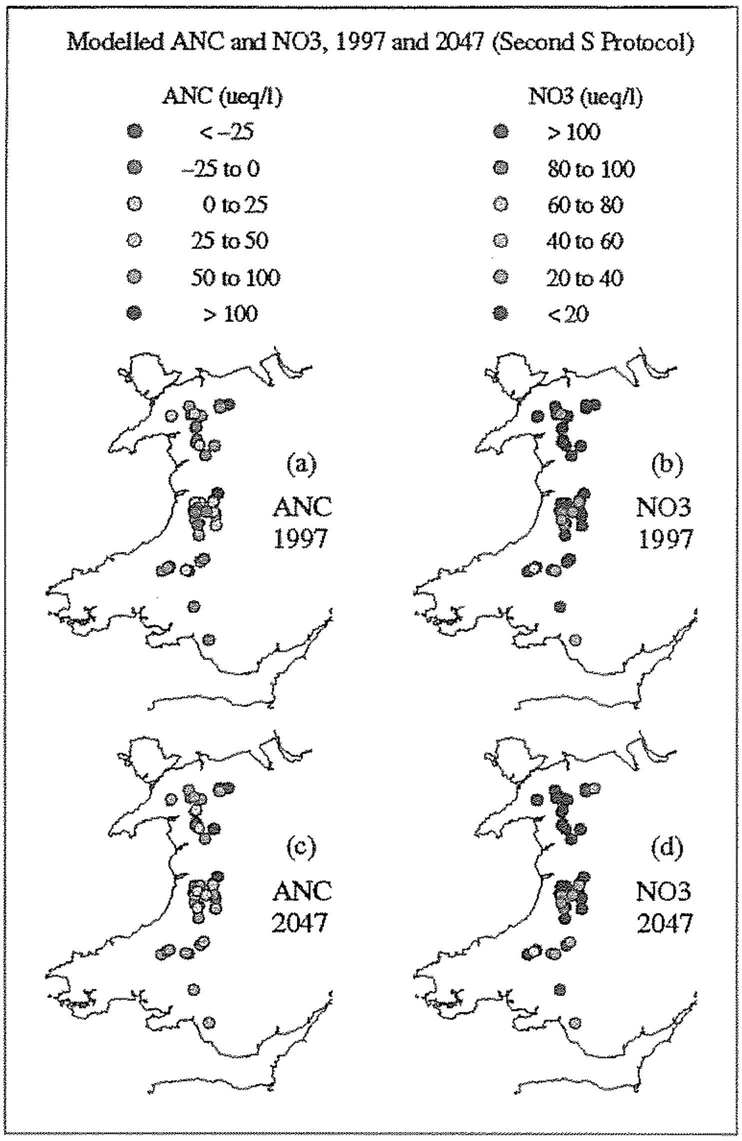
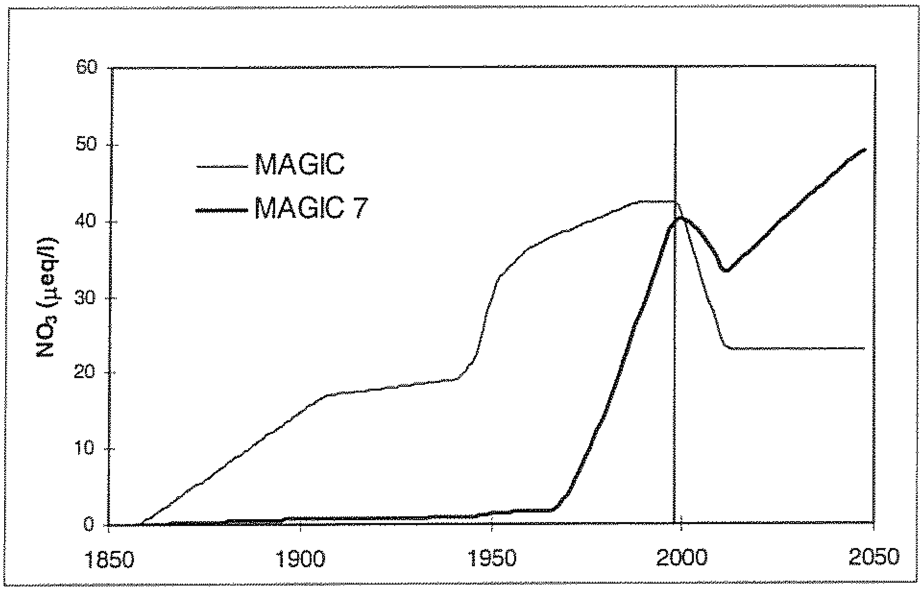


Figure 15. Comparison of NO_3 simulations using MAGIC and MAGIC 7 at Gorpley Reservoir, South Pennines (forecasts based on 2^{nd} Sulphur Protocol)



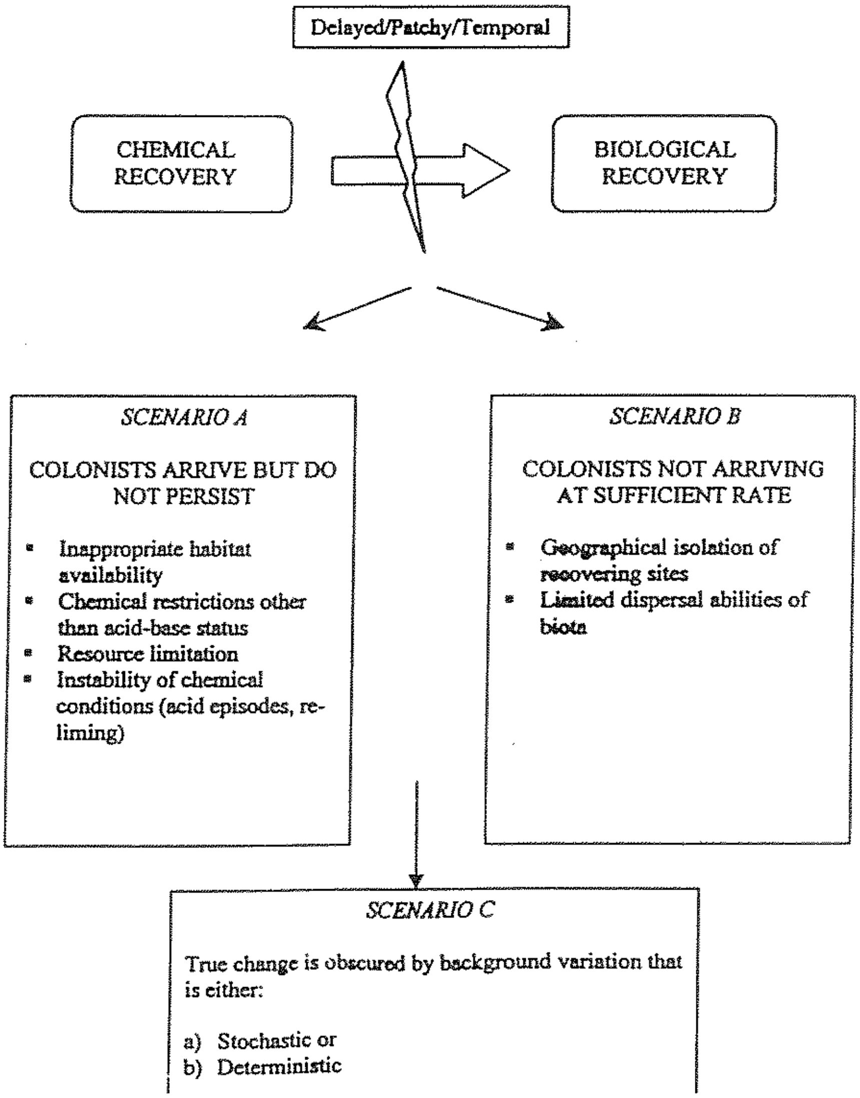
2.3 Complete a desk review of ecological information available on the concepts, rates, timing, mechanisms and constraints on biological recovery in aquatic ecosystems affected by large scale disturbance

Understanding biological processes of recovery is central to understanding how aquatic ecosystems will respond to deposition reduction. Contrasting schools of thought indicate:

i) that chemical remediation is sufficient to allow biological recovery,
ii) that other processes might interfere to cause hysteresis or shortfalls in biological recovery,
iii) that chemical changes associated with recovery (i.e. reduced base cation concentrations) will be damaging in their own right.

A draft review of processes affecting biological recovery was completed early in the programme. Drawing on published experience at Welsh sites at Llyn Brianne and in the Welsh Acid Waters Survey (e.g Rundle *et al.* 1995), the review outlines why mismatches between biological and chemical recovery can sometimes occur (Figure 16). However, new developments from the long-term analysis of Llyn Brianne data (see 2.2.1, below) reveal additional complications about recovery, so that completion of the review is being deferred until understanding is clearer.

Figure 16. Three scenarios under which chemical recovery will not lead to biological recovery from acidification.



2.4 Assess the value of analogues in defining target communities for recovery of acidified waters

A desk review has been prepared which examines the assumption that pre-acidification conditions act as suitable targets for lake restoration and evaluates the usefulness of analogue sites as ecological targets. A copy of this has been submitted to DETR.

Summary and Recommendations

i) Palaeolimnological techniques have been widely employed to study lake acidification. This approach has been central in testing the cause-effect relationship between acid deposition and lake acidification, and in assessing the magnitude and extent of surface water acidification across the UK.

ii) Most of these palaeolimnological applications have been based on diatom analysis and the use of diatom-pH transfer functions to reconstruct hydrochemical change in upland lakes associated with acidification.

iii) Following the signing of the Second Sulphur Protocol, attention is now focusing on emissions reductions and the reversibility of surface waters acidification. There is a clear need for criteria against which to evaluate the recovery process.

iv) In order to evaluate future recovery, Flower *et al.* (1997) have proposed a palaeolimnological technique for defining targets for the recovery of acidified surface waters. This is based on the technique of analogue matching of lake sediment diatom assemblages. Multivariate statistical methods are used to identify modern analogues for the pre-acidification diatom assemblages of acidified lakes. The chemical and biological status of modern analogue lakes can then potentially provide recovery targets for acidified systems.

v) This approach has been successfully applied to several acidified lakes, and modern analogue systems defined for the pre-impact (pre-acidification) status of these impacted sites. An advantage of the approach is that it can provide recovery targets for both chemical and biological status of acidified lakes.

vi) Modern analogue matching as currently applied makes several key assumptions:

> (a) that analogue matches based on a single biological group (diatoms) effectively represent the hydrochemical and biological variation of low alkalinity systems;
> (b) that the modern datasets used to identify modern analogues contain the range of hydrochemical conditions represented by the fossil assemblages;
> (c) that a suitable stable 'baseline' (pre-impact) status can be defined.

vii) Prior to more comprehensive application of the modern analogue approach to acidified lakes in Britain, these assumptions require evaluation. Three studies are required.

(a) Extension of the current modern lake dataset used for analogue matching by the inclusion of minimally impacted low alkalinity sites from northern Scotland.

(b) Development of the current technique by including two more fossil groups (chironomids and clodocera) in the modern surface sediment dataset used in the matching procedure. This will allow the assumption that diatoms represent wider ecosystem variation to be tested, and should result in more robust analogue matches.

(c) A study of hydrochemical and biological variation in the pre-acidification conditions of acidified lakes through high-resolution palaeolimnological study of selected Acid Waters Monitoring Network lakes. This will allow the stability of baseline (pre-acidification) conditions to be evaluated.

2.5 Where appropriate, assess composition of target communities by the study of selected analogue streams and lakes in non-acidified regions

Following the completion of the desk review (workpackage 2.4) it was apparent that to apply this approach there would be a need to build on existing datasets (see above). Within the period of this contract it is proposed to develop the modern analogue approach by including chironomids and cladocera in the analyses (see (vii) (b) above) and extend the current modern analogue dataset by including low alkalinity sites from Northern Scotland (see (vii) (a) above).

2.6 Develop and analyse the data in the CLAG and national chemical-biological databases to improve the understanding between fish, birds, invertebrates, aquatic macrophytes, diatoms and chemistry

Critical loads are defined as "the highest deposition of acidifying compounds that will not cause chemical change leading to long-term effects on ecosystem structure and function" (Nilsson and Grennfelt 1988). By definition, our ability to predict the biological implications of different levels of critical load exceedance, and to set target loads to allow biological recovery, depends on a detailed knowledge of the relationships between water chemistry and biological communities. These relationships could be generated by field or laboratory experiment, but in either case the generation of sufficient data to relate the large number of potential biological targets to the full range of water chemistry parameters would be a vast undertaking. An alternative method is to derive statistical relationships between biological status and chemical conditions empirically, using field survey data collected from a range of sites spanning the appropriate chemical gradients (Ormerod 1994).

To this end, an important aspect of the biological modelling work has been the development of a high quality chemical – biological database focused on diatoms and invertebrates. These groups of organisms are ubiquitous in freshwaters, they are relatively easy to sample and identify, and they are extremely sensitive to changes in acidity status (Battarbee 1984; Ormerod and Edwards 1987). They are thus excellent "indicator" groups for assessing freshwater acidification status.

This report describes progress in developing the CLAG chemical – biological database, and presents an analysis of diatom and invertebrate assemblage distribution in relation to chemical parameters using the Welsh Acid Waters Resurvey dataset.

Database Development

Data Sources

The CLAG chemical – biological database has been assembled by merging existing datasets from previous CLAG contracts and wil incorporate new data collected during the current contract. All data were required to meet the AQC criteria concerning sampling techniques, chemical and biological analyses used in the UKAWMN (Patrick *et al.* 1991). After screening, four datasets with matching chemical, diatom and invertebrate data have so far been incorporated in the database. These are listed in Table 9.

These data are currently stored as a series of tables in a relational database managed using Microsoft Access97 software. All biological data are stored using the analyst's original determinations and taxonomic nomenclature. However, as different analysts frequently work to different taxonomic levels, and use different naming conventions for diatom and invertebrate data, a process of taxonomic harmonisation was carried out prior to merging the datasets. This involved screening the individual taxon lists for synonyms and differing levels of taxonomic resolution between datasets. All datasets, with the exception of WAWS have been taxonomically harmonised using this procedure. Current work is focussing on harmonisation of the WAWS data.

Table 9 Data sources for the CLAG biological – chemical database

Dataset	*Source*	*Sampling Date*	*N*	*mean pH*	*min pH*	*max pH*
Scot Base	Scottish Baseline Survey (Doughty 1989).	1986	144	6.70	4.42	8.49
UKAWMN	UKAWMN Survey Data Stream sites	1990-92	33	5.52	4.53	6.68
IF / OF	Inflow / outflow validation study, this contract	1996	31	5.97	3.70	7.05
Sea Salt	Sea salt study, this contract	1996	17	5.77	4.89	6.98
WAWS	Welsh Acid Waters Resurvey	1995	118	6.21	4.0	8.29
Total			**343**	**6.03**	**3.7**	**8.49**

Species – environment relationships

Canonical correspondence analysis has previously demonstrated the strength and statistical significance of pH, total monomeric aluminium, conductivity and chloride in determining patterns of species distributions in the merged diatom and invertebrate datasets. Prior analysis also used Gaussian logistic regression to identify individual diatom and invertebrate taxa that showed significant relationships with pH. This analysis was also used to develop response models that could be used to predict individual taxon occurrence and abundance from mean stream-water pH.

In this report we explore an alternative approach to the analysis of species / environment relationships using the recently obtained Welsh Acid Waters Resurvey dataset, and focus on the distribution and prediction of diatom and invertebrate communities, rather than individual taxa.

This section presents results of a preliminary classification of the WAWS diatom and invertebrate data and relates the distribution of these to their chemical and physical environment using generalised additive modelling (GAM) and classification and regression tree (CART) techniques.

All chemical variables except pH were $\log_{10}$ transformed prior to analysis as they showed highly skewed distributions. Abundances of diatom and invertebrate taxa were expressed as relative proportions of the total assemblage. The WAWS dataset contains 102 stream sites and 16 lake sites. Only stream sites were used in this analysis as lake data were unavailable for invertebrates.

Classification of diatom and invertebrate communities

Diatom and invertebrate communities were classified using the method of two-way indicator species analysis (TWINSPAN, Hill 1979). Results identified a total of five diatom and five invertebrate assemblage groups. The distribution of common taxa across the groups is listed in Appendices 1 and 2. Tables 10 and 11 summarise each group according to their dominant taxa.

Table 10 Description of TWINSPAN diatom groups according to dominant taxa

Group No.	Dominant Taxa
1	*Eunotia exigua, Achnanthes austriaca var. helvetica*
2	*Eunotia vanheurckii var. intermedia, Eunotia exigua, Peronia fibula*
3	*Tabellaria flocculosa, Eunotia exigua, Achnanthes minutissima*
4	*Achnanthes minutissima, Diatoma hyemale*
5	*Achnanthes minutissima, Cocconeis placentula, Gomphonema spp.*

Table 11 Description of TWINSPAN invertebrate groups according to dominant taxa

Group No.	Dominant Taxa
1	*Amphinemura sulcicollis, Leuctra nigra*
2	*Leuctra inermis, SIMIULIIDAE, Amphinemura sulcicollis*
3	*Isoperla grammatica, Leuctra inermis, CHIRONOMIDAE*
4	*Baetis rhodani, Rithrogena semicolorata, Leuctra inermis*
5	*Rithrogena semicolorata, Baetis rhodani, Gammarus pulex*

Relationship between diatom and invertebrate community types to their chemical and physical environment

The relationship between the TWINSPAN-derived diatom and invertebrate community types and their chemical / physical environment is visualised using simple graphical analysis. Figures 17 and 18 show, for each dataset, boxplots of key physico-chemical parameters by community type.

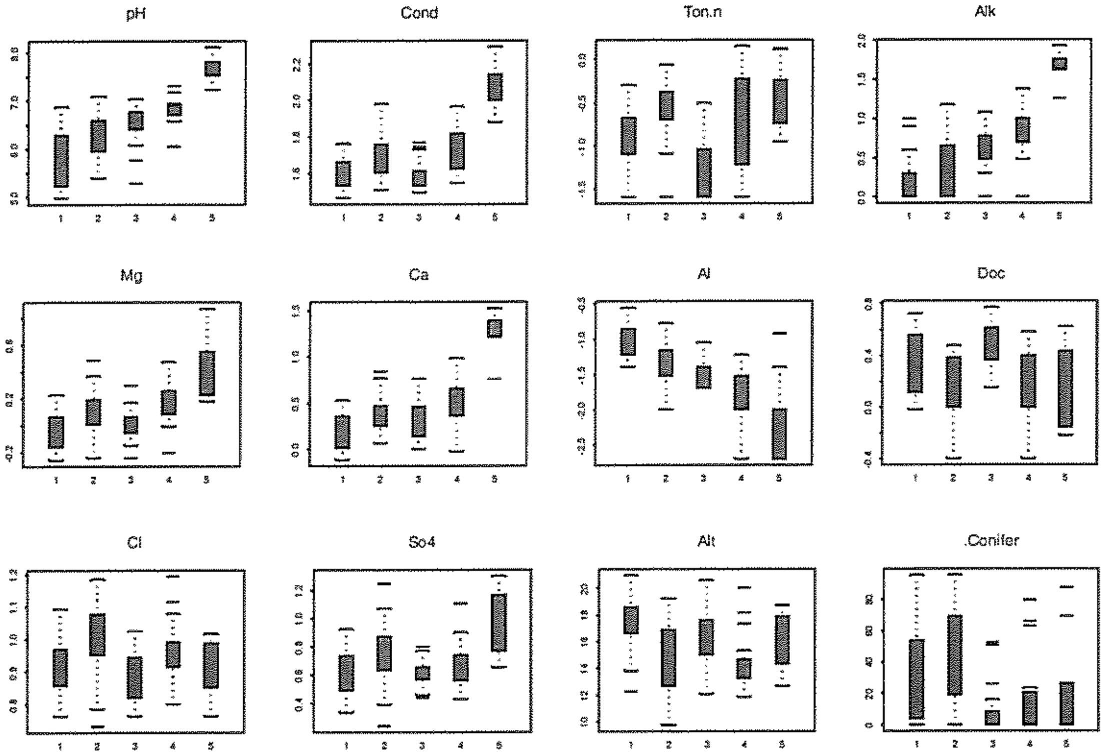


Figure 17. Boxplots of selected physico-chemical parameters against diatom community types

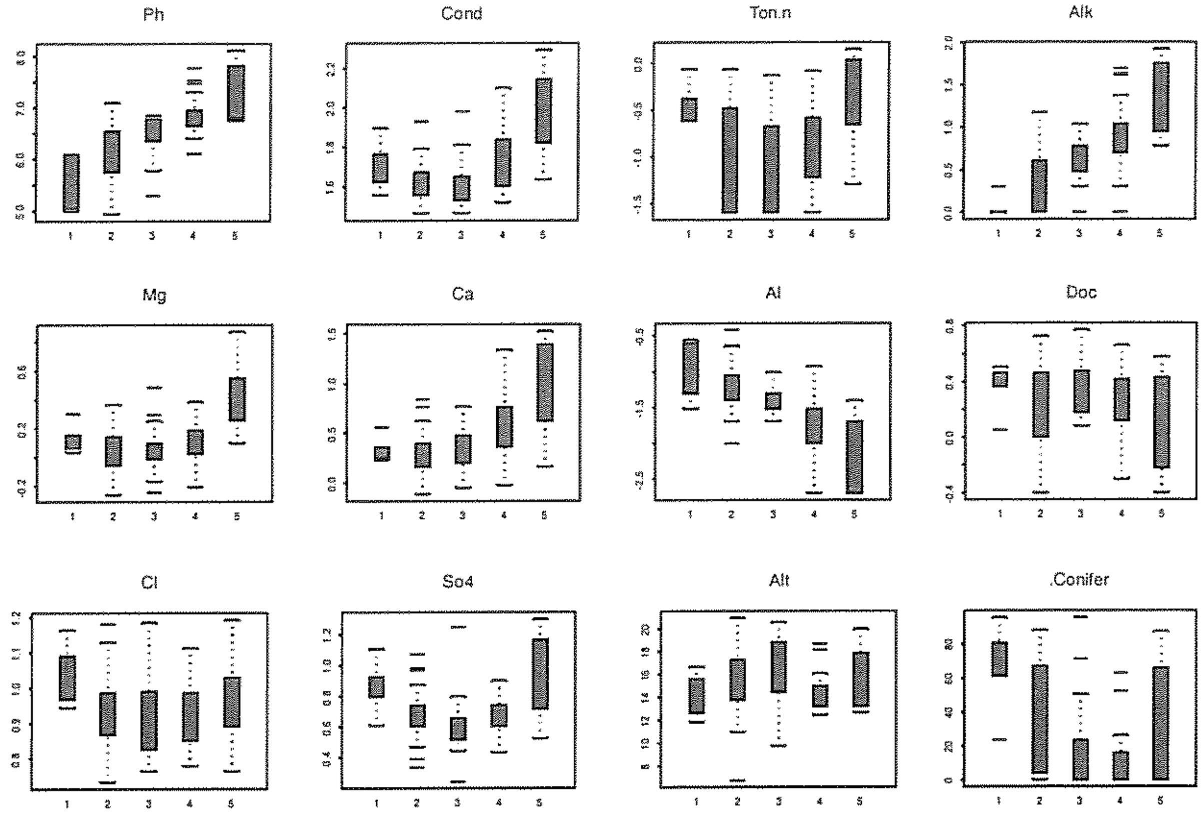


Figure 18. Boxplots of selected physico-chemical parameters against invertebrate community types

As might be expected, diatom communities show a strong relationship to stream-water pH, alkalinity, total organic nitrogen (Ton.n) and aluminium. DOC does not appear to be a determinant of community distribution in this dataset. Similarly, stream-water pH, alkalinity, and aluminium are also major determinants in influencing the distribution of invertebrate communities. Total organic nitrogen and DOC also appears to be an important factor in the distribution of invertebrate group 1.

Predicting the occurrence of diatom and invertebrate communities using physico chemical data

One of the main aims of the biological database work is to develop predictive models that relate the distribution of plants and animals to their chemical and physical environment. Results of section 3.1 show that the WAWS biological datasets can be summarised into a series of distinct and spatially persistent diatom and invertebrate communities. Furthermore, the exploratory analysis of 3.2 shows that the distribution of these communities is strongly related to their chemical environment. In this section we develop simple models to quantify these relationships.

Figures 19 and 20 show the predicted occurrence of the five diatom and invertebrate TWINSPAN community types respectively, modelled in relation to mean stream-water pH using a generalised additive model (GAM). This approach is an extension of generalised linear modelling used previously (e.g. Juggins *et al.* 1995), and has the major advantage in being able to fit non-linear and non-symmetric response curves.

The fitted response curves show the succession of community types with increasing pH, and can be used to (1) predict the probability occurrence of each community type at a given pH, or to (2) predict the chemical conditions necessary to sustain a given community type, or to (3) predict the pH change needed to achieve a replacement of one community type by another.

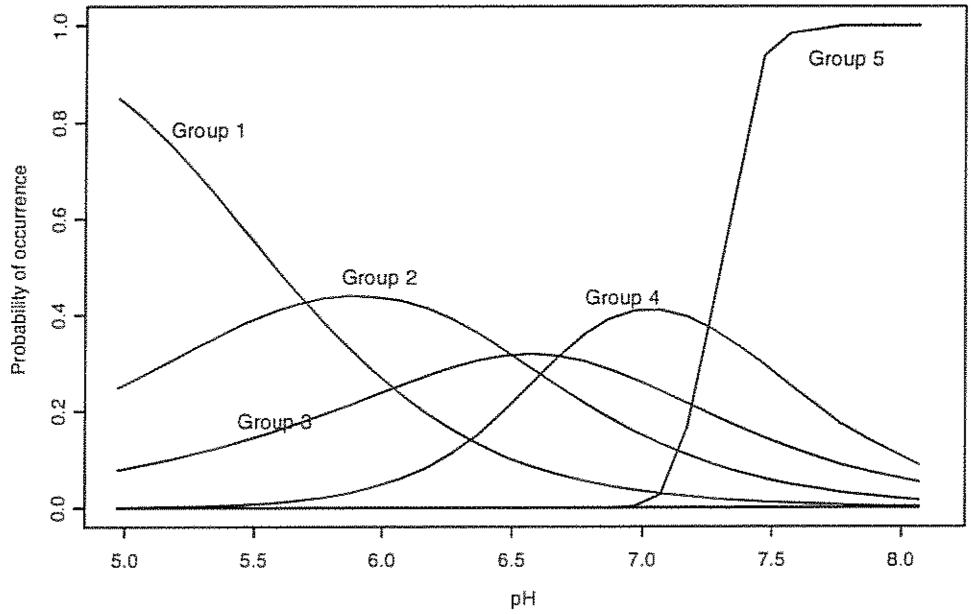


Figure 19. Predicted occurrence of TWINSPAN diatom groups vs. stream-water pH

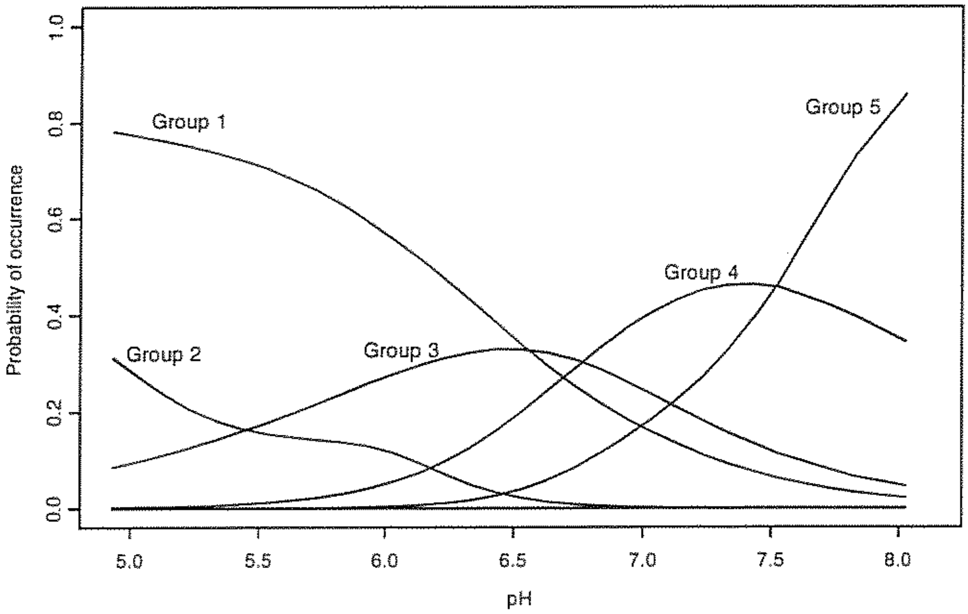


Figure 20. Predicted occurrence of TWINSPAN invertebrate groups vs. stream-water pH

The above analysis and previous work has demonstrated that stream-water acidity is the dominant parameter controlling the distribution of diatom and invertebrate taxa and communities. However, it also suggests that other variables are important in determining biological distributions in acid waters. While it is possible to extend the GAM modelling to include additional parameters, this approach is problematic, given the relatively small size of the WAWS dataset. An alternative approach uses decision trees to identify important chemical parameters that can be used to build a classification function for predicting community type. Figures 21 and 22 show results from this analysis in the form of classification trees. Details of the method are given in Hand (1991), and Bell (1996) shows an ecological example.

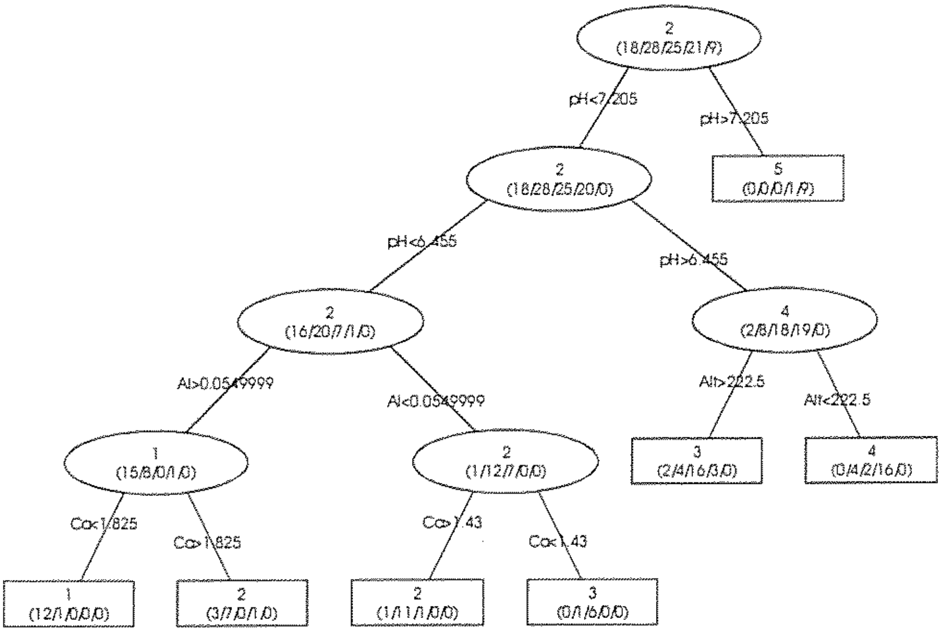


Figure 21 Classification tree for TWINSPAN diatom groups

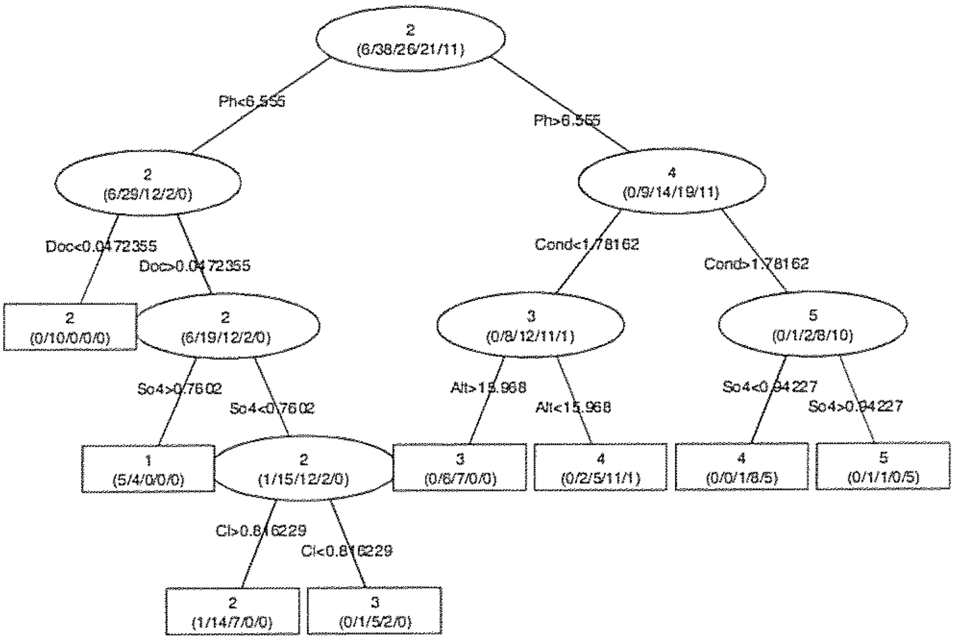


Figure 22 Classification tree for TWINSPAN invertebrate groups

The classification trees show a hierarchical decision tree with majority group number and group membership at each level (ellipses) and final group membership (rectangles), together with key variables and criteria (ie. decision rules). For diatoms, four chemical variables are selected and used to classify sites into one of the five community types: pH, Ca, aluminium, and altitude. For invertebrates six variables are used: pH, DOC, SO4, Cl, conductivity, and altitude.

The predictive ability of the classification trees is best assessed through the so-called confusion matrix of observed group vs. predicted group. These are shown in Tables 12 and 13. Results show the models perform well, with 77 of the 101 diatom sites allocated to the correct diatom group using the three selected chemical parameters and site altitude. Performance is slightly worse for the invertebrate data, with 65 of the 102 invertebrate sites being correctly classified.

Table 12 Confusion matrix for diatom classification tree results

	Actual group				
Predicted Group	1	2	3	4	5
1	12	1	0	0	0
2	4	18	1	1	0
3	2	5	22	3	0
4	0	4	2	16	0
5	0	0	0	1	9

Table 13 Confusion matrix for invertebrate classification tree results

	Actual group				
Predicted Group	1	2	3	4	5
1	5	4	0	0	0
2	1	24	7	0	0
3	0	7	12	2	0
4	0	2	6	19	6
5	0	1	1	0	5

Conclusions

1. Diatom and invertebrate counts, together with associated water chemistry and catchment data have been added to the CLAG biological database. Taxonomic harmonisation of these data is underway as a prerequisite to combined species - environment modelling using the entire merged dataset.

2. Preliminary classification of the WAWS data identified five diatom and five invertebrate groups, or community types. Exploratory analysis showed that the distribution of these assemblages is strongly related to stream-water acidity (and its correlates), total organic nitrogen, and DOC.

3. Generalised additive modelling was used to relate the occurrence of each community type to mean stream-water pH. The fitted models provide a quantitative description of the distribution of each community type in relation to pH, and can be used to predict the probability of occurrence of each community, or to predict the pH necessary to sustain a particular community.

4. Classification trees were used to explore the extent to which community type could be predicted from simple functions of multiple chemical parameters. For diatoms, the correct community type could be predicted from pH, Ca, Al and site altitude for 76% of sites. For invertebrates 64% of sites could be correctly predicted using six environmental parameters.

5. Future work will focus on (1) taxonomic harmonisation of the WAWS data, (2) continued development of predictive species and community response models using the expanded, combined dataset, and (3) linking the biological models to chemical predictions to produce mapped predictions of taxon and community occurrence under various abatement strategies.

2.7 Evaluate the importance of hysteresis, stochasticity and episodicity in delaying and detecting change

Stochasticity

Initial ideas on this item were that year-to-year variations in the stability of invertebrate communities in upland streams represented stochastic variations. These, in turn, were larger than trends apparently due to 'recovery' evident from the Welsh Acid Waters Survey (WAWS). However, in parallel with assessments from the UK Acid Waters Monitoring Network, there is now evidence that long-term biological cycles might be occurring in upland British streams. They are large, and occur independently of trends in stream chemistry. They occur across all stream types (circumneutral, acid, moorland, forest). These cycles, apparently driven by climate, have major ramifications for the detection of recovery and the interpretation of previous data (e.g. on the effects of liming (Rundle *et al.* 1995).

This item has formed the bulk of work of the Cardiff group. It shows:

- Year-to-year patterns in invertebrate species abundance, species richness and stability follow an approximately decadal cycle.
- The pattern is common to nearly all the experimental catchments at Llyn Brianne - irrespective of differences in land use and chemistry; this indicates a supra-catchment influence on inter-annual variation.
- The only streams not showing the cycle were those affected by liming, indicating that one of the major liming effects on invertebrates was to disrupt natural trends.
- Cyclical patterns are equally apparent across stream-habitats, and in common vs rare taxa; this indicates it is a large community-wide effect.
- Measures of stability, persistence and composition in invertebrate communities at Llyn Brianne do not vary more or less with increasing elapsed time, so that there is no evidence of further deterioration or recovery from acidification.

What drives long-term invertebrate cycles in upland streams at Llyn Brianne ?

We have examined a range of hypotheses, including intermittent drought effects and longer-term climatic effects. Current indications are that:

- The winter North Atlantic Oscillation index (NAO) is significantly correlated with invertebrate stability and persistence for all streams combined, but relationships are strongest for circumneutral streams and acid-forest streams (Figure 23);
- Significant relationships with chemistry or hydrological pattern are not marked, and, while they might be involved, do not appear to provide the major NAO effect.

Papers on this work for major international journals are now being prepared on the following themes:

i) Stability and persistence of upland aquatic invertebrates and the effect of the NAO.
ii) The effects of liming on long-term invertebrate cycles in upland streams.

iii) Consequences of long-term invertebrate cycles for the detection of recovery from acidification and other trends

Episodicity

This work aims to advance our understanding on the role of episodes in offsetting or affecting biological recovery.

Work to evaluate the effects of episodes was undertaken during summer 1999. It involved experimental transplantation experiments with two mayfly species, *Ephemerella ignita* and *Baetis rhodani*. These species are both absent from acid streams, and their absence is a classical indicator of acid conditions. The factorial design has involved transplanting between a range of streams (acid, neutral, limed), with contrasting food quality (sourced from acid, neutral and limed streams) and under contrasting flow conditions (summer dry weather flow, summer wet-weather flow). The results show that:

- Both *E. ignita* and *B. rhodani* are able to survive in large numbers - even in acid streams - at typical dry-summer flows.
- Moreover, both *E. ignita* and *B. rhodani* were able to survive in either acid or neutral streams with typical food available from acid streams.
- At wet-weather flow, mortality in *B. rhodani* was dramatically increased in acid streams (Tywi; Figure 24), although survivors still reached emergence. *E. ignita*, by contrast, was still able to survive to emergence.

Together, these data support the hypothesis that stream chemistry (rather than food quality) limits the occurrence of some mayflies in acid streams. The data confirm also the importance of acid episodes in preventing the survival of *B. rhodani*. However, the contrast between *E. ignita* and *B. rhodani* indicate that limits on occurrence are inter-specifically variable for reasons that are not currently undertood. Severity and frequency of episodes may be important. Moreover, continued episodicity might be sufficient to offset recovery.

A manuscript describing the results of this work is currently in preparation.

Figure 23 Long-term trends in average invertebrate community persistence in streams at Llyn Brianne in relation to the winter NAO.

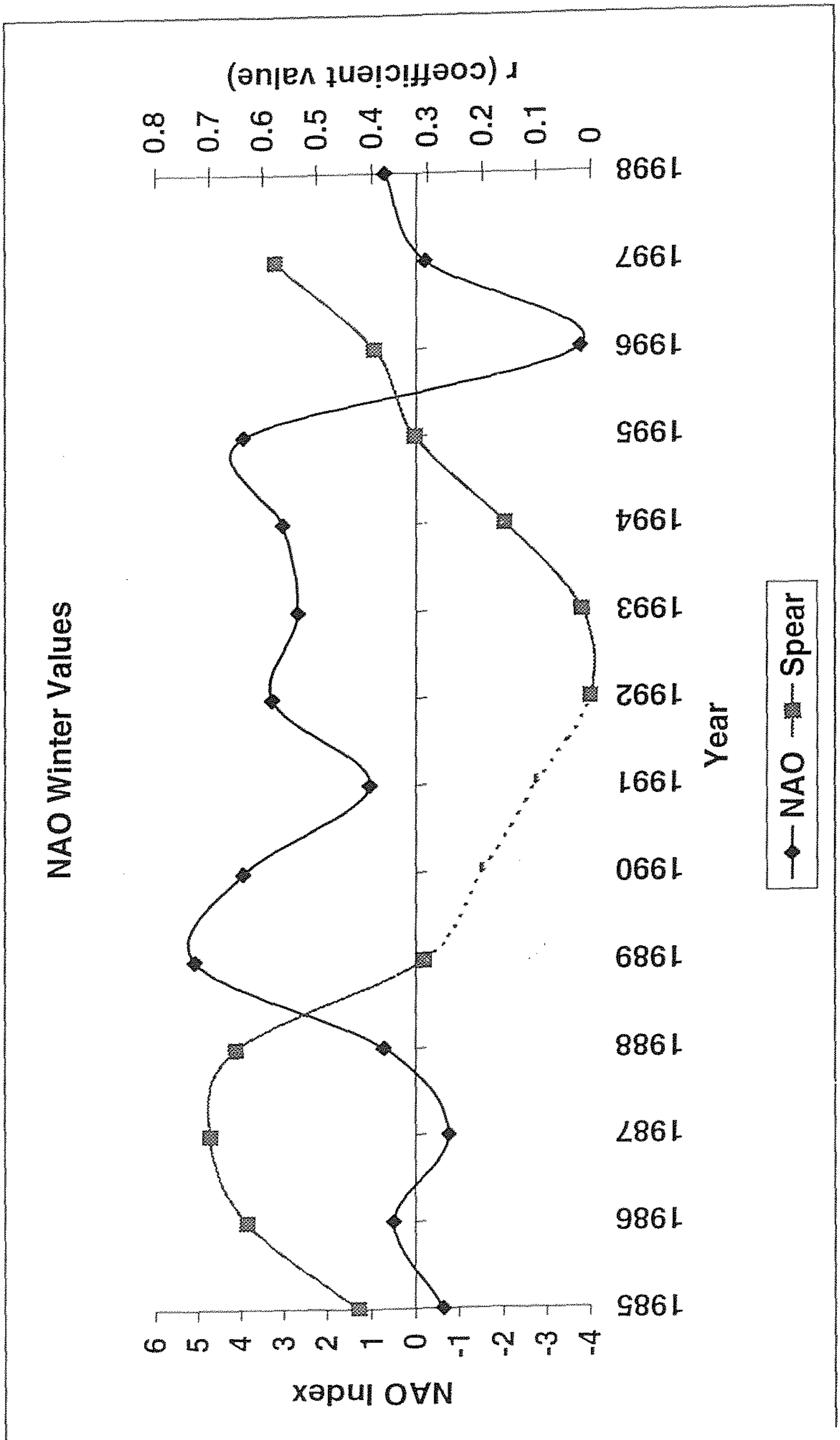
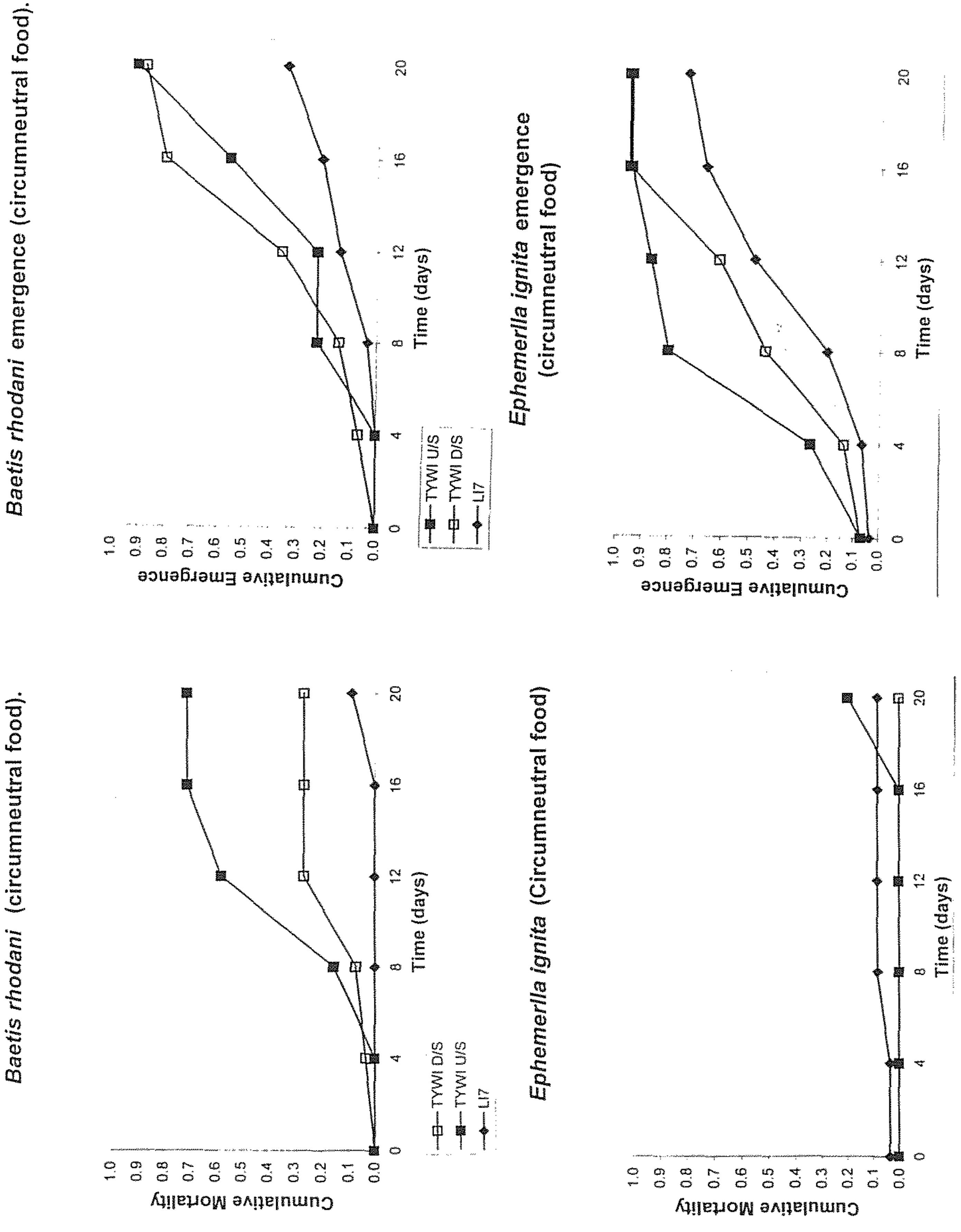


Figure 24 Survival and emergence patterns in two mayfly species in streams at Llyn Brianne following factorial transplantation. All data refer to summer-wet periods.



2.8 Develop linked hydrochemical-biological models to predict biological outcomes from MAGIC7 and other dynamic models

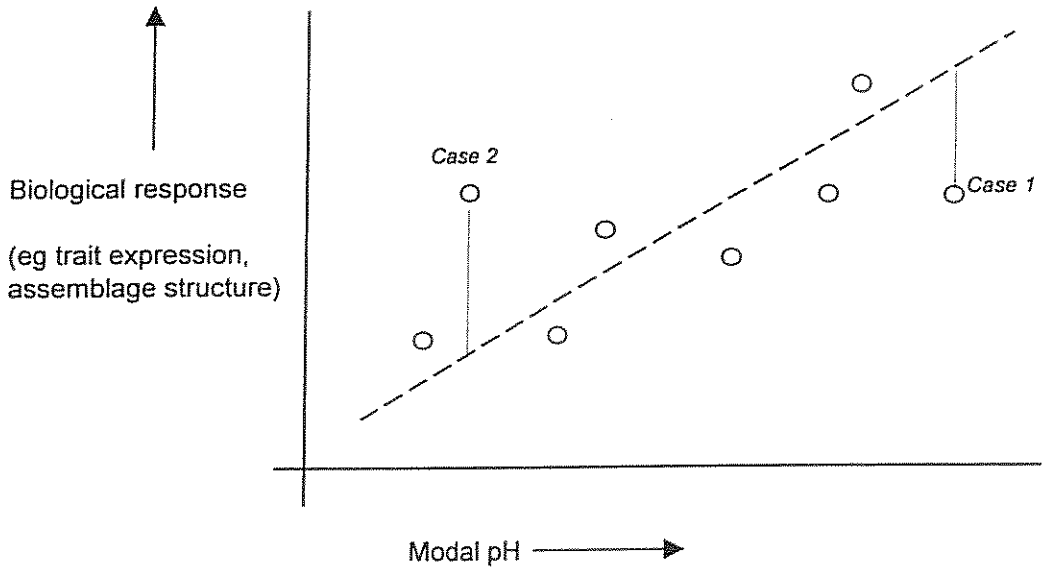
Work on other parts of the contract have taken precedence over further developments to linked hydrochemical models. However, as reported previously we now have a statistical method for incorporating episodes into biological models. It involves examining differences for model chemistry (Figures 25a and 25b). This incorporation will form the next step.

Additionally MAGIC 7 will be used to provide biologically relevant indicators, identified by those working on components 2.6 and 2.7, for linkage to biological models.

Work on this part of the programme will recommence during 2000.

Figures 25 a and b. Conceptual developments for incorporating acid episodes into linked hydrochemical-biological models.

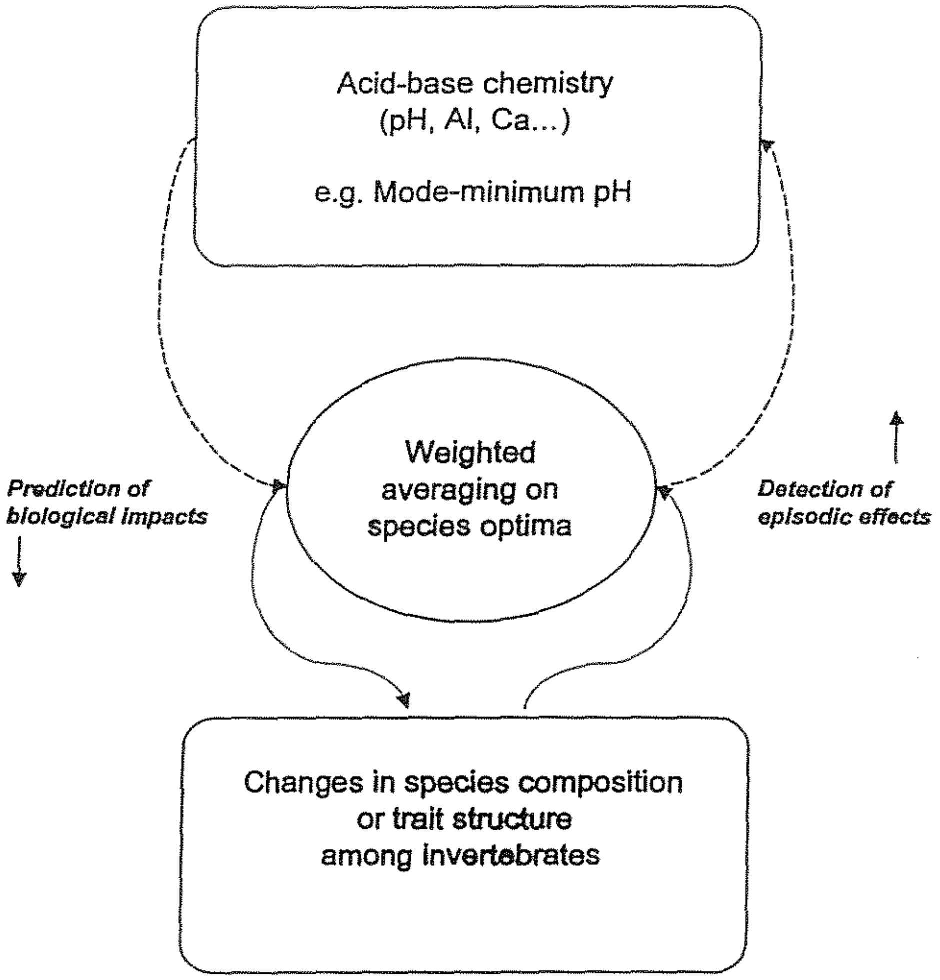
a)



Case 1: Biotic character 'worse' than expected from modal pH: suspect episodic effects

Case 2: Biotic character 'better' than model pH: no episodic effects likely.

b)


Acid-base chemistry
(pH, Al, Ca...)
e.g. Mode-minimum pH
Weighted averaging on species optima
Prediction of biological impacts
Detection of episodic effects
Changes in species composition or trait structure among invertebrates

2.9 Run MAGIC7 scenarios that include (i) different afforestation strategies; (ii) different non-forest vegetation nitrogen uptake strategies; (iii) different temperature regimes

MAGIC 7 simulations have been carried out under different forestry scenarios for the Wales and Galloway datasets (the Pennines are unsuitable for this analysis, since few sites are forested).

Thirty six of the sixty catchments in the region of Galloway are forested ranging from 10-100% forest cover. Future afforestation policy is expected to have a significant effect on acidification status of soils and surface waters in this region. Two forestry scenarios have been implemented in MAGIC 7 simulations namely: Scenario 1 (SC1) 'remove all forest as it reaches 50 years of age and allow land to revert to moorland vegetation', and Scenario 2 (SC2) 'remove forest as it matures but immediately replant a second rotation forest'. These land use scenarios combined with the agreed sulphur reductions (REF deposition scenario) cause the response of soil and surface water quality to differ markedly within the region. MAGIC 7 predictions under the 'best case' forestry scenario (Scenario 1) indicate a significant recovery in the surface water Acid Neutralising Capacity (ANC) compared to the ANC under the more realistic scenario which assumes forest rotation at 50 years i.e. planting a second rotation forest (Figure 26).

Despite emission reductions, soil base saturation (BS) is predicted to decline from 1997 to 2047 for the majority of catchments in the region (Figure 27). This implies that sulphur deposition is still greater than base cation supply from weathering. Changing land use at these forested sites complicates the future recovery of the base cation status of the soil. Clearly, a second rotation forest (SC2) exerts an additional stress on the soil base cation pool and so tends to exacerbate soil acidification in 2047.

Work is ongoing to incorporate the effects of upland improvement within the model. Methods have been developed to separate deposition and agricultural sources of S and N for regional applications, which will allow more accurate forecasting for partially improved catchments. Work in the remainder of the programme will consider impacts of non-forest vegetation uptake, nutrient addition and temperature, taking account of results from intensive study sites.

Figure 26 Change in surface water ANC under alternative forest management strategies

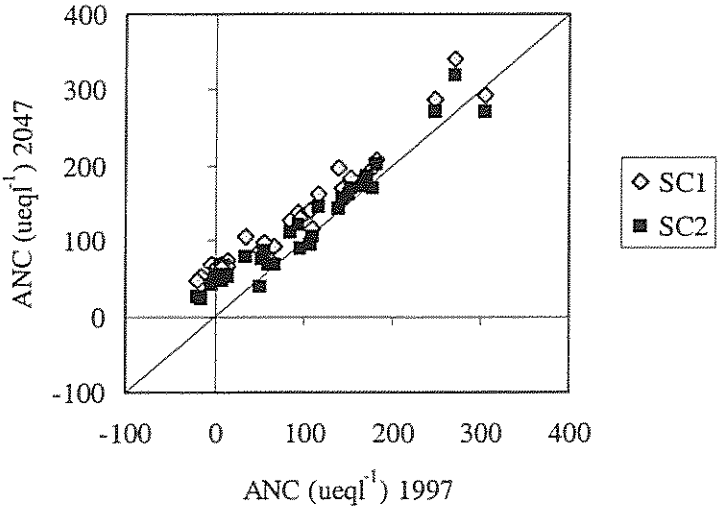
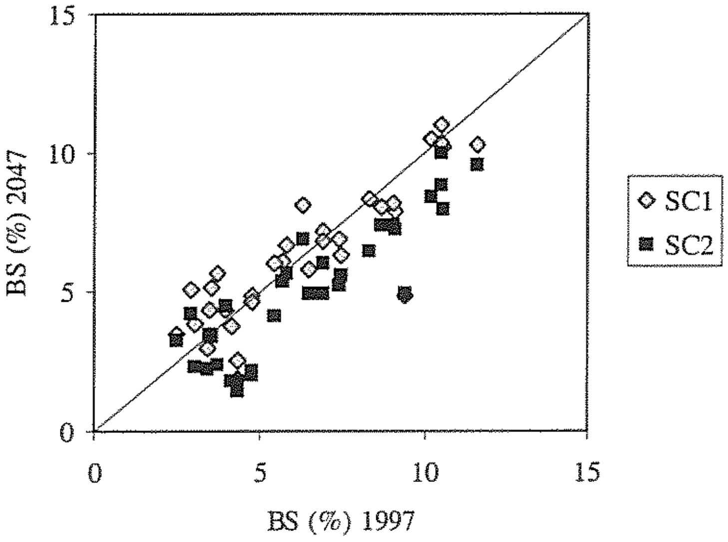


Figure 27 Change in soil base saturation under alternative forest management strategies



2.10 Organise a workshop(s) with environmental economists to ensure cost benefit modellers are well informed of the relevant science output.

DETR have expressed a wish to reconsider the scope of this meeting. It will be organised once DETR specifications are clarified.

WORKPACKAGE 3: HEAVY METAL DEPOSITION TO UPLAND SURFACE WATERS

3.1 Scoping study

The study "Atmospheric deposition of heavy metals: An assessment of monitoring in the UK with reference to critical loads and forthcoming legislation" produced by Phil Henderson was completed in July 1999 and submitted to the DETR. This part of the metals programme is thus complete although there is an intention to try and synthesise this report into a paper.

3.2 Metal deposition and cycling at Lochnagar

This section of the work is ongoing throughout the period of the contract. Hg, Cd, Pb, Zn and Cu are being measured in the following samples:

- Fortnightly bulk deposition samples (monthly for Hg)
- Fortnightly water samples taken from near the outflow (monthly for Hg)
- Annual sediment trap samples
- Annual samples of epilithic algae and zooplankton
- Annual samples of catchment vegetation (*Calluna vulgaris, Vaccinium myrtillus, Vaccinium vitis-idaea, Hylocomium splendens, Pleurozium schreberi*)
- Annual samples of aquatic macrophyte species (*Nardia compressa, Isoetes lacustris, Scapania undulata, Sphagnum* sp.)

All annual data except the sediment traps are now available up to 1998 whilst bulk deposition and lake water sample data are available up to May 1999. Hg data in bulk deposition and lake water samples are available up to September 1999. There has been a contamination problem in the latest Hg samples, unfortunately only identified in September 1999 and the data from June 1999 - September 1999 have been affected. It is hoped that this problem has now been rectified in time for the October sampling.

Annual plant and trap samples for 1999 were collected in August and have been 'made safe' prior to analysis.

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Appendix 1 Relative abundance of common diatom taxa in TWINSPAN diatom groups

TaxonId	TaxonName	1	2	3	4	5
AC001A	Achnanthes lanceolata	0.0	0.3	0.1	0.3	1.3
AC013A	Achnanthes minutissima var. minutissima	1.5	9.5	16.6	44.4	38.1
AC014C	Achnanthes austriaca var. helvetica	7.7	0.6	3.1	0.3	0.0
AC028A	Achnanthes saxonica	0.1	0.5	4.4	5.5	0.0
AM012A	Amphora pediculus	0.0	0.0	0.0	0.0	1.2
BR001A	Brachysira vitrea	0.6	2.0	2.9	0.0	0.1
CM003A	Cymbella sinuata fo. sinuata	0.0	0.0	0.0	0.1	2.9
CM031A	Cymbella minuta var. minuta	0.0	0.0	0.0	0.3	1.1
CO001A	Cocconeis placentula var. placentula	0.0	0.0	0.0	0.0	10.0
DT002A	Diatoma hyemale var. hyemale	0.2	0.2	0.1	16.8	0.1
EU002E	Eunotia pectinalis var. minor fo. impressa	0.0	0.2	1.0	0.2	0.0
EU009A	Eunotia exigua var. exigua	78.4	21.5	22.3	1.4	0.1
EU047A	Eunotia incisa	0.4	2.1	0.5	0.0	0.0
EU048A	Eunotia naegelii	0.2	0.3	3.6	0.0	0.0
EU049A	Eunotia curvata var. curvata	0.0	0.1	1.8	0.0	0.0
EU051B	Eunotia vanheurckii var. intermedia	3.6	38.2	0.9	0.8	0.0
FR007A	Fragilaria vaucheriae var. vaucheriae	0.0	0.4	0.7	8.0	1.4
GO001A	Gomphonema olivaceum	0.0	0.0	0.0	0.0	1.5
GO014A	Gomphonema intricatum	0.0	0.0	0.0	0.2	6.2
GO014B	Gomphonema intricatum var. pumilum	0.0	0.0	0.0	1.0	2.5
HN001A	Hannaea arcus var. arcus	0.0	0.0	0.0	2.2	3.8
MR001A	Meridion circulare var. circulare	0.0	0.1	0.2	1.9	0.1
NI9985	Nitzschia [cf. palea]	0.0	0.1	0.0	0.5	3.9
PE002A	Peronia fibula	0.0	8.5	0.1	0.0	0.0
PI022B	Pinnularia subcapitata var. hilseana	0.8	0.6	1.1	0.1	0.0
SU004A	Surirella biseriata var. biseriata	0.0	1.7	0.5	0.1	0.0
SY010A	Synedra minuscula	0.0	0.2	1.2	2.5	0.6
TA001A	Tabellaria flocculosa var. flocculosa	2.1	1.8	18.7	0.3	0.0
ZZZ996	Temporary sp. 4	0.0	0.0	0.0	0.0	1.6
ZZZ999	Temporary sp. 1	0.1	1.0	13.1	8.2	14.3

Appendix 2 Relative abundance of common invertebrate taxa in TWINSPAN invertebrate groups

TaxonId	TaxonName	1	2	3	4	5
SP003	AGAPETUS_FUSCIPES	0.0	0.0	0.0	0.3	3.1
SP004	AMPHINEMURA_SULCICOLLIS	49.1	18.8	6.6	8.3	5.0
SP008	BAETIS_MUTICUS	0.0	0.0	0.0	0.4	2.3
SP009	BAETUS_RHODANI	0.0	0.0	1.3	14.1	17.3
SP010	BRACHYPTERA_RISI	2.0	8.9	2.1	2.0	2.0
SP015	CHIRONOMIDAE	0.4	3.9	15.4	6.9	6.6
SP016	CHLOROPERLA_TORRENTIUM	0.8	4.8	6.9	2.0	1.5
SP017	CHLOROPERLA_TRIPUNCTATA	0.8	2.5	0.4	1.6	0.8
SP022	DINOCRAS_CEPHATOTES	0.0	0.0	0.0	0.1	1.7
SP026	DRUSUS_ANNULATUS	0.1	0.9	0.7	1.4	0.2
SP032	ECDYONURUS_VENOSUS	0.0	0.0	0.0	1.2	1.0
SP033	ELMIS_AENEA	0.0	0.2	1.3	1.8	1.1
SP036	GAMMARUS_PULEX	0.0	0.0	0.0	0.3	10.1
SP040	GLOSSOSSOMA_CONFORMIS	0.0	0.0	0.0	0.2	1.6
SP048	HEPTAGENIA_LATERALIS	0.0	0.1	1.2	4.7	0.9
SP052	HYDROPSCYCHE_INSTABILIS	0.0	0.1	0.4	1.2	2.3
SP054	HYDROPSCYCHE_SILTALAI	0.0	0.5	2.5	2.9	0.2
SP055	ISOPERLA_GRAMMATICA	0.2	7.6	20.3	8.5	2.8
SP056	LEPIDOSTOMA_HIRTUM	0.0	0.0	0.2	1.0	0.0
SP058	LEUCTRA_HIPPOPUS	7.6	1.2	1.7	0.2	1.0
SP059	LEUCTRA_INERMIS	4.8	20.0	12.0	10.1	6.5
SP060	LEUCTRA_NIGRA	15.2	1.2	0.2	0.1	1.3
SP064	LIMNIUS_VOLCKMARI	0.0	0.4	3.0	4.4	0.4
SP065	LIMONIINAE	1.6	1.0	0.8	0.9	1.4
SP073	NEMOURA_CINEREA	1.2	0.1	0.1	0.0	0.0
SP079	OLIGOCHAETA	0.3	3.5	5.0	2.2	1.2
SP081	OULIMNIUS_TUBERCULATUS	0.0	0.0	1.3	0.4	0.0
SP090	PLECTROCNEMIA_CONSPERSA	3.1	0.8	0.2	0.1	0.2
SP097	PROTONEMURA_MEYERI	2.3	1.3	2.0	0.4	0.3
SP101	RHITHROGENA_SEMICOLORATA	0.3	0.2	0.2	11.6	17.5
SP102	RHYACOPHILA_DORSALIS	0.3	1.2	1.3	0.5	0.6
SP104	SERICOSTOMA_PERSONATUM	0.0	0.0	0.3	1.1	0.3
SP107	SIMIULIIDAE	3.2	15.3	6.3	1.7	3.2